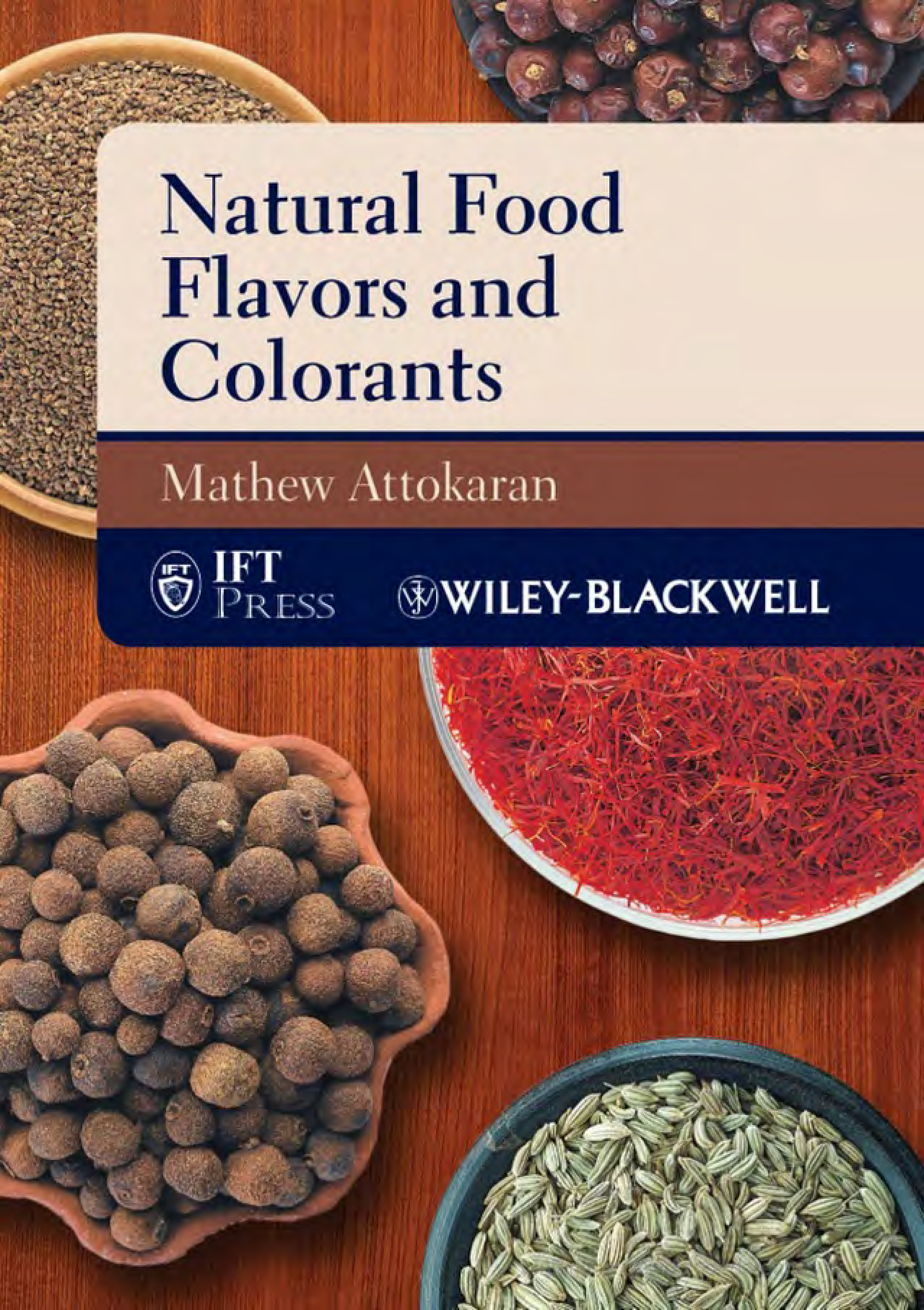

# Natural Food Flavors and Colorants

Mathew Attokaran

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# Natural Food Flavors and Colorants

*Natural Food Flavors and Colorants* Mathew Attokaran

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# Natural Food Flavors and Colorants

Mathew Attokaran, *Technical Director,*
*Plant Lipids Limited, Cochin, India*

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*Color plates appear between pages 240 and 241*

# Preface

Ever since man started adding crushed roots, fruits, and leaves to food with a view to improving its organoleptic appeal, the search for more and more diverse flavors had continued. In addition, consumers want their food to be pleasing to the eye. It was soon found that some plant materials gave a good color to the food. One of the distinctive features of humans that differentiates us from other animals is our innovative approach to improve the quality of our food. This enabled the production of such plant material in ground, crushed, distilled, and extracted forms so as to obtain the flavor and color in a convenient and effective form, to be used as an excellent natural additive.

With the development of modern chemistry, synthetic chemical molecules capable of producing delicious flavors and attractive colors started emerging. But as man became more and more conscious of his own physiology and the interference of external molecules, leading to allergy, toxicity, and carcinogenicity, he took a decisive step back to natural substances. After all, the human body is a biological engine and compatibility with bio-derived materials is only natural.

A recent survey (Food Technology, IFT, 2010, April) of the top 10 food trends reports that blending foods and drinks with naturally rich nutrients to be the second most popular trend, and avoidance of chemical additives and artificial colors as the fifth most important trend that Americans seek now.

It was Ernest Guenther who pioneered the production of a six-volume treatise, *The Essential Oils*, which covers the largest group of natural aroma and flavor materials used in food. Even after 60 years, the volumes are widely consulted by food scientists and technologists. Brian M. Lawrence continued the great tradition of reviews in the form of "Progress in Essential Oils," which appears in the journal *Perfumer and Flavorist*. While the aroma-contributing natural flavors of essential oils are well treated, the same cannot be said regarding nonvolatile natural flavors.

There are many books on spices, but only a few deal with the chemical constituents that are referred to in this book. For spices and other materials, the compilation by Albert Y. Leung and Steven Foster, *Encyclopedia of Common Natural Ingredients*, is indeed a very valuable one. There are some good books and reviews on food colors. Nevertheless, the author believes that there is room for a book that includes all the available natural food flavors and colorants with adequate coverage of plant products, tips on extraction procedures, the chemistry of active principles, guidance on analytical methods, and links to regulatory bodies. This book is designed to assist people associated with food science, technology, and industry to realize the newfound dream of consumers for a return to natural substances that can be added to food to improve its appeal.

Almost all the products dealt with in this book may indeed be familiar to ordinary people. However, their scientific significance, methods of production, and recognition in food laws are matters that laypeople will not be fully conversant with and will be a great help to students, researchers, and those in the industry.

The book is divided into three parts. Part I deals with matters connected with analysis, general properties, and techniques. Part II describes the various natural flavors and colorants that are available. Part III covers the future prospects that can be pursued by research workers and manufacturers.

Mathew Attokaran

# Acknowledgments

This book has been the fulfillment of one of my cherished dreams. In making available this publication, it is my humble wish that it will serve food scientists, technologists, and industrialists the world over, to move toward flavors and colors of natural origin, a trend that is preferred by today's consumers. However, this effort of mine would never have seen the light of day had it not been for the benevolent and generous support and encouragement I received from C.J. George, Managing Director of Plant Lipids Limited, a natural flavor and color producing company that is in the forefront of technical excellence and quality management.

Furthermore, I wish to express my indebtedness to all staff members of Plant Lipids for their excellent cooperation throughout this effort. In particular, may I express my gratitude to C.P. Benny, K.V. George, Thomas Mathew, and Binu V. Paul for useful discussions; John Nechupadom for his keen interest; Neelu Thomas for making the figures; Moby Paul for assistance in word processing; and the scientific staff for helpful hints. I must also acknowledge Professor Madhukar Rao for his valuable advice on the usage of language.

I will be failing in my duty if I do not express my gratitude to Salim Pushpanath for the beautiful photographs. (All photographs copyright © Salim Pushpanath.)

I am indeed grateful to the authorities of the Food Chemical Codex (FCC) for allowing me to quote the relevant descriptions of physical specifications of about 40 natural ingredients, most of which are essential oils. They are reprinted with permission, the United States Pharmacopeial Convention, copyright 2009, all rights reserved.

Last but not least, I thank the Institute of Food Technologists, USA, for the encouragement and acceptance of my proposal for publication.

Mathew Attokaran

# About the Author

Mathew Attokaran (formerly A.G. Mathew) was born in Kerala State in India. He has taken his MSc. in Oils, Fats, and Aromatics and Ph.D. in Food Chemistry. He has carried out research in Food Science and Technology for over 28 years in the Central Food Technology Research Institute, Mysore and Regional Research Laboratory (CSIR), Trivandrum, before moving to the industry. He has guided Ph.D. students and published over 200 scientific papers.

Many of his research findings have been successfully developed into viable technologies, which have been effectively utilized by the industry. His team developed the highly successful two-stage process for making spice oleoresin.

Twice he has been the leader of the Indian Delegation for the International Standards Organization (ISO) Committee meetings on Spices and Condiments held in Hungary (1983) and in France (1986). He was the President of Essential Oils Association of India for two terms. He has widely traveled in the United States, Europe, and Asia for visits to research and industry centers as well as for participation in international conferences. He has completed Short-term Missions in three United Nations agencies: the Food and Agricultural Organization of the United Nations, Rome; the United Nations' Industrial Development Organization, Vienna; and the International Trade Centre, of the UN and WTO, Geneva.

He is happily married and lives with his wife in Cochin, where he continues to work as the Technical Director of Plant Lipids Limited. He has two daughters and five grandchildren. Dr. Attokaran can be reached at info@plantlipids.com.

# Part I
# General

## Introduction

Before we discuss various flavors and colorants, many general aspects will have to be understood. There are several eminent organizations, which on a regular basis, review methods of determination, specifications, and safety assessments of these. This part deals with techniques and general characteristics of certain classes of flavors and colors that are necessary for a better understanding of the food technology related to these ingredients.

Various chapters cover subjects related to analysis, techniques in extraction, and modifications necessary for application in foods. General characteristics of some important classes of products like spices, essential oils, flavors, and colors have also been given some emphasis so as to help researchers, manufacturers, and formulators of food.

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# 1 Analytical Matters

The analysis of natural flavors and colorants involves three different types of determinations: (1) chemical analysis of constituents, (2) analysis of residues, and (3) microbiological analysis.

## Chemical Analysis

The most important determination is the content of the active components. Some indications are given under each item. In these, in addition to conventional analysis, instrumental analysis may be needed. For many constituents, estimation based on UV or visible spectra is relevant. Furthermore, some volatile components can be analyzed by gas chromatography (GC) and nonvolatile components by high-pressure liquid chromatography (HPLC). An advanced method is GC/MS where GC is combined with a mass spectrometer (MS) to identify compounds separated by GC.

In the case of many substances containing volatile oils, such as spices, the moisture content cannot be determined by loss of weight. The American Spice Trades Association, Inc. (ASTA) describes the toluene distillation method; the volatile oil content can be determined by distillation using the Clevenger trap.

The AOAC's *Official Methods of Analysis* is a veritable bible as far as analysis of plant products is concerned. The U.S. Food and Drug Administration (FDA) and European Union (EU) have the Code of Federal Regulations (CFR) and the European Food Safety Authority (EFSA), respectively, where regulatory, specification-based, and analytical matters are described. Similarly, in the case of flavoring materials, IOFI gives some details. Codex Alimentaris also specifies and gives directions for analysis. A wide range of flavors, colorants, and test methods are very well described by the Food Chemicals Codex (FCC).

## Residue Analysis

Generally, the residues that are unwelcome but likely to be present in natural flavors and colorants are (1) solvents (in the case of extracts), (2) aflatoxins, (3) pesticides, and (4) heavy metals.

The **residual solvent** is limited according to food laws (see Chapter 8 on solvent extraction). This residue is determined by taking 50 g of the extract and collecting the residual solvent in 1 mL of toluene by water distillation under specified conditions. The solvent present is determined by GC.

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This is a method based on the paper by Todd (1960) done about half a century ago. Many efforts have been carried out to standardize an improved method but without success. Details of the determination are given in the FCC.

**Aflatoxins** are produced by the fungus *Aspergillus flavus* (from which the name is derived) and a few members of *Aspergillus* and *Penicillium* species. EU limits are 5 ppb for B1 and 10 ppb for total. The FDA limit is 20 ppb for total aflatoxins. Methods are available from AOAC and ASTA (for spices only).

The EU has recently included limits on ochratoxin contamination. The recommended limit is 30 ppb. The AOAC gives methods of analysis. Aflatoxins are determined using HPLC with a fluorescence detector.

For the analysis of **pesticide residues**, detailed methods are given by the *Pesticide Analytical Manual* published by the FDA. The AOAC is also a good reference source. The residues come under organo-chlorine, organo-phosphorus, and pyrethroids. These are determined using GC. For organo-chloro compounds and pyrethroids, electron capture detection (ECD) is required, while for organo-phosphorus compounds, flame photometric detection (FPD) is used.

**Heavy metal residues** that are considered to be harmful and frequently found include mercury, cadmium, arsenic, copper, lead, and zinc. Methods of testing are given by the AOAC. The measurement is carried out using atomic absorption spectrometry (AAS).

**Artificial colors** became the focus of attention when there was an attempt to adulterate red chili extract with Sudan dyes. This is not a general problem of all flavors and colorants, and its emphasis is slowly vanishing. For capsicum and turmeric, restriction was introduced by the EU for the following dyes: butter yellow, fast garnet GBC, methyl yellow, metanil yellow, orange II, para red, p-nitro-analine, rhodamine, Sudan black B, Sudan orange, Sudan red B, Sudan red I to IV, and toluidine red. Bixin was also introduced more as a measure of preventing cross contamination.

The initial limit for these artificial dyes was 10 ppb, which means the analysis needs LC/MS/MS, in which a liquid chromatograph (LC) is combined with two mass spectrometers to quantify low levels of target compounds. Now the limit may be increased to 500 ppb, which can be determined by HPLC. This is a point that must be checked.

There is a general feeling that adulteration at these levels is not an advantage that can be exploited. Additionally, contamination can result from many other means. Pesticide manufacturers use colors like rhodamine for color coding their products for farmers to identify. Lubricants for machines used in farm operations and grinding are sometimes color coded. Farmers use dye to write on the bags, details such as weight, date, and lot number.

## Microbiological

For steam-distilled essential oils and solvent-extracted flavors and colorants, microbial contamination is not a major issue due to the sterilizing effect of processing. However, for plant products and aqueous extracts, microbial contamination is important. In ordinary cases where hygiene is well maintained, an evaluation of total plate count, yeast, and mold will suffice. However, in badly contaminated cases, the following pathogenic bacteria need to be tested for: coliforms, especially *Escherichia coli*; *Salmonella*; *Staphylococcus aureus*; and *Bacillus cereus*.

## Important Agencies

The FCC has described a wide range of flavoring and coloring materials. AOAC and ASTA (for spices) have given analytical procedures. Identification numbers of different natural flavorings and colorants are given by the Flavor Extract Manufacturers Association (FEMA) and the Chemical Abstracts Service (CAS). The EU gives E-numbers to various items after examining all aspects that make them safe for use. To date, they have covered food colors and a few other items. Spices and their active components are yet to be given numbers. The FDA gives specifications and CFR numbers. FEMA, CAS, CFR, numbers and E-numbers, wherever available, are given under each item.

The full name and address of each of these valuable agencies are given below:

American Spice Trades Association, Inc. **ASTA**
560 Sylvan Avenue
P.O. Box 1267
Englewood Cliffs, NJ 07632
Official Analytical Methods
(for methods of analysis on spices)

AOAC International **AOAC**
481 North Frederick Avenue, Suite 500
Gaithersburg, MD 20877
(for methods of analysis of plant products and impurities)

Food Chemicals Codex **FCC**
Legal Department of United States
Pharmacopeial Convention
12601 Twinbrook Parkway
Rockville, MD 20852
(for specification and test methods)
European Union

European Food Safety Authority **EFSA**
(for food regulation, standards, and award of E-number)

U.S. Food and Drug Administration **FDA**
10903 New Hampshire Avenue
Silver Spring, MD 20993
(for regulatory matters and standards)
Code of Federal Regulations (CFR)

Codex Alimentaris **CODEX**
Secretariat
Viale delle Terme di Caracalla
00153 Rome, Italy
(for food safety, standards, and related matters)

International Organization of the Flavor Industry **IOFI**
Secretariat, 6 Avenue des Art
1210, Brussels, Belgium
(consisting of national association of flavor manufacturers of several countries)

Flavor Extract Manufacturers Association **FEMA**
1620 1 Street NW, Suite 925
Washington, DC 20006
(generally recognized as safe [**GRAS**] list)

Chemical Abstracts Service **CAS**
American Chemical Society
Columbus, OH 43202

FCC (FCC 6 2008–2009) is a body that gives descriptions, specifications, and testing methods for a wide range of food additives, including natural flavors and colorants. Today, the body has become an authority on food additives. It is being operated by the U.S. Pharmacopeial Convention (USP), and it is certain that professionalism of the USP will also be extended to food chemicals.

The following are the abbreviations for **units of measurements** used.

| | |
|---|---|
| % | percentage |
| °C | degree Celsius |
| $\mu$g | microgram ($10^{-6}$ g) |
| $\mu$m | micrometer ($10^{-6}$ m) |
| g | gram |
| kg | kilogram (1000 g) |
| km | kilometer (1000 m) |
| L | liter |
| m | meter |
| mg | milligram ($10^{-3}$ g) |
| mL | milliliter ($10^{-3}$ L) |
| mm | millimeter ($10^{-3}$ m) |
| mt | metric tonne (1000 kg) |
| ng | nanogram ($10^{-9}$ g) |
| nm | nanometer ($10^{-9}$ m) |
| ppb | part per billion |
| ppm | part per million |
| v/w | volume/weight |

## References

FCC 6. 2008–2009. *Food Chemicals Codex*, 6th edition. Rockville, MD: United States Pharmacopeial Convention.

Todd, P.H. 1960. Estimation of residual solvents in spice oleoresin. *Food Technol.* **141**, 301–308.

# 2 Flavors

## Sources of Natural Flavors

In today's world, there is great preference for natural materials for use in food. As chemistry has developed, a large array of wonderful chemicals were synthesized. Thus, the chemist could create compounds that give aroma, taste, and color. But as some chemicals, upon testing, were found to be toxic and carcinogenic, consumers of food have made a decisive retreat to nature. Development of organic foods, opposition to genetically modified items, avoidance of unwanted residues during processing, and strict limits to mycotoxins, pesticide residues, and heavy metals are all manifestations of man's urge to get back to nature as far as food materials are concerned.

One of the largest groups of flavors is spices. Spices have been used in food for a very long time. They contain essential oils, which contribute toward the fine aroma. In addition, many of them have pungency or hotness, which gives piquancy to the food. Man started using spices to make bland food more attractive for consumption. Since spices are important, Chapter 3 is devoted to them.

The only other major group that is valuable in flavoring through the fine aroma contributed by the essential oils contained in them is citrus fruits. The peel of various citrus fruits contains fine essential oils. These oils can be extracted from the cells without the need to resort to steam distillation. In fact, the peels are valuable only for the essential oils, as they do not contain any nonvolatile component that contributes toward flavor. Only in some rare cases is the whole peel used as a flavorant, such as in cakes, some pastries, and orange marmalade. The whole lime or lemon with peel is used in pickles. In most other cases, separated essential oil is used.

There are also flavoring materials whose attractiveness is due to the alkaloids and polyphenols present in them. But unlike spices, these are not used as such in food. They are mainly used as extracts either in beverages or for mastication.

## Perception of Flavor

Flavor is a combination of taste, odor, and mouthfeel. Sweet, sour, salty, and bitter were regarded as the true tastes. Now "umami," the brothy, meaty, or savory taste of glutamates, is also included in the list. A true taste is felt at a specialized nerve ending on the tongue.

Sweetness is given by sugar and other sweeteners, while a salty taste is provided by sodium chloride. Both of these categories play a vital role in food and its

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preparation. Sourness, caused by $H^+$ ions of acids, is provided by products such as tamarind, garcinia fruit, lime, tomato, citric acid, and vinegar. Bitterness, as in quinine, is generally appreciated at an appropriate level only along with other tastes. Bitterness is contributed by alkaloids as in cocoa and coffee, by saponins as in fenugreek, and by burned sugar as in caramel.

In addition to true tastes, there are other sensoric factors that do not require specialized nerve endings. They are felt all over the body, but when felt in the mouth along with other factors, they are perceived as a desirable factor in some food. Pungency, astringency, coolness, and warmth belong to this class. Pungency is caused by chemicals such as capsaicin in red chili, piperine in black pepper, and gingerol in ginger. It is essentially a pain reaction. Astringency is a touch feeling caused by polyphenols as in tea and coffee, which temporarily link to proteins in the mouth. It is somewhat similar to the tanning of leather. Coolness or warmth is an effect of temperature as in the cool feeling of ice cream or the warmth of hot coffee. Some chemicals such as menthol also create a sense of coolness. Alkaloids in general affect the nervous system and cause a sensation that will modify the flavor as one feels.

Mouthfeel includes the texture of the food, such as hardness, toughness, tenderness, or crispness. Flavoring and color extract have a minor role in texture, as they are added at low levels.

Odor or smell is caused by volatile compounds in food. Generally, such compounds are organic. When a desirable odor is referred to in food, it is called aroma. There are two steps in the perception of a smell. When a volatile compound diffuses, the stimuli are captured by the receptors in the nose. These are then processed by a section of the brain responsible for olfaction.

The science of smell and its detection is much more complicated than the detection of taste. Over the years, many studies have been conducted. According to the molecular size and shape, molecules are divided into some primary odors such as camphoraceous, pungent, ethereal, floral, pepperminty, musky, and putrid.

The overall feeling of taste, mouthfeel, and aroma defines the flavor of a food. All of the flavor ingredients described in this book contribute significantly toward taste and aroma. But however attractive the flavor is, the appearance (especially color) is very important. Attractive and appropriate colors improve the appreciation of flavor and satisfaction of eating (see Chapter 5 on food colors).

# 3 Spices

Spices are a vast reservoir of good flavors. Even in ancient times, Europe has shown its acceptance of the appetizing flavors of spices. In the fifteenth century, many daring maritime expeditions were undertaken to get to the source of the spices of the Orient. The voyages of Columbus and Vasco da Gama are two examples. While Columbus stumbled upon the great continent of America, Vasco da Gama came around the Cape of Good Hope in South Africa and landed in Calicut, a thriving port in those days on the southwest coast of India. Earlier Arab tradesmen were doing business with the Middle East, the Mediterranean region, and European countries mainly using land routes combined with sea routes from southwest India and the East Indies. Marco Polo in the thirteenth century experienced the attractions of spices from the Orient in his travels. But the successful landing of Vasco da Gama and his team made the export of Asian spices to Europe a thriving business.

Barring leafy spices, such as Mediterranean herbs and mint, most of the major spices need the warm humid weather conditions of the tropics. Even in the case of chili, the hot variety needs warm weather, and only paprika, which is primarily used for color, is grown in colder weather conditions. To Asians, spices are indeed the soul of their food. In the Western world, they evoke dreams of tropical lands, exciting expeditions, and the rise and fall of empires.

Spices come from different parts of a plant. They can be fruits (cardamom, chili), berries (juniper, black pepper, pimenta), seeds (celery, cumin, fennel), kernels (nutmeg), aril (mace), flower parts (saffron, clove), bark (cassia, cinnamon), leaves (mint, marjoram, bay), rhizome (turmeric, ginger), or bulbs (garlic, onion).

In trade, black pepper, chili, ginger, and turmeric are regarded as the major spices. Seed spices, tree spices, and others are minor spices. In India, because of high trade rate, it is a general practice to treat cardamom as a major spice. However, it may be noted that many of the seed spices, such as coriander, cumin, anise, and celery, are really the fruits, which when dried are called seeds.

Spices, especially major spices, are in general used in savory foods. This is because of the high level of hotness they impart. Black pepper, capsicum, and ginger are called hot spices. However, many seed spices and herbs are used in sweet preparations, such as cardamom, mint, and cinnamon.

While almost all the spices are described in Part II, some general aspects need further consideration. In almost all spices except chili the aroma is contributed by the essential oil present. Many major spices and, in fact, all spices (barring herbal and

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some seed spices), have nonvolatile pungent constituents, which give piquancy to the food. A few of them, such as paprika, turmeric, and saffron, give an attractive color to the food. The pungent and color-contributing components as well as essential oils are discussed below for the relevant spices. However, essential oils have some common properties and therefore need some examination (see Chapter 4).

## Spice Oils and Oleoresins

During World War II, soldiers and some civilians had to spend long periods in a totally alien world. It was therefore necessary to have convenient foods and additives that reflected preferred flavors. This convenience food trend grew after the war, and the development of standardized spice oils and oleoresins was the natural result of such a need.

As already indicated, the spices have two main flavor attributes. The one that catches the immediate attention of a consumer is the spice aroma. This is contributed by the essential oil or spice oil, which is detected by the olfactory organ of the nose. Spice oils can be separated by steam distillation.

The other flavor attribute is the hot, pungent taste felt in the mouth while masticating. Pungency is caused by chemicals that are nonvolatile. Spices also have color, although only some of them are considered to be attractive as in the case of paprika and turmeric. The coloring components are also nonvolatile. If all the flavor attributes of aroma, taste, and color are required, only solvent-extracted oleoresin will be a complete extractive. Even the volatile spice oils will be found in the extract.

Before the improved two-stage method of preparation of oleoresin was introduced in India in the 1970s, oleoresins used to be produced in a single stage of solvent extraction. However, there are drawbacks in that the quality of oil is not as good because of interference of solvent. During the removal of solvent, some fine aroma can be lost.

In the two-stage process, spice oil is separated by steam distillation as the first step. The deoiled spice, after drying and lump breaking, is extracted with an appropriate solvent for nonvolatile fraction. The solvent chosen can be the best suited for nonvolatile components only, as the essential oil has already been recovered. The resin fraction, so obtained after removal of solvent, is blended with an adequate quantity of oil collected in the first stage to obtain oleoresin.

The spice oils removed in the first stage are unaffected by solvent. Generally, the yield of the oil is so high that only about half the quantity need be used for blending with the resin extract. In fact, during steam distillation of the first stage, oil can be collected as two fractions. The first fraction will be richer in the harsher smelling monoterpenes. The second fraction will be richer in sesquiterpenes and oxygenated compounds. This second fraction can be used as salable oil. The first fraction with its strong top note will be ideal for blending with nonvolatile resin obtained in the second stage by solvent extraction. Due to the improved two-stage process, production of quality spice oils became a part of the oleoresin industry, thus making the process more commercially viable.

# 4 Essential Oils

Essential oils are volatile, generally aroma-contributing liquids produced by plants. The term "essential oil" is derived from "essence," as it carries the distinctive scent or essence of the plant material. Because they are volatile, they are also called volatile oils. Specific essential oils are named after the plant from which they are extracted, for example, ginger oil, nutmeg oil, and orange oil. As a group they are also called spice oils and citrus oils.

An essential oil is a concentrate of lipophilic and hydrophobic chemical compounds, which are volatile. Plants also produce fixed oils or fatty oils, which are not volatile. Fixed oils are fatty acid esters of glycerol called triglycerides. Triglycerides, which are also present in the animal kingdom, are viscous materials. They can be used as cooking oil and are nutritionally significant. The role of essential oils in food is to provide aroma and flavor. In some cases, they have a medicinal role. Essential oils are extensively used in the fragrance industry. In recent times, the popularity of aromatherapy has given a boost to essential oils. Aromatherapy is an alternative medicine wherein it is believed that specific notes of odor, contributed by essential oils, have curative power.

An essential oil is composed of terpenes. More than 100 years ago, it was seen that the hydrocarbons found in essential oils are $C_{10}$, $C_{15}$, and occasionally $C_{20}$ compounds. $C_{10}$ hydrocarbon typically has $C_{10}H_{16}$ formula. They can be considered to be derived from two isoprene units of $C_5H_8$. Similarly, $C_{15}$ and $C_{20}$ compounds are derived from 3- and 4-isoprene units, respectively. Thus, $C_{10}$, $C_{15}$, and $C_{20}$ compounds are called monoterpene, sesquiterpene, and diterpene, respectively. Monoterpenes can be acyclic, as in $\alpha$-pinene; monocyclic, as in limonene and *p*-cymene; dicyclic, as in camphene; and even tricyclic. $C_{10}H_{16}$ terpene acyclic hydrocarbon has three double bonds, while a monocyclic has two, dicyclic one, and tricyclic none. With additions of hydrogen or other derivatives, this rule of number of unsaturation may be different.

$C_{15}H_{24}$ hydrocarbons are sesquiterpenes and can be considered to be made up of three isoprene units. Here, an acyclic compound will have four double bonds, monocyclic three, dicyclic two, and tricyclic one. Sesquiterpenes will have a higher boiling point than monoterpenes, usually above 250°C. In general, significant aroma-contributing terpenes will be derived from a monoterpene or a sesquiterpene structure. Diterpenes, being less volatile, are not commonly seen as aroma-contributing compounds in most essential oils.

The terpene and sesquiterpene compounds occur as oxygenated derivatives. Monoterpenes can be alcohol (citronellol, geraniol, menthol), aldehyde (citral,

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cinnamaldehyde), ketone (menthone, carvone), phenols (thymol, eugenol), esters (acetyl derivatives of alcohols), and oxides (cineole). There are also acids, lactones, and coumarins. Sesquiterpenes also occur as oxygenated derivatives as above.

Since volatility reduces with increased molecular size, sesquiterpenes are less volatile than monoterpenes. Oxygenated derivatives also have lower volatility than hydrocarbons. Despite these, sesquiterpenes and high boiling oxygenated derivatives are very important in food flavoring. While chewing, the food containing the flavor is kept for some time in the mouth, which is very close to the olfactory organ. In such cases, the molecules do not have to travel a long distance. Spices are generally used in savory foods that are eaten after warming; heating will increase the volatility. Very volatile molecules, such as monoterpene hydrocarbon, will be very harsh on the olfactory system, if held very close to the nose for a long duration or if heated.

It should be borne in mind that in many salable spice oils, the quality is measured by the content of a marker compound represented by heavy oxygenative terpene or sesquiterpene (Table 4.1). A higher percentage of high boiler markers ensures that it has sufficient of oxygenated terpenes and sesquiterpenes.

A higher level of sesquiterpenes and oxygenated derivatives in salable spice oil is obtained by resorting to fractional steam distillation. In India, an improved two-stage extraction procedure is employed for making oleoresin. In this process, spice oil is first steam-distilled. In the second stage, deoiled spice is extracted with solvent. As mentioned earlier, in the first stage of steam distillation, the oil is collected into two fractions. The first fraction will have more of the low boilers such as monoterpenes and the second will have more of high boilers such as sesquiterpenes and oxygenated derivatives (Table 4.2). The first fraction, with stronger top notes, will be very good for blending with the solvent-extracted nonvolatile resin to get a good oleoresin. The

**Table 4.1.** Quality marker constituents of major spice oils

| Spice Oil | Quality Marker | Chemical Nature |
|---|---|---|
| Nutmeg oil | Myristicine | Dicyclic oxygenated terpene |
| Celery seed oil | Selinene | Dicyclic oxygenated sesquiterpene |
| Ginger oil | Zingiberine, ar-curcumene | Sesquiterpenes |
| Pepper oil | $\beta$-Caryophyllene | Dicyclic sesquiterpene |

**Table 4.2.** Distribution of high boiler marker compounds in the first and second fractions during fractional steam distillation

| Spice Oil | First Fraction | | | Second Fraction | | |
|---|---|---|---|---|---|---|
| | % of the Total Oil | High Boiler Marker | % of the Marker in Oil | % of the Total Oil | High Boiler Marker | % of the Marker in Oil |
| Nutmeg oil (Sri Lankan) | 25 | Myristicine | 0.2–0.5 | 75 | Myristicine | 2.5–3.5 |
| Celery seed oil | 40 | Selinene | 3–5 | 60 | Selinene | 16–18 |
| Pepper oil | 50 | $\beta$-Caryophyllene | 4–6 | 50 | $\beta$-Caryophyllene | 25–27 |
| Ginger oil | 10 | Zingeberene | 8–12 | 90 | Zingeberene | 42–44 |

second fraction, with enriched high boilers, will be good salable spice oil. Again, the way to further increase the sesquiterpene and oxygenated derivatives is by using prolonged steam distillation.

Some of the simple hydrocarbons can undergo oxidation during storage. This happens in limonene, which is the major monoterpene hydrocarbon in citrus oils. On oxidation, limonene gives off an unpleasant camphoraceous odor and flavor. Excessive presence of hydrocarbon not only dilutes the desirable flavor given by oxygenated compounds, but also limits oil's dispersibility in water and dilute alcohol when used in beverages. To avoid these problems, terpene hydrocarbons are removed to obtain terpeneless citrus oils. The hydrocarbons, being more volatile, can be separated by fractional vacuum distillation. Liquid partitioning using aqueous alcohol and hexane is also possible, but residual solvent can be a problem. Oxygenated compounds, being more polar, go into aqueous alcoholic fraction, while nonpolar hydrocarbons go to hexane. Since residual hexane is unwelcome in a refreshing beverage, generally a single liquid fractionation with appropriately dilute alcohol is recommended. It must be stressed, however, that fractional vacuum distillation is the preferred procedure as it is more efficient.

Although it is old, the exhaustive six-volume books of Ernest Guenther (1948–1952) is still a valuable reference source for essential oils. For more detail, it would be worthwhile to look into the recent book by Baser et al. (2010).

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# 5 Food Colors

According to food technologists, food is first "eaten" by the eye. An attractive and appropriate color of a food product will gain the approval of consumers. Consumers also expect a certain color for a particular food, for example, light yellow for pineapple juice, orange for orange juice, and pink for strawberry juice. If these are interchanged, the result will not be satisfactory. Similarly, some foods are plain white, such as cooked rice or milk. If these are deeply colored, however attractive the color is, it will not be accepted. Generally, browning of a food like cut apple is regarded as unwelcome, but consumers accept browning as a desirable attribute in the case of baked products.

During processing and storage, some color could be lost. Similarly, some off-season fruits may not have adequate color. In such cases, color has to be added to make the product acceptable. For products for children, especially, a colorful appearance is welcome as in the case of candy, cereal, ice cream, and so on. The color of a food can influence the opinion of a consumer and can suppress or increase the appetite.

## Mechanism of Color Perception

Color is derived from the spectrum of light, which then interacts in the eye with specialized light receptors with spectral sensitivities. These receptors are referred to as cone cells. Varying types of cone cells present in the retina react appropriately to various parts of the spectrum, enabling the subject to identify and to quantify the color by the degree to which each component can stimulate these cells.

The human eye can identify light radiation of any wavelength between 380 and 740 nm; toward the lower wavelength is blue and toward the upper wavelength is red. This range is called visible spectrum. Below the wavelength of visible light is the ultraviolet region and above is infrared. When the eye looks at an object, three types of cones yield three signals based on the extent to which each is stimulated. These values are called tristimulus values. But suffice it to say that the eye sees the object as a whole and the perceived color is the sum total of the stimulation in the various cones. In such cases, the background color can influence our reading of the color, since the eye sees the situation in totality.

Pigments are chemicals that selectively absorb and reflect different spectra of light. While the background color is influential, the overall color is described assuming the background color as white. However, the same food viewed in sunlight and artificial

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light may appear different. When light is dimmed, the judgment can also be influenced. This is a factor to be noted when food is displayed in a supermarket or a restaurant.

## Food Colors

From the early days of food processing, efforts to make food attractive through the addition of color and color-contributing ingredients were made. Even in household cooking, the value of the ultimate color of the food is well understood. With the development of synthetic pigments, artificial colors were in demand for use in food. However, quite a few of them were subsequently identified as toxic and some as carcinogenic. After much screening based on toxicological studies, food laws of major countries now allow only a small number of synthetic colors. The Code of Federal Regulations (CFR) of the U.S. Food and Drug Administration (FDA) allows only seven synthetic colors for use in food. Their E-numbers and color shade are given in Table 5.1.

A recent study conducted by the University of Southhampton and published in *Lancet* has shown evidence of higher levels of hyperactivity among children when they were consuming a mixture of artificial colorings as well as sodium benzoate, which is used as a preservative. Unfortunately, the colors were not tested individually but only as mixtures; this makes it difficult to pinpoint the source of the physiological disorder that was noticed. Confirmatory and more systematic research is planned, and it would be prudent to wait for the results.

University experts and the European Food Safety Authority are convinced that artificial colors have a role in creating hyperactivity in children. It is possible that the European Union (EU) may look into these aspects. However, so far the FDA has not been convinced of these results.

Consumer concerns surrounding synthetic dyes have projected natural color as a very desirable alternative. Food colors are tested for safety by different organizations around the world. In the United States, FDA approval indicates that the colorant is usable in foods, drugs, and cosmetics. The European Commission of the EU is now engaged in a detailed testing and approving process. An E-number indicates safety for use. Many advanced countries have their own regulations and a list of approved food colors that can be used, including maximum daily intake.

Natural food colors are not generally required to be tested by a number of regulatory bodies and very rarely is a maximum limit for intake insisted on. Almost all the

**Table 5.1.** Synthetic food colors allowed in the United States

| Serial No. | Synthetic Color | E-No. | Color Shade |
|---|---|---|---|
| 1 | Brilliant blue FCF | E. 133 | Blue |
| 2 | Indigotine | E.132 | Blue |
| 3 | Fast green FCF | E. 143 | Bluish green |
| 4 | Allura red AC | E. 129 | Red |
| 5 | Erythrosine | E. 127 | Pink |
| 6 | Tartrazine | E. 102 | Yellow |
| 7 | Sunset yellow FCF | E.110 | Orange |

natural food colors presently used in food are described in Part II. Many regulatory bodies consider caramel to be a natural color.

## Measurement of Color

Color measurement of foods can be done with a Lovibond tinctometer. Here, filters of three primary colors, red, yellow, and blue, with graduation are provided. There are also filters of white to account for haziness and turbidity. Color can be matched for both transmission (for liquids) and reflectance and expressed in red, yellow, blue, and white units. It is a subjective but standardized determination. Later objective spectrophotometric reflectance was used with tristimulus combination filters designed to be similar to the three cones, human retina, and brain use.

An objective method is the determination of L, a, and b values that describe the color of a product as the eye perceives. In the determination, the L value stands for white to black. If the reading is 100, then the product has 100% whiteness. A reading of zero stands for 100% blackness. Value a represents red and green. If the value is +ve, it is red, and if –ve, green. Value b represents yellow and blue, with +ve value showing yellow and –ve value blue. Both reflective and absorption color values can be described objectively using equipment specially made for this end. Equipment made by Minolta Lab Services, Hunter, and Associates Laboratory, Inc., are well accepted.

Some spices contribute toward making food colorful. In addition to spices, there are vegetables and fruits that can make food attractively colored. However, color sources like green leaves, flowers, microbes, and insect materials have to be extracted for use in food, as the whole material does not have any flavor or food value. Constituents that give color, such as curcumin, xanthophylls, and anthocyamins, can also be quantitatively determined by spectrophotometric or HPLC methods.

# 6 Preparation of Plant Material for Extraction

Processing of natural flavoring and color materials requires some unit operations, especially while making extractives. Two major steps, steam distillation (Chapter 7) and solvent extraction (Chapter 8), are dealt with later. Some of the other operations are briefly mentioned in this chapter. There are many theories, finer details, and modifications that are needed in these operations when it comes to applying to a specific product. Therefore, readers are advised to refer to specialized books and articles if in-depth understanding is required.

## Drying

Almost all plant materials, whether for use as such or for making extractives, require drying. A few exceptions are when extracts with fresh flavor or with a water-soluble colorant such as anthocyanin are required. Drying ensures protection from spoilage. It also helps to break down the cells, enabling active components to flow out when steam or solvent is applied. The bulk of these materials, especially in the tropics, are sun dried. A few materials are dried in a dryer where previously heated air is passed through the material by either cross flow or through flow. Normally, drying is carried out as part of the agricultural operation or in premises close to the growing area. The processors of extractives buy dried material. In some rare cases, the processor has to do some finishing drying using either sunlight or a dryer.

In rural areas, smoke drying is not uncommon, but this is not a desirable option as smoke can affect the flavor. Natural flow hot pipe drying rooms are often used in crops such as cardamom, when an assured electricity supply is not available. The ideal drying is done by previously heated air obtained using a heat exchanger.

## Size Reduction

All natural flavoring and coloring materials require size reduction. Even when they are used as such, size reduction ensures proper distribution in the manufactured or cooked food products. For the preparation of the extractive, size reduction is needed so that access to the inside of the cells becomes easier.

Impact, attrition, shearing, and compression are the forces that can be used for size reduction of agricultural products. For products that are brittle, such as black pepper and nutmeg, compressive strength is very useful for size reduction. For a sheath-like

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material, as in the case of red chili, attrition and shearing action will be useful. For tough and hard products such as ginger, coffee, turmeric, and chicory, a combination of these forces will be needed. Jaw and gyratory crushers, which are very useful in the mineral industry, are not very useful in the food industry. Similarly, ball mills are not usually applicable for powdering dry plant products.

## Hammer Mill

In this process, swinging hammer-like heads attached to a disk rotate at high speed inside a metal case. The material is pulverized due to the impact of the swinging hammers, which rotate inside the casing with only a small clearance. The escape opening in the bottom of the mill can be fitted with screens with different sieve sizes. The material will be subjected to impact until the size of particles is small enough to pass through the selected sieve.

The hammer mill is a very efficient type of size-reducing equipment for tough products. The major disadvantages are possible high heat formation and difficulty in regulating the particle size.

## Fixed Head Mills

Here, instead of a swinging hammer arrangement, fixed stout projections rotate against a fixed casing with narrow clearance. A modification in the design is a moving disk with two or three rows of thick pins, which will move inside rows of fixed pins with narrow clearance. This type of mill is also called a pin disk mill. Since the grinding is done by pins that are well distributed, there is less heat development.

## Plate Mill

In this type of mill, material is ground between two circular plates, one of which is moving. Material passing through will be ground, primarily through shearing and attrition actions. The surface of plates can be made suitably rough. Although in the plate mill, plates are placed vertically, it is similar to hand-rotated stone mills where the movement is horizontal. Because of high friction, the heat developed will be normally high.

## Roller Mill

Here, the material is passed through two heavy rollers rotating in opposite directions. The roller mill is used in wheat flour milling. Modifications can be two rollers moving at different speeds, grooved instead of smooth rollers, two pairs of rollers placed one below the other, and so on. Here, the main force acting will be compression with some amount of shearing, especially when rollers move at different speeds. Heat development usually will be low.

In the case of black pepper, passage through two sets of rollers will flatten each berry into a flake. Rather than size reduction, it is the squeezing effect that opens up cells that is more important.

Plant products that are large and tough such as rhizomes of ginger, turmeric, and galangal need a preliminary size reduction in a hammer mill or pin disk mill before passing through the rollers.

For spices, passage through a roller mill will help to break up the cells without an increase in temperature. With impact mills, heat is generated. Higher yields of volatile oils are obtained in the case of celery seed (Sowbhagya et al. 2007) and cumin seed (Sowbhagya et al. 2008) when a roller mill is used instead of a hammer mill.

## Cutter Mills

Here, thin blades rotate at high speed in a case with high clearance. This type of mill is useful for fresh undried plant materials and is somewhat similar to a kitchen mixer. For slicing, sharp thin knives rotate such that the plant product is kept somewhat perpendicular to the motion of the blades.

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# 7 Methods of Extraction of Essential Oils

Essential oils are volatile, and therefore the most logical method of extraction would be distillation. However, the most essential oil constituents—terpenes, sesquiterpenes, and their oxygenated derivatives—are destroyed or charred before they reach boiling point.

Liquids boil when their vapor pressure becomes equal to the external (atmospheric) pressure. However, as mentioned earlier, an essential oil cannot be heated to a level where its vapor pressure becomes equal to atmospheric pressure due to decomposition. In such a case, there are two ways to proceed. One is to reduce external pressure, that is, through vacuum distillation. In many essential oil-containing materials, the amount of volatile matter is very low, and therefore resorting to vacuum distillation is very expensive and impractical. For the removal of fractions or compounds from an essential oil, vacuum distillation can be employed as in deterpination of citrus oils. The other method is steam distillation (see below).

## Size Reduction

To hasten the release of oil from the cells, it may be necessary to grind the material. However, care should be taken to avoid fine grinding. Fine particles will pack tightly in the still, making it difficult for steam to pass through the bed uniformly. This will encourage channeling of steam. Coarse grinding is more advantageous in such cases.

In some plant products such as black pepper, merely passing through a roller mill once or twice will be sufficient. The berry will flatten into a flake, and cells will open up.

In hard materials such as rhizomes, an initial coarse grinding using a hammer mill or a pin disk mill may be required before passing through a roller mill. In a hammer mill, because of the heavy impact, the temperature rise of the material can be significant. Because of the distribution of points of impact, pin disk mills produce less heat. In cardamom, the essential oil is in the seeds, but they are covered by husk. So the capsules are led to a loosely adjusted plate mill, when the husk opens without damaging the seeds, which are then separated from the husk. Seeds alone are taken for steam distillation.

## Steam Distillation

Steam distillation is a practical method that does not require the use of a vacuum to recover essential oils. When a mixture of two immiscible liquids is heated, with

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agitation, to increase the vapor pressure, each liquid independently exerts its own vapor pressure. This pressure, which is dependent on the temperature, exerts as if other constituents are not present. This results in an increased total vapor pressure contributed by individual constituents of the mixture. Boiling starts at a much reduced temperature when the sum of partial vapor pressures of the constituents is more than the outside (atmospheric) pressure. Thus, in steam distillation, essential oil vapors distill along with water vapor at a temperature close to the boiling point of water.

Steam distillation is the most common method of collecting essential oil from a plant product. On cooling of the mixture of vapors, essential oil that is immiscible with water at ambient temperature separates. Generally, most of the essential oils are lighter than water, and in such cases, they float on top of water. However, there are some essential oils that are heavier than water. In some cases, it may be a mixture of lighter and heavier fractions.

Steam distillation was developed from water distillation. Here, the plant material after size reduction is boiled with water to produce steam, which along with vapor passes on to a receiving vessel after cooling. In crude distillation, there may be no condenser to cool the vapor. Cooling is carried out by keeping the receiving vessel immersed in water or, better, in a stream of running water. As improvements were made, an external source of steam and an efficient water-cooled condenser were introduced.

A modern-day steam distillation unit consists of an external source of steam, in the form of a boiler, and a distillation unit with a false bottom to hold the size-reduced plant product, water circulated condenser, and a receiver where water and essential oil can be collected and separated. The condenser is so designed that vapors are effectively cooled with minimum quantity of water. To obtain this efficiency, the heat exchange area is increased by providing multiple tubes for the passage of vapors. The tubes are surrounded by cooling water. The cold water enters the outlet end of the condenser so that the partially cooled vapors are effectively further cooled. As the cooling water gets partially warmed and moves up toward the inlet end of the condenser, emerging hot vapors will be cooled to some extent, which by further moving down will be completely cooled to ambient temperature.

The cooled mixture of essential oil and water then enters a receiver. In the case of steam distillation of essential oil, because of the high boiling point, the mixture coming out after cooling will be over 90% water and a small quantity of essential oil. It may not be practical to collect the large volume of mixture in order to recover a small quantity of essential oil. In such cases, collection, separation, and removal of water are carried out in a Florentine flask receiver. Most of the essential oils are lighter than water, and an arrangement for such oil separation is presented in Figure 7.1. In the receiver flask, oil floats on top and water collects at the bottom. Discharge is at the bottom so that only water flows to the next compartment. To avoid loss of essential oil in the form of entrapped drops, generally two or three flasks are combined.

Since the outlet is on the bottom, no loss of the lighter oil collected at the top will occur. However, if the oil is heavier, then the outlet should be on the top. In this arrangement, no oil will be lost as it will be collected at the bottom and the separated water flows from the top to the next flask. Here, also to save entrapped drops of oil going with the water, two or three flasks can be arranged. However, in most cases of

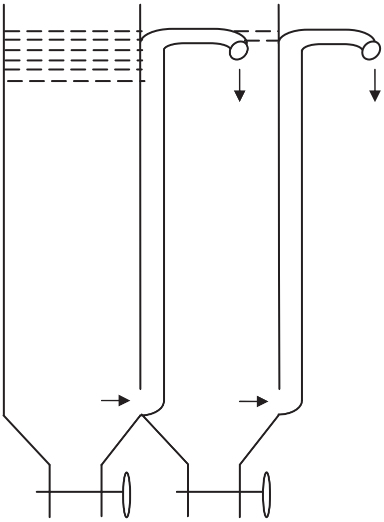

**Figure 7.1.** Receiver for lighter-than-water oil with no heavy fraction.

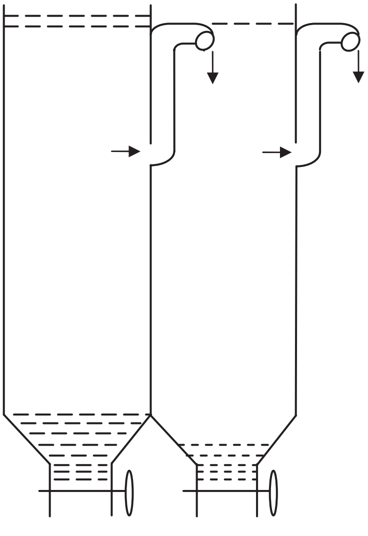

**Figure 7.2.** Receiver for heavier-than-water oil with minute amount of lighter fraction.

heavier oils, some fractions that are lighter may collect at the top. In such cases, the outlet should start from a little below the top but with a siphoning effect so that water column will be maintained as shown in Figure 7.2. Depending on the proportion of lighter fraction in the oil, the point of outlet of separated water should be properly adjusted.

## Separation of Water from the Oil

Generally, one can separate the oil from water from the receiver itself. Considering the high cost of flavor essential oils, every effort to recover oil is often worth it. There is no set procedure, although certain steps can be helpful. In the case of heavy oils such as clove bud oil, the interphase of oil and water may not be very clear. In such cases, the use of a glass separating funnel for the separation of oil and water from the foamy interphase will be helpful. In large commercial firms, unseparated portions from several batches are stored in a stainless steel vessel with a conical bottom and a tap for removing liquid. After some days, water dispersed in the oil will collect, and this can be drawn out and the oil removed.

If the oil is hazy, then it can be treated with anhydrous sodium sulfate, which will absorb the moisture to leave the oil crystal clear. Using a large amount of chemical to clarify essential oil can be expensive. So this treatment is carried out judiciously. The oil absorbed by sodium sulfate can be liberated by adding water. Oil separates easily from the aqueous sodium sulfate. This fraction can be added to the next batch.

Salting out is an old process to separate lighter essential oil from water, when the separation is difficult. Salt dissolves in water, increasing its density. Lighter oil gets pushed to the top of the water phase. This technique is not possible for heavy oil, where oil will be occupying the lower layer. Long storage and careful separation is the way this is accomplished. Some people add the emulsion of oil and water, which is difficult to separate, to the next batch of steam distillation.

Some of the other methods for obtaining essential oils from plant sources are solvent extraction, enfleurage, and cold pressing.

Essential oils being hydrophobic and nonpolar can be extracted by organic solvents, especially petroleum solvents. But the main problem in solvent extraction is extraction of nonvolatile components in the plant material. In the case of spices, such solvent extracted product is known as the corresponding oleoresin. This is described in Chapter 8.

Enfleurage is a classic method for extracting aroma from flowers. Here, flowers are spread on a fat-smeared chassis, which is really a framed glass plate. The aroma and the essential oil get transferred to the refined fat. After the removal of the flowers the next day, the fragrance-containing oil is extracted with alcohol to obtain an "absolute." This process is not common these days. Instead, flowers are extracted by hexane followed by the removal of hexane by distillation to obtain what is known as the "concrete." From the concrete, the absolute is prepared by extraction with alcohol, removal of waxes by wintering and filtering, and partial or full removal of alcohol by careful distillation. It must be stressed here that the above method is generally relevant for fragrance essential oils.

The cold-pressing method is used in the case of fresh citrus peels. Scratching will open the oil cells and pressing will liberate the oil. Scratching is sometimes carried out by rotating in a vessel with a rough surface or with pins. Raspers are also used. Pressing can be by hand, gadgets, or a screw press. Recovery of oil is generally low. More details are given in relevant chapters on citrus oils.

# 8 Solvent Extraction

Chemical constituents that contribute toward taste and color are nonvolatile. To extract such compounds, solvent extraction is the standard practice. In the case of major spices, the most important taste contributed is pungency, or hotness. Black pepper has piperine, capsicum has capsaicin, and ginger has gingerol. Some of the sulfur-containing essential oil components, as in the case of garlic, onion, mustard, and so on, do contribute toward pungency along with powerful aroma. They are exceptions as they can be extracted by steam distillation.

Pungency, or hotness, is not a true taste like sweetness, sourness, bitterness, and saltiness, which are felt by specialized nerve endings in certain regions of the tongue. Pungency, like astringency, coolness, and warmth, are felt almost anywhere in the body especially in the soft and sensitive tissues. Pungency is a pain reaction. When it is felt in the mouth in the right dosage along with other desirable taste and aroma components in a food, it is perceived as a desirable sensoric factor.

Flavoring materials such as coffee, tea, cocoa, and coca leaves contain alkaloids. While bitterness is a distinct taste in these components, they are also capable of affecting the nervous system, which is a desirable sensation at the right concentration. Alkaloids are nonvolatile.

Paprika, turmeric, annatto, and other colored plant products contain natural colorants. They are also nonvolatile and require solvent extraction to produce a concentrate.

Solvent extraction is the process of transferring a substance from any matrix by the use of a liquid in which the substance is soluble. When the extractable component is a solid, as is the case with dried, ground plant material, it is a form of leaching.

The simplest process is batch percolation at ambient temperature. Here, ground dried powder of the plant material to be extracted is filled in a vertical vessel with false bottom. A cloth cover at the bottom will prevent passage of fine particles along with miscella. The packing should be uniform to avoid channeling. Additionally, size reduction should be such that easy and uniform flow of solvent is possible. Recently, countercurrent methods are used in what is known as batch countercurrent extraction. A battery of two or more vessels is used. The early extract will be richer, and this is taken for distillation to produce the extract. The following weaker miscella is directed to the next percolator filled with fresh ground plant material. Since the concentration of the solute is highest at this stage, exchange of this with the weak miscella will occur. Progressively weaker and weaker miscella passes through progressively

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partially extracted plant material. Finally, fresh solvent passes through nearly completely extracted material to complete the process. This procedure goes on in an unbroken manner using two or more extraction vessels.

Generally for spices, organic solvent at ambient temperature is satisfactory. For coffee or tea, hot water is the ideal solvent. In the case of solvent, there is a need to recover the residual solvent adhering to the spent material. Otherwise, the process will become uneconomical. For this, the percolator is provided with a steam jacket and arrangements to connect to a condenser and receiver. Since flavor and color extracts are used in food, it is necessary to have stainless steel in all contact parts.

The batch-type extraction vessels come in different sizes capable of holding half a tonne to 5 tonnes. They require manholes at the top for feeding ground material and at the bottom for removing spent material. These openings should have closures to prevent leakage of solvents. The percolator should also have a discharge opening with tap to withdraw the extract. When plant material is heat-treated while removing adhering solvent, a cake tends to form, causing a problem in removal. Bottom-unloading vessels are often used so that when the bottom is opened on a hinge, the material will flow down and can be collected in a suitable wheeled tray arrangement capable of being pulled out by a motor tractor. The bottom closure should be perfectly made so that when it is shut and secured by bolts, there is no leakage of solvent.

Much of the problem of loading and unloading can be avoided if a continuous extraction facility is used. Here, the dried, size-reduced material is fed into a moving metallic chain. Solvent is sprayed from the top, and fresh solvent at the discharge end where there is nearly extracted material. The partially enriched miscella is pumped up and sprayed at the next segment. Usually, the spraying is carried out in segments numbering between six and 12. From the fresh solvent at the discharge end, each segment progressively enriches the miscella until in the final segment, the enriched miscella will come in contact with fresh plant material, which will have solute at maximum concentration.

Fully enriched miscella after the final segment is taken for distillation, when the extract freed of solvent will be obtained. The spent material at the discharge end is taken out and passed through a heated toasting arrangement to recover the adhering solvent. For feeding of plant material and discharge, a special rotary arrangement to prevent leakage of solvent and its vapors is needed.

While continuous extractors are quick and efficient, they are high on capital cost. In the case of spices, there are many seed spices whose oleoresins will be required in smaller quantities. Even in major spices such as black pepper and ginger, spice oleoresin of different distinct origins is required. Because of this, batch countercurrent extraction cannot be avoided. Continuous extractors are very valuable in the case of *Capsicum annuum*, where oleoresins are specified according to the content of active components rather than the origin. Moreover, such extracts are required in very large quantities. In continuous extraction, the particle size, rate of movement of the chain, thickness of bed, and the number of stages of spraying are all determined according to the type of plant material. A few experimental runs to standardize the process may be required to get maximum efficiency.

Removal of the last traces of solvent is of paramount importance since the extracts and oleoresins are used in food. If water or ethyl alcohol is the solvent, then residue is no problem. But for organic solvents used for extraction, there are strict limits, as shown in Table 8.1. This table is a digest of the regulations; these laws are also updated from time to time. The limit of methanol residue in oleoresin was brought down from 50 to 10 ppm only recently by the European Union (EU).

The removal of solvent from the miscella is best done in two stages. In the first stage, the bulk of the solvent, for example, 90%, can be removed by simple distillation. By resorting to thin-layer continuous distillation, the negative effect of heat on the active components can be avoided, even without use of vacuum.

**Table 8.1.** Limits of residual solvent allowed in oleoresins in different countries

| **FDA in ppm** | **European Union in ppm** | **Japan in ppm** | **Korea in ppm** |
|---|---|---|---|
| Acetone 30 | Et Ac | MDC 30 | MDC, ETC |
| MDC 30 | Acetone *n*-butanol | Acetone 30 | Less than 30 |
| EDC 30 | Hexane | IPA 50 | Singly or in combination |
| | | | Acetone 30 |
| IPA 50 | Ethanol | Methanol 50 | IPA 50 |
| Methanol 50 | Not more than 50 ppm singly or in combination | Hexane 25 | Methanol 50 |
| Hexane 25 | Methanol 10 MDC 10 | EDC not allowed | Hexane 25 |

EDC = ethylene dichloride; MDC = methylene dichloride; Et Ac = ethyl acetate; IPA = isopropyl alcohol; ETC = ethylene trichloride; ppm = parts per million; FDA = U.S. Food and Drug Administration.

**Table 8.2.** Residual solvent in final food

| | **Maximum Residues in Final Food in mg/kg (Parts per Million)** | | |
|---|---|---|---|
| | **EU** | **IOFI** | **Codex** |
| Acetone | GMP | 2 | 30 |
| Benzyl alcohol | | P | GMP |
| Butan 1-ol | 1 | 10 | 1000 |
| Butan 2-ol | 1 | P | 1 |
| Carbon dioxide | GMP | GMP | GMP |
| 1,2-Dichloroethane | | | |
| Dichloromethane | 0.02 | 2 | 2 |
| Ethanol | GMP | P | GMP |
| Ethyl acetate | GMP | 10 | GMP |
| Glycerol | | | |
| Hexane | 1 | 1 | 0.1 |
| Petroleum ether (light) | | 1 | 1 |
| Isopropyl alcohol | 10 | P | |
| Methanol | 10 | 10 | |
| Toluene | | 1 | 1 |

EU: European Union. Council Directive 88/344/EEC as amended by Directive 92/115-94/52-97/60.
IOFI: Code of Practice E12. January 1997. Codex Alimentarius Vol. 1A, 1999 Section 5.
P: Permitted as flavoring or carrier solvent.
GMP: An extraction solvent is considered as being used in compliance with good manufacturing practice if its use results in the presence of residues or derivatives in technically unavoidable quantities presenting no danger to human health.
Blank box indicates no reference to the solvent in the relevant legislation.

The distillation vessel for the second stage should have the ability to connect to the vacuum; a stirring arrangement without affecting the vacuum; the introduction of direct, open steam; and, of course, a steam jacket to raise the temperature. Generally, judicious use of vacuum with stirring during heating will give the necessary reduction in residual solvent content. If needed, steam can be introduced during distillation when traces of solvent will be steam-distilled out. In rare cases, one can admit a small amount of a liquid allowed in food, such as ethyl alcohol, and azeatropic distillation can be carried out with stirring and under vacuum.

However, the EU has now changed its stance regarding the limits of residual solvent in the final food. The values of specified residual solvent limit must be followed. Manufacturers of food items must determine the level of use and other contributing ingredients and then will have to arrive at the amount of residual solvent in the food. The maximum residual solvent permitted in final food is presented in Table 8.2. A longer list of solvents and diluents is given by the various agencies; however, here, relevant solvents only are selectively included.

# 9 Supercritical Fluid Extraction

Any gas above the critical temperature of the substance will not liquefy, even if high pressure is applied. Such a gas acts as a fluid with some special properties. It can pass through solid material easily like a gas and dissolve components like a liquid solvent. In addition, by manipulating pressure, its solubility can be regulated. Thus, there is a great potential to effect fractional extraction of specific components.

Carbon dioxide can exist as a solid, liquid, or gas. It has a critical temperature of around 31°C; above this, the compound will remain a gaseous fluid. The removal of solvent can be performed simply by releasing the pressure. Even if residual solvent is present, carbon dioxide is a safe and natural component present in the atmosphere, inside the body, and in some foods. Water can also be used as a supercritical fluid (SCF), but its critical temperature is very high and therefore inconvenient except in very special cases.

The advantages and disadvantages of supercritical carbon dioxide extraction are as follows.

## Advantages

1. Carbon dioxide is chemically inert, inflammable, nontoxic, noncorrosive, and cheap.
2. Extraction can be carried out at a low temperature, so that temperature-sensitive and very volatile compounds in the extract are unaffected.

## Disadvantages

1. More solvent is required to achieve the same degree of extraction as compared with conventional solvents. However, this can be partly overlooked, as SCF is recycled.
2. Since carbon dioxide is nonpolar, it is a good solvent for nonpolar compounds only. It cannot dissolve sugars, glycosides, salts, or similar compounds. However, this property may be a boon for flavors, as the flavor will not be contaminated or diluted with unwanted polar nonflavor compounds.

While it is not our intention to go through the finer details of SCF extraction, some general aspects will be described. SCFs have properties between those of a gas and

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liquid. Since there is no interphase between liquid and gas, there will be no surface tension. Thus, by changing the pressure and temperature (above critical temperature), the SCF can be adjusted to be more gas-like or liquid-like. At the same temperature, solubility generally increases with the density of the SCF.

Making use of these aspects, SCF extraction is used in a wide range of operations such as dry cleaning, dying, nanotechnology, and pharmaceutical extractions. Its use in flavor and color materials is somewhat limited at the present. The main disadvantage of SCF extraction is that expensive equipment (pressure vessels) are required. There are also limitations in the capacity that can be achieved. One of its chief advantages, the absence of harmful residual solvent, cannot be exploited effectively, since food laws of various countries allow 25–50 ppm of common organic solvents used in extractions.

Removal of carbon dioxide does not require the heat treatment generally needed in the case of solvents such as petroleum ether and alcohols. But many natural flavor and color materials such as black pepper, ginger, coffee, turmeric, and chili are already exposed to heat during drying or curing. Furthermore, in many cases, cooking or food processing involves heating. In flavor materials, some of the flavor is thermally generated. However, SCF extraction will be quite beneficial for flavor from undried plant products or for fragrance materials where absence of heat during processing will be a great advantage.

Supercritical carbon dioxide extraction is used in the decaffeination of coffee. Generally, it is difficult to remove the last traces of solvent from the extracted solid plant material. In decaffeinated coffee and denicotinized tobacco, it is the solid material after extraction that is important. This technique is also used for extraction of acids from hops. Here, the specificity of SCF at different pressures can be used to concentrate either on $\alpha$-acid, which contributes to bitterness, or $\beta$-acid, which contributes to aroma.

Many efforts have been made to produce spice oleoresins using SCF extraction. However, extra capital cost, limitation of capacity, and the allowance of residual conventional solvent up to a level as per existing food laws have limited its popularity. Citrus oils are produced without heat or solvent, and therefore, there is no necessity to use SFC extraction.

Liquid carbon dioxide is used in some extractions, but then there is no SCF effect. It is used merely to reduce the temperature of extraction and to avoid residual solvent.

# 10 Homogenization of Extracts

Many extracts, especially those obtained through extraction with organic solvents, may not be uniform in consistency. There will be a lot of lipophilic constituents that give a turbid appearance. In both solvent-extracted and water-extracted materials, there can be impurities such as sediments, fine particles, and thick liquid globules, which will give a hazy appearance. Sometimes the extractives may contain two major components like essential oil and nonvolatile components, which may not form a homogeneous body. To solve such problems there are various operations, described below.

## Diluents

Diluents are necessary for strength reduction and standardization. When the extracts are aqueous, then dilution can be carried out with water. However, sufficient total soluble solids strength is necessary for the extract to be safe from contamination. A total soluble strength of above 65° Brix is regarded as safe, especially if the pH is low. To standardize the strength of an active component, a small quantity of water can be added.

In oily extracts, special diluents are required. The final criterion is good solubility. It should also be safe for use in food. Some of the more commonly used diluents are listed below.

**Fixed oil diluents.** Many vegetable oils are used as diluents. At one time, soybean oil was popular. However, the problem with oils derived from beans and nuts is the possibility of allergy. Today, sunflower seed oil is a commonly used diluent for standardization of strength. Castor oil with ricinoleic acid will give a mild water dispersibility.

**Propylene glycol**, or 1,2-propanediol ($CH_3CHOHCH_2OH$), is not an emulsifier but a diluent. It has miscibility in water and oil and therefore can bring about homogeneity. It is a viscous clear liquid with a density of 1.0362 g/mL at 25°C. (FEMA: 2940; CAS: 57-55-6; US/CFR: 184.1666; E-no. 1520.)

**Triacetin**, or triacetyl glycerin, is also a diluent. It also has solubility in both water and oil. It is a colorless, slightly oily liquid with a bitter taste. It has a boiling point of 258–260°C and a density of 1.1562 g/mL at 25°C; therefore, it is useful as a diluent for heavy oils like garlic oil. (FEMA: 2007; CAS: 102-76-1; US/CFR: 184.1901; E-no. 1518.)

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Apart from these, many liquids usually used in food can be diluents. They include ethyl alcohol, acetic acid, and glycerol. Even chemical liquids not associated with natural foods but regarded as reasonably safe such as ethyl acetate, benzyl alcohol, and isopropyl alcohol are used as a diluent in special cases.

## Emulsifiers

Heterogeneity can appear due to the presence of lipophilic and hydrophilic components. A similar case is when one wants to make an oily extract into a water-soluble or water-dispersible emulsion. In some cases, emulsifiers can help solve the problem.

Emulsifiers are surfactants, which are useful as detergents, wetting agents, antifoaming agents, and so on. Such molecules will have a hydrophilic end (e.g., sodium of a soap) and a lipophilic end (e.g., aliphatic end of a fatty acid). The hydrophilic/lipophilic balance based on the structure of the molecule determines its efficiency to function as an emulsifier. In an oil-in-water dispersion, the lipophilic end will be attached to the oil droplet. Micelles are formed with oil droplets with surrounding molecules of emulsifier with the hydrophilic ends outside in water. Such a system can form a stable dispersion.

Emulsifiers are either oil-in-water or water-in-oil type. Based on the molecular mass of the hydrophilic end and the mass of the whole molecule, the hydrophile/lipophile balance (HLB) value of an emulsifier is fixed on an arbitrary scale of 0–20, with 0 corresponding to a completely hydrophobic molecule and 20 corresponding to a completely hydrophilic molecule. A good emulsifier for a water-in-oil type of emulsion will have an HLB value of 4–6, while an oil-in-water type will have an HLB value of 8–18.

Some commonly used emulsifiers are presented below.

**Polysorbates** are excellent emulsifiers, which can be used to bring about water solubility for spice oleoresins. It can be described as polyethylene glycol sorbitan monooleate when it is supplied as polysorbate 80. While it is also supplied as derivatives of saturated fatty acids for use in liquid spice extracts, the oleic acid derivative is the most satisfactory. With unsaturated fatty acids, the HLB will be 10–16. The oleic acid derivative is a yellowish viscous liquid. In recent years, some countries in Europe, as well as Japan and Korea, have raised doubts about its safety, although it is still legal to use it. (Polysorbate 80: FEMA 2917; CAS: 9005-65-6; US/CFR: 172.515; E-no. 432.)

**DATEM**, or diacetyl tartaric acid esters of mono- and diglycerides of fatty acid, are partially soluble emulsifiers, which make oleoresins water dispersible. HLB for DATEM will be 7–8.

Fatty acid esters of many polyhydric compounds are also emulsifiers. Of these, **sucrose esters of fatty acids** are good emulsifiers with a high HLB value (7–16) and polarity. (FEMA 4092; US/CFR: 182.1101; E-no. 472e.)

**Glyceryl monooleate** is a good emulsifier, especially to make lipid products more dispersible in oil. During esterification of glycerol with a limited quantity of fatty acids, generally about 20% will come as diglycerides and the rest as monoglycerides. Therefore, these are sometimes referred to as mono- and diglycerides. For oleoresins that are liquids, oleic esters are more suitable than esters of saturated acids. HLB for glyceryl monounsaturated fatty acid will be 3–4. (FEMA: 2526; CAS: 111-03-5; US/CFR: 172.515; E-no. 471 [unsaturated].)

**Glycerol-polyethylene glycol oxystearate** (macrogol-glycerol hydroxyl stearate) produced from hydrogenated castor oil is a new class of emulsifier, which is very effective in making oily extracts water-soluble. Food laws of major countries have not allowed this as yet. It is manufactured by BASF with the name Chremophor and by ICI/Uniquema (now by Creda Chemical Co.) with the name Cresmer.

**Lecithins** are a complex mixture of phosphatides and glycolipids. They are obtained from soy, corn, sunflower, and rapeseed. It comes as a cream- to brown-colored viscous liquid. It increases miscibility in oil. The HLB will be around 3–4. (US/CFR: 184.1400; E-no. 322.)

## Mechanical Homogenizers

Homogenization is a process that makes a solution or extract become uniform. Chemical emulsifiers can do this to a point, but even when they are used, mechanical homogenizers can complete the process more efficiently. Homogenizing can also help to reduce the quantity of emulsifiers used.

In homogenization, pressure is used on liquids to subdivide the particles or droplets present into even smaller particles. By breaking down liquid coagulates and globules to submicron size, a stable dispersion can be created. In an ordinary household, the same techniques are used when working with an egg beater or mortar and pestle. The following are some of the techniques used in the food industry to obtain a stable suspension of a dispersed liquid, generally thick, in the main product.

### Colloid Mill

When a thick extract is heterogenous, the best way to bring it to homogeneity is by passing it through a colloid mill. The action of a colloid mill is like the size reducing of solids in a plate mill.

In a colloid mill, fluid shear is caused by a high-velocity stream to disperse particles or liquid droplets. Small particles so formed will give a stable dispersion or emulsion. Sometimes in addition to size reduction, weakly bonded agglomerates are disrupted. The particle size of the globules will usually be below 5 $\mu$g when stability is attained.

In a typical colloid mill, the feed liquid is fed through a hopper to pass through closely spaced surfaces, one of which will be moving at a speed greater than that of the other surface. One design involves liquid passing through a disk-shaped rotor and casing, with the clearance being adjusted to below 20 $\mu$m. To avoid heating due to friction, cold water is circulated.

### Ball Mill

This type of mill is generally used to reduce the size of hard brittle materials, like minerals. However, moderate-sized mills can also be used to break the globules in food extract into a small size to obtain homogenization. The action is more like a mortar and pestle.

Since the materials handled are food items, a stainless steel drum has to be used with heavy ceramic balls. A typical ball mill used for homogenization of black pepper oleoresin consists of a stainless steel horizontal drum, which can rotate on a horizontal axis. A large opening is provided for introducing the ceramic balls inside. From a point opposite to the main opening, another opening with a tap is provided to withdraw the homogenized liquid product. A convenient size is about 1000-L capacity, filled to about one-third capacity with 1000 kg of ceramic balls of 30-mm diameter. About 500–600 kg of oleoresin is poured from the main opening, which will fill about half the drum containing the balls. The drum and its contents are rotated using a motor. The speed and duration of revolution can be adjusted according to the nature of the extract to be homogenized.

### *Sand Mill*

The modern pressurized horizontal sand mill is a natural extension of the ball mill for use as a homogenizer. In a sand mill, there are a series of disks rotating at high peripheral speed. The centrifugal force transmits the power, making small glass beads (1.5- to 2.0-mm size) rotate inside a jacketed chamber. The movement of beads closer to the disk is greater than that of those further inside. When the slurry passes through such a system, the globules are broken down by shear caused by differential rotational velocities of the beads. The speed of rotation and packing of beads can be adjusted according to the viscosity of the product slurry and nature of the globules. The equipment can also be used to homogenize fractions of different densities.

### *Pressure Homogenizer*

Various well-known brands of pressure homogenizers of different capacities are available. In this, the product to be homogenized is passed at a very high pressure through a specially designed homogenizing valve with an adjustable gap. The design will include a single-acting reciprocating multiple pump to force the liquid through the valve. The pressure created on striking a stationary surface is able to break globules to micron-sized droplets.

This type of homogenizer is particularly useful to homogenize liquid slurries of water, flavor extracts, and hydrocolloids used for spray drying. When oily extracts are made water-soluble or dispersible by use of an emulsifier, passing through a pressure homogenizer will improve efficiency and decrease the quantity of emulsifier required.

### *Sediments and Impurities*

Sometimes oily extracts may contain unwanted thick globules. If these globules tend to settle to the bottom, then a super centrifuge will be useful. In a super centrifuge, slightly heavier globules will be collected in the central collection tube, while clarified material will pass through the outlet. In capsicum and paprika oleoresins, this is a nice way to get a clear product free of sediments. In aqueous coffee and tea extracts, there can also be sediments that can be clarified by super centrifuge.

When the impurities are of solid nature and in larger quantity, they can be filtered away. A basket centrifuge with appropriate filter cloth will be satisfactory. Filtration by basket centrifuge will be considerably cheaper than a super centrifuge where the separation is based on gravity.

### *Water Solubilization*

Many natural flavors and colors obtained by extraction with organic solvents are mostly lipid in nature and have very low dispersibility in water. Water solubility or dispersibility can be introduced using emulsifiers. Polysorbates are satisfactory for this purpose. In some cases, only a temporary dispersibility is required, since after this, the intermediate product is taken for secondary processing. In such cases, a lesser quantity of emulsifier is required, or a less efficient one like DATEM can be used. Needless to say, in all these cases, mechanical homogenizing will be beneficial.

When the lipid extracts are required to be in an aqueous phase with plenty of solids, as in bread dough, oily extracts can be used without emulsifiers, because the solids will help in making the dispersion stable.

In the past, constituents that have a carboxylic or hydroxyl group were converted to a potassium or sodium derivative to introduce water solubility. With efficient emulsifiers available today, the trend is to avoid the use of alkali in food processing.

Size reduction of the dispersed phase by mechanical homogenization is the key to obtaining a stable colloidal solution. Additionally, the use of an emulsifier will be very beneficial.

Diluents such as propylene glycol with solubility in both water and oil are not emulsifiers, but they can be used judiciously to reduce the quantity of more expensive emulsifier to be used.

# 11 Suspension in Solids

Many extractives like essential oils, oleoresins, and color extracts are oily liquids. For some applications, these must be made into a solid powder. Two methods of suspension in solid matrix are plating and microencapsulation by spray drying.

## Plating

When an oleoresin has to be made into solid suspension for use in solid food products like cookies, cakes, or other bakery items, it can be mixed with an appropriate percentage of a solid that will not interfere with the final food. Sugar, dextrose, salt, corn or other cereal flour, and rusk powder can be used. The appropriate amount of flavor extract is mixed with any of the above in powder form. The flavor strength will be lower per unit weight.

If a mild water dispersibility is desired, then maltodextrin or other modified starch will be helpful. An emulsifier like polysorbate can also be added to increase the water solubility of the plated powder. Mixing is very important for uniform spread and avoidance of lumps.

## Microencapsulation by Spray Drying

Microencapsulation is a process in which tiny particles or droplets are surrounded by a coating to produce very small capsules with many useful properties. It is a specialized form of edible packaging of a food ingredient. Of course, the material used to form the protective packaging must be safe for eating.

In its simplest form, a microcapsule is a tiny sphere having a uniform wall and with a hollow inside to hold a droplet of the desired ingredient. The material inside is referred to as the “core” and the protective outside sphere as the “wall.” Generally, the particle size ranges between 1 and 200 $\mu$m.

Many flavors and extracts used in candies, soup powders, other foods, and cosmetics are liable to be subjected to oxidative deterioration and loss due to evaporation. For example, if cardamom oil is blended with tea to be filled in a tea bag, the volatile oil will be lost gradually by evaporation. If the oil is protected by microencapsulation, this will not happen during a specified shelf life. When the bag is dipped in hot water at the time of consumption, only then will the volatile oil be released, giving the rich flavor of cardamom to the tea.

One of the most successful methods of microencapsulation is spray drying. The first step in microencapsulation is to make a colloidal suspension of the core material

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in an aqueous solution of wall material. Two classic wall materials are maltodextrin and gum acacia. Both of these give emulsion with low viscosity capable of being pumped through the atomizer of the spray dryer. Of the two wall materials mentioned above, gum acacia is more efficient; maltodextrin is cheaper. In fact, among the naturally occurring gums or hydrocolloids, gum acacia has the lowest viscosity in solution form. Recently, some specialized starch-based gums have been made available for use in spray drying with greater efficiency.

A typical mixture of various ingredients taken for homogenization can be as follows: water 70 L, gum acacia 22.5 kg, and oil (such as cardamom oil) 7.5 kg. Oil represents 25% of the mixture other than water, which will be evaporated. In the final spray-dried powder, oil will be less than 25% due to loss. Maltodextrin gives a much lower loading in the final powder, while higher loading can be obtained by special modified starch designed for spray drying. This mixture, after being stirred with a ladle, is passed through a pressure homogenizer where a stable colloid will be formed. Each colloid particle will consist of a droplet of core material surrounded by an aqueous solution of the wall material. When such a suspension is passed through the atomizer of the spray dryer, each colloidal particle will dry into a powder. As explained earlier, the powder will consist of a central core of volatile oil surrounded by a spherical dry wall formed by the evaporation of water during the passage through the hot zone of the spray dryer.

Lipophilic materials like essential oil and oleoresins when spray dried with modified starch or gum acacia will become easily water-soluble. When viscous products like oleoresin are to be spray dried, for the stability of colloid suspension, it may be necessary to add an emulsifier such as polysorbate, in addition to the hydrocolloid, to the slurry.

In some materials like coffee extract, which is soluble in water, there is no colloid formation. Very small quantities of coffee extract, in the form of tiny droplets, when sprayed will dry to tiny particles. In this case, there is no wall or core to be discerned.

## Spray Drying

A spray dryer is a device used for converting a liquid solution or suspension of an extract or other ingredient into a dry powder. Usually, since the liquid passes through the drying zone as spray particles, drying will be effected in only a few seconds.

The main part of the spray dryer is a tall metallic cylindrical chamber with a conical bottom. The upper zone is kept hot by admitting hot air from an external furnace. The inlet temperature will be around 185–195°C and the outlet temperature generally around 90–95°C, depending on the material to be dried. At the top end, there is an arrangement to spray a water solution or a suspension of the material to be spray dried. Spraying is done using a pump, which will allow liquid to be sent through a nozzle in the form of a spray. Depending on the material to be sprayed and final particle size desired, there are many designs of nozzles. As the sprayed drops fall down and pass through the hot zone in the upper section of the chamber, they are dried by the removal of moisture to form solid particles. Other features of the equipment are an opening at the bottom for removal of dried particles collected at the conical section, insulation of the chamber to avoid heat loss, and a tapping or vibrating device to encourage particles to fall into the bottom of the cone. An outlet is provided at the bottom for an airstream carrying moisture to escape through a cyclone or a bag filter to recover any escaping spray-dried product. Instead of two points of collection of the product, modifications can be made to have a single point of collection. It may be a good idea to make an air-conditioned or dehumidified enclosure around the withdrawal opening at the bottom to protect the hygroscopic powder.

A moderately sized spray dryer will have a chamber of about 3 m in diameter and 6 m in height, half of which will be the conical bottom. The angle of the cone side to perpendicular will be around 60°. The chamber must be made of stainless steel when the spray-dried material is used in food.

The heart of the equipment is the nozzle through which the colloidal solution of the slurry is sprayed. A high-speed rotary atomizer revolving at a speed of 15,000–35,000 revolutions per minute, with cocurrent swirling action, will yield a fine powder. A high-pressure nozzle at the top yields a coarser powder. Here, the spray is directed downward with less swirling. For this, a much thinner and taller chamber will be suitable. There are many specialized nozzles depending on the material and nature of the powder required. One such is the two-fluid nozzle fixed at the middle portion of the chamber. Here, air and slurry to be dried are sprayed upward.

The size of the powder particle is important. This depends on the food material with which the microencapsulated product is to be mixed. For example, if the tea particles are larger, a comparable size of spray-dried particles will be required to regulate the desired proportion during the filling of the tea bags. Fine spray-dried instant coffee tends to form lumps while dissolving in water. The above defects can be corrected by increasing the size of particles by a technique known as agglomeration. In this process, particles are critically wetted and made to stick together by collision caused by the turbulence introduced. When particles adhere to form the desired size, it is made into a nonsticky agglomerate by drying.

# 12 Deterioration During Storage and Processing

During the storage of plant products like spices, if drying is not carried out properly, there is a chance of fungus contamination. This could lead to a musty flavor, which will be transferred to the extractives. An even greater danger in the case of extensive contamination is the possibility of formation of mycotoxins. When plant material is partially dried and stored, there is the danger of loss of color in products like chili and cardamom. Excessive exposure to sunlight can also cause loss of color, especially in the case of curcumin of turmeric and chlorophyll. Carotenoid pigments are also affected by light, though to a lesser extent.

During processing, there can also be chemical changes. Heat treatment of extract of paprika, marigold, and tomato gives traces of toluene and *m*-xytene (Rios et al. 2008). A temperature of 80°C and below during processing ensures that these artifacts are indeed very low. The presence of other compounds such as methyl benzaldehydes or isophorones indicates carotenoid oxidation.

Formation of breakaway small molecules is a possibility when complicated molecules, such as those in flavoring materials, are subjected to processing. The presence of toluene and acetone has been reported in ginger (Chen and Ho 1988). This may not be a case of thermal degradation, as the study is on the extract of freeze-dried ginger powder by liquid carbon dioxide. Benzene and toluene have been noticed in another study on ginger oil (Erler et al. 1988). In turmeric extraction, acetone has been detected even when no acetone was used for extraction (Binu et al. 2007). The damage may be due to the heating carried out during estimation itself. Oleoresin analysts are sometimes intrigued by the presence of an unaccounted-for quantity of residual methanol.

In the case of ginger oleoresin, excessive heat, above 80°C, may result in gingerols being converted to shogaols. Gingerol content is important when ginger oleoresin is used for pharmaceutical purposes. In such cases, there is a need to restrict the temperature of processing, preferably below 70°C, but never above 80°C.

When the two-stage extraction procedure was introduced in India, there was fear that piperine would be lost due to prolonged heating during the first stage of the steam distillation step to recover volatile oil. To remove the moisture prior to the second stage of solvent extraction, some manufacturers resorted to sun drying. However, experience has shown that if shade drying is used, there is no noticeable loss of piperine.

Loss of xanthophylls occurs during heat treatment of extracts such as paprika and marigold. Curcumin of turmeric is remarkably stable during the heating carried out

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during normal processing. However, curcumin, especially in extract form, is sensitive to light. In fact, all natural colorants are affected by exposure to light and therefore need protection.

## Autoxidation

Autoxidation is a process where molecules such as unsaturated lipids are converted to peroxide through the influence of atmospheric oxygen. It is a free radical chain reaction. Unsaturated fatty acids of an oil get converted to peroxide and further to carbonyl compounds and can even result in breakdown products. In food, propagation of the reaction can lead to rancidity, which will cause an unwelcome off-flavor. During the process of secondary reaction, an autoxidized molecule can give off energy to another unsaturated molecule, which then continues the chain reaction through formation of peroxide, oxygenated carbonyl derivative, and breakdown products with unwanted rancid odor.

Keeping material protected from light and heat will reduce the intensity of autoxidation. An effective method is the addition of antioxidant, which acts as a chain breaker. Iron and other metals act as prooxidant; therefore, keeping the material in metal containers will increase autoxidation. Storage has to be in food-grade stainless steel, appropriate polymer, or glass packaging containers. Some of the antioxidants used in natural flavors and colors are listed below.

## Antioxidants

Antioxidants are required in the case of carotenoid colors, especially when dissolved in a fatty oil as is the case with paprika oleoresin. While there are many synthetic antioxidants like butylated hydroxyl anisol (BHA), butylated hydroxy toluene (BHT), tertiary butylated hydroxy quinone (TBHQ), and ethoxyquin (EQ), many people prefer natural antioxidants.

Tocopherol mixture (vitamin E) is a valuable natural antioxidant. It is usually a mixture of $\alpha$, $\beta$, $\gamma$, and $\delta$ tocopherol. Commercial tocopherol manufactured for antioxidant use comes in a strength up to 70%. The product is a golden brown-colored oily liquid with a mild characteristic odor. China has become a good source for tocopherols.

Rosemary extracts are now considered to be a valuable natural antioxidant. The active component in these is carnosic acid. Commercial preparations are available from 5% carnosic acid, but can be found as high as 50%. Recently, rosmarinic acid of rosemary has been found to be even more effective as an antioxidant.

Ascorbic acid is a synergist and works more effectively with a proper antioxidant. While it is available as a salt, one derivative that is effective is ascorbyl palmitate. Both ascorbic acid and ascorbyl palmitate come as a white powder.

## References

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Erler, J.; Vostrowsky, O.; Strobel, H.; and Knobloch, K. 1988. Uber atherische ole deslingwer, *Zingiber officinale* R. *Z. Lebensm. Urters. Forsch.*, **186**, 231–234 (see Lawrence, B.M., Progress in essential oils, *Perfumer Flavorist* 1990, **15**, 167).

Rios, Jose J.; Fernandez-Gracia, Elisabet; Minguez-Mosquera, Maria Isabel; and Perez-Galvez, Antonio. 2008. Description of volatile compounds generated by the degradation of carotenoids in paprika, tomato and marigold oleoresins. *Food Chem.* **106**, 1145–1153.

# Part II
# Individual Flavors and Colorants

## Introduction

This part deals with a wide range of natural materials that are already in production and use. In each case, there is a description of the plant (or animal) material, matters relating to extraction, a bit of the chemistry of the active components, and their properties. Identification numbers of major regulatory bodies will help students in obtaining more details. Some relevant references are listed for each item.

It can be seen that some colorants are from microbial and others from entomological sources. In fact, these two sources have a very promising future. Biotransformation of molecules by microorganisms and tiny insects is a dynamic tool which produces biologically oriented molecules that have the desired flavor and color useful in making foods more appealing and safe.

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# 13 Ajwain (Bishop's Weed)

*Trachyspermum ammi* L Sprague (*Umbelliferae*)

## Introduction

Ajwain (spelled "ajowan" outside the United States) is also known as Bishop's weed. It is a small caraway-like seed which belongs to the parsley family and is sometimes mistaken for lovage seeds. It is not clear how it acquired the name Bishop's weed. It is very important in Ayurvedic therapy as a medicinal product. The name originated from Sanskrit and almost all over the world it has a similar sounding name. In Arabic, it translates as "cumin of the king." It grows wild in Africa and its Ethiopian name is "azmud." The plant most likely originated in the eastern Mediterranean, probably in Egypt. Thymol is its principal constituent and therefore its flavor has some resemblance to thyme.

## Plant Material

Ajwain is an annual herbaceous plant, growing to a height of 90 cm, with a profusely branched stem. The leaves are primately divided with 24 × 14 cm size and with clasping leaf base. The inflorescence is a compound umbel, each containing a few hundred flowers. The fruit is 2–3 mm long. On drying, the gray-brown fruit becomes the spice, generally referred to as seed. Often, the seed will have a hair-like attachment to the plant. Mild roasting gives it an enhanced aroma.

India is a major producer of ajwain, as it is used in many vegetarian dishes. It is also grown in Egypt, Afghanistan, and Iran. Ajwain has 15.4% protein, 18.1% crude fat, 38.6% carbohydrates, and 11.9% crude fiber. It is rich in minerals: calcium 1.42%, phosphorus 0.30%, and iron 14.6 mg % (Pruthi 1976).

## Essential Oil

In India, the seeds are mostly distilled in primitive stills, but there are also modern facilities that produce quality oil. The yield is reported to be 2.5–4%. In early twentieth century, some seeds were exported to Europe and the United States for distillation. Most likely this was for the separation of thymol, which has demand in medicinal preparation. However, with the introduction of synthetic thymol, export for this purpose died out.

Some monoterpenes have been reported in the literature (Akhtar et al. 1988). They include $\alpha$-pinene 1.8%, camphene 0.5%, $\beta$-pinene 3.5%, myrcene 0.3%, $\delta$-3-carene

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**Table 13.1.** Analysis of ajwain oil

| Constituent | Content as % v/w |
|---|---|
| $\alpha$-Pinene | 0.2–1.0 |
| $\beta$-Pinene | 2.0–5.0 |
| Limonene | 0.1–0.6 |
| *p*-Cymene | 20.0–25.0 |
| $\gamma$-Terpinene | 40.0–45.0 |
| Thymol | 20.0–30.0 |

0.5%, limonene 5.1%, $\alpha$-terpene 34.9%, and *p*-cymene. The major oxygenated derivatives are thymol (45.2–48.5%) and carvacrol L (4.5–6.8%).

In the author's lab, oil is produced by steam distillation. The oil is a colorless to brownish liquid possessing a characteristic thyme aroma.

Physical characteristics are as follows.

| | |
|---|---|
| Optical rotation | –1° to +5° |
| Refractive index | 1.490–1.499 at 25°C |
| Specific gravity | 0.895–0.910 |

No oleoresin is known to be produced.

In the author's lab, a sample of oil produced and analyzed on gas chromatography (GC) is presented in Table 13.1. The major constituents seen are $\gamma$-terpinene, *p*-cymene, and thymol. However, for producing the best quality oil, generally during distillation the first fraction is cut off and the second fraction is taken. This will show a thymol content of 40–42%, with corresponding reduction in *p*-cymene (12–18%) and $\gamma$-terpinene (30–38%).

Analysis of a sample from Algeria and several samples from India was complied by Lawrence (2006). The major components are thymol, isothymol, $\gamma$-terpinene, limonene, and *p*-cymene. However, there are also some significant minor components.

## Uses

Ajwain has a characteristic phenolic/medicinal flavor due to its thymol content. Its herbaceous and acrid taste is used in some vegetarian dishes. Ajwain could be useful in processed foods such as caramelized onion soups and similar dishes, where it can give an interesting flavor variation.

The main uses of ajwain and its oil are in medicinal preparations for stomach and intestinal treatment. It also has use in the treatment of bronchitis and asthma.

## References

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Pruthi, J.S. 1976. *Spices and Condiments*. New Delhi: National Book Trust, pp. 6–8.

# 14 Allspice (Pimenta)

## *Pimenta officinalis* Lindley (*Myrtaceae*)

### Introduction

When Spanish explorers under Columbus entered the West Indies, they thought that they had discovered the source for black pepper when they saw the berries of the allspice tree. This is because the dried berries are round with a dark wrinkled surface similar to that of pepper. Consequently, the explorers gave the tree the name *pimenta*. The berries have the same astringency and aromatic flavor as black pepper, though they lack the extreme hotness. Allspice berries are also a bit larger than pepper berries. It is reported that Azetics used them to flavor the cocoa drink. Pirates of the Caribbean Islands used it to flavor their meat; it used to be called Jamaican pepper. The name "allspice" was earned because the flavor appeared to be a combination of cloves, cinnamon, nutmeg, and black pepper.

### Plant Material

Jamaica is the major producer of allspice. It is also grown in Mexico, other West Indian islands, and countries of Central America. The Jamaican government prevented the spread of the plant for some time by restricting the export of the plant and its seedlings. Many early efforts to germinate the seed in other tropical lands met with failure, so much so it was thought that it would not grow outside Jamaica or other nearby areas. It is now understood that passage through the digestive tract of birds is helpful to prepare the seeds for germination. With better knowledge of biochemistry, allspice is now making its appearance in places such as the Kerala state in India, Sri Lanka, and Indonesia, where the agro-climatic conditions are favorable for tree spices like allspice.

Allspice is a bushy tree with a height of 6–9 m. The vegetative growth is profuse and spreads in a globe of 4–7 m wide. In the main growing region of Jamaica, the tree is semiwild. The trees are either male or female, so cultivation has to be performed in such a way that male and female trees grow side by side for easy pollination.

The leaves are about 15 cm long and oblong in shape. Leaves are aromatic and yield an essential oil. The aroma characteristic resembles that of the bay leaf. The berries are hard and round (Photo 1). Mexican berries are larger, with a diameter of 5–7 mm, while Jamaican berries have a diameter of 4–6 mm. On drying, the berries resemble dried black pepper, except for a larger size and slightly less black color.

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**Photo 1.** Dried allspice (pimenta). See color insert.

**Table 14.1.** Analysis of pimenta of different origins

| Origin | Volatile Oil (vo) Content Clevenger Method, Water Distillation % v/w | Resin % by Hexane extraction | Total Yield of Oleoresin (vo + Resin) |
|---|---|---|---|
| Jamaica | 3.2 | 5.0 | 8.2 |
| Mexico | 2.3 | 4.7 | 6.8 |
| Guatemala | 1.8 | 4.0 | 5.8 |

## Chemistry

Typical allspice, on analysis, shows about 6% protein, 6.6% crude fat, 52.8% carbohydrate, 21.6% crude fiber, minerals such as calcium, phosphorus, sodium, and potassium, and water-soluble vitamins.

However, the most important constituent of allspice is the essential oil, which is present to a level of 3–4.5% on dry basis. The characteristic aroma is influenced by the main constituent eugenol (see Chapter 36 on clove).

## Essential Oil

Allspice seeds from three origins have been analyzed for volatile oil content and yield of resin by solvent extraction of the deoiled residue. For this, deoiled material is dried and extracted by cold gravity percolation using hexane as the solvent. The results are presented in Table 14.1. Jamaican allspice shows a higher yield of both oil and oleoresin.

**Table 14.2.** GC analysis of Jamaican pimenta oil (area percentage)

| Constituent | Percentage Range |
|---|---|
| Eugenol | 80–87 |
| $\beta$-Caryophyllene | 4–8 |
| $\beta$-Phyllandrine | 0.2–0.5 |
| 1,8-Cineole | 1–3 |
| $\alpha$-Pinene | <0.3 |
| $\beta$-Pinene | <0.3 |
| $\delta$,-3-Carene | 0.5–2 |
| Limonene | <0.5 |

Commercial steam distillation using external steam and a stainless steel still is carried out. Size reduction is done using a roller mill where round berries are turned into flat flakes. Steam is let in at a slow rate at normal pressure for a period of 18 hours. Most of the oil is heavier than water, with a small quantity being lighter. On mixing, the total yield is 4.0%.

A typical GC analysis of Jamaican allspice oil is presented in Table 14.2.

Much analytical work carried out in recent years shows that the allspice oil contains mainly methyl eugenol and eugenol. There are some minor components that will naturally influence the quality of the oil. Lawrence (2006) has compiled this list into a useful review for further information.

Pimenta berry oil is a heavy yellow to reddish-yellow clear oil with a fine aroma reminiscent of clove, cinnamon, nutmeg, and black pepper. It turns darker on keeping.

According to the Food Chemical Codex (FCC), *pimenta* oil occurs as a colorless, yellow, or orange liquid that becomes darker with age. It has the characteristic odor and taste of allspice. It is soluble in alcohol, in propylene glycol, and in most vegetable oils.

Physical characteristics as defined by the FCC are as follows.

| | |
|---|---|
| Optical rotation | −4° to 0° |
| Refractive index | 1.527–1.540 at 20°C |
| Specific gravity | 1.018–1.048 |
| Solubility | 1 mL dissolves in 2 mL of 70% alcohol |

## Oleoresin

Hexane is a satisfactory solvent for extraction of deoiled Jamaican allspice. Deoiled material is packed in a percolator and extracted using hexane by cold percolation. The combined miscella on removal of solvent yields 3.8% of resin on the basis of whole allspice. Resin can be blended with the required quantity of previously collected oil.

*Pimenta* oleoresin is a dark greenish-brown, viscous liquid with a pleasing spicy aroma and flavor of clove, cinnamon, nutmeg, and pepper.

## Uses

Allspice flavor is very important in Caribbean cooking. It is used in sausages and other meat products. Its flavor is well liked in sauces and in pickling. In the Middle East, the flavor is also popular. It is used in American desserts and European sausages. When included in processed food, pimenta oil and oleoresin are very convenient to use. Generally, oleoresin gives a fuller and rounded flavor compared with essential oil. Having a reasonable amount of eugenol, it has some antimicrobial and deodorant properties. However, for these uses, clove extractive will be more appropriate.

## Allspice Leaf Oil

Allspice leaves on drying give an essential oil with a yield of 0.7–2.9%. The flavor of this oil is considered inferior. Leaf oil has a pale yellow to brownish-yellow color. Its main constituent is eugenol, which is present to an extent of 65–95%.

Leaf oil of *Pimenta dioica* shows eugenol (76.02%) as the main constituent. Other compounds include methyl eugenol and $\beta$-caryophyllene (Jirovetz et al. 2007a). *Pimenta racemosa* leaf oil exhibits eugenol (45.60%), myrcene (24.97%), and chavicol (9.31%) (Jirovetz et al. 2007b).

*Pimenta* leaf oil, according to the FCC, is a pale yellow to light brown-yellow liquid when freshly distilled, which becomes darker with age. In contact with iron, it acquires a blue shade, turning dark brown. It is soluble in propylene glycol and is soluble with slight opalescence in most fixed oils. It is relatively insoluble in glycerin and in mineral oil.

Physical characteristics as defined by the FCC are as follows.

| | |
|---|---|
| Optical rotation | −2° to +0.5° |
| Refractive index | 1.531–1.536 at 20°C |
| Specific gravity | 1.037–1.050 |
| Solubility | 1 mL dissolves in 2 mL of 70% alcohol, a slight opalescence may occur when additional solvent is added |

Allspice leaf oil is also used for the flavoring of food items such as ice cream, confectionary, chewing gum, baked goods, beverages, and medical preparations. The leaf oil generally is cheaper than the berry oil.

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| *Pimenta* berry oil | 2018 | 8006-77-7 | 182.20 | – |
| *Pimenta* leaf oil | 2901 | 8006-77-7 | 182.20 | – |
| *Pimenta* oleoresin/extract | 2019 | 8006-77-7 | 182.20 | – |
| | | 84929-57-7 | | – |

## References

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Jirovetz, L.; Buchbauer, G.; Stoilova, I.; Krastanov, A.; Stoyanova, A.; Schmidt, E. 2007b. Spice plants: chemical composition and antioxidant properties of Pimenta Lindl. essential oil. Part 2: *Pimenta racemosa* (Mill) J.W. Moore leaf oil of Jamaica. *Ernaehrung (Vienna)* **31** (7/8), 293–300 (English).

Lawrence, Brian M. 2006. Progress in essential oils. *Perfumer Flavorist* **31** (5), 52–62.

# 15 Anka-Red Fungus

## *Monascus anka* or *M. purpureus*

### Introduction

Anka red natural pigment is produced from *Monascus* fungus, known in Japan as *koji* fungus. A Chinese medical book first mentioned the pigment as “ang-kak” or “red mold rice,” which has been used since 1884. Philippe van Thieghem later isolated and named the mold *Monascus ruber*. In 1895, mold from red mold rice was obtained in Indonesia. The fungus was named *Monascus purpureus*. After this, several species were studied and isolated.

Red mold rice is produced in Southern China, Japan, and Southeast Asia, using the traditional Koji process. There have been several modifications and more than 50 patents are registered. The pigments used as traditional natural food color in China and Japan are a mixture of yellow (monascin, anka flavin), orange-red (rubropunctatin, monascorubrin), and red-purple (rubropunctamine, monascorubramine) compounds (Chiu and Poon 1993).

### Microbial Material

*Monascus* fungus grows in substrates that contain plenty of carbohydrates (Delgado-Varghas and Paredes-Lopez 2003). In the Koji process, substrates such as rice, wheat, soybeans, or corn are inoculated. The major fungus used in Asia is *M. purpureus*. The first stage is a solid state but may be continued at a later stage using submerged culture (Chiu and Poon 1993).

In pigment production, the fungus produces an antibiotic, monascidin A, which is unwelcome in a food product. Improvements in strains and process have avoided this defect. Regulation of oxygen and carbon dioxide during the process has yielded higher efficiency for production (Delgado-Varghas and Paredes-Lopez 2003).

### Extractive

The traditionally produced red color is poorly soluble in water but soluble in alcohol. The color is sensitive to light. At lower acid pH, the color is more orange, while at higher pH it is purplish red.

Water-soluble red pigments are produced by reacting extracted pigments with amino acetic acid and amino benzoic acid (Wong and Koehler 1983). The modification gives the same characteristics as those obtained with glutamic acid or gelatin. The red

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pigments can be dissolved in ethanol and propylene glycol and freeze-dried for use as a food color. Use of complex culture media containing glucose or sucrose, corn steep liquor, and monosodium glutamate results in better production of the red pigment than with semisynthetic medium (Hamano and Kilikian 2006).

## Use

The pigment can be used in processed meat, fruit products, various sauces, and ice cream. The *Monascus* pigments are not approved for use in the United States. The European Commission has not yet assigned it an E-number. It would appear that this pigment is more often used in Asia but is becoming less and less important as other natural dyes such as paprika and annatto become more popular.

## References

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Wong, Hin-Chung; and Koehler, Philip E. 1983. Production of red water-soluble *Monascus* pigments. *J. Food Sci.* **48**, 186–189.

# 16 Aniseed

## *Pimpinella anisum* L (*Umbellifereae*)

### Introduction

Aniseed (anise seed) has been known to mankind for a long time, reported to have been found in Egypt more than 1000 years before Christ. Its aroma was believed to prevent bad dreams while sleeping. In the past, it was believed to increase sexual feeling and the flow of milk. Among the many beneficial effects attributed to aniseed is its ability to cure insect bites, control mites and lice, be a good bait for rodents, and have some medicinal effect: It is particularly effective for preventing gas and discomfort due to overeating, for preventing bad breath, and for use as a diuretic.

There have been conflicting reports of the seed being taxed and encouragement by government bodies to propagate the crop. All these point to the importance of the seed. In India, aniseed is often confused with other similar seeds like fennel, which also has digestion-improving qualities. Its flavor is similar to that of star anise, but the two are botanically quite different.

### Plant Material

Aniseed, which belongs to the ajowan family, is native to the Mediterranean region, especially Egypt, Greece, Turkey, and Lebanon. In recent times, its cultivation has extended to many countries. They include American nations such as Argentina, Chile, the United States, and Mexico; Mediterranean countries such as Cyprus, Spain, and Syria; Asian nations such as China, India, and Pakistan; and the island of Madagascar. The United States is a net importer.

The plant is an herbaceous annual that grows to about 1 m in height. It has long stalked leaves at the base and short stalked leaves at the top. The seeds have a yellowish-gray to yellowish-brown color. It is oval in shape with a length of 3–5 mm. The seed has longitudinal ridges, usually with a bit of thin stalk attached. It has a sweet aroma and flavor, reminiscent of licorice, and can be pleasant to chew.

### Chemistry

The chemical composition may vary slightly among seeds grown in different places. Generally, on dry basis, it has protein 18%, fixed oil 8–23%, total sugar 3.5%, starch 5%, crude fiber 12–25%, and essential oil 2–7%. The major component of volatile oil is anethole (Fig. 16.1).

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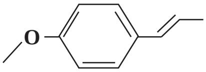

**Figure 16.1.** Anethole.

## Essential Oil

An average quality dry seed, on crushing and steam distillation, gives about 2–3% volatile oil. Anethole accounts for 80–90%, which gives the characteristic flavor. Star anise also has a high anethole content. The quantity of aniseed oil produced worldwide is only a fraction of volatile oil from star anise. Other components from aniseed include $\alpha$-pinene, camphene, linalool, anisaldehyde, acetoanisole, and safrole.

Aniseed oil has rich aromatic odor and flavor and can be considered to be slightly more pleasant than the oil of star anise. According to the FCC, anise oil occurs as a pale yellow liquid with the characteristic odor and taste of anise.

Physical characteristics as defined by the FCC are as follows.

| | |
|---|---|
| Optical rotation | −2 to +1 |
| Refractive index | 1.553–1.560 |
| Specific gravity | 0.978–0.988 |
| Solubility | 1 mL dissolves in 3 mL 90% alcohol |

## Uses

Aniseed oil is well suited for flavoring various processed meat preparations of Europe. It is particularly well liked in Italian dishes, including sausages. It is also used in alcoholic liquors and liqueurs. It has many medicinal properties and is useful in mouthwashes, digestive, and antiseptic preparations. There are unconfirmed reports of its use in aromatherapy and for perfumery.

Anethole separated from the oil has many uses; it can be added to give flavor to foods and beverages. Anethole is reported to have the property of spontaneous formation of microemulsion, which gives alcoholic beverages their cloudy appearance. This has potential for use in many beverages and pharmaceutical preparations.

Anethole has antinemetode, antimicrobial, and anti-insect properties.

## Identification Numbers

| | FEMA No. | CAS | US/CFR | E-No. |
|---|---|---|---|---|
| Anise oil | 2094 | 84775-42-8 | 182.20 | – |
| Anise oleoresin | – | 84775-42-8 | – | – |

# 17 Annatto

## *Bixa orellana* L (*Bixaceae*)

### Introduction

Annatto is used both as a spice and as a coloring material. The plant can be described as a bush. The Mayans of Central America used the dye as war paint. It was known to Latin Americans as *achiote*. Writers of the nineteenth century have glorified it as having the "color of fire." Presently, it is used on cosmetics and food.

### Plant Material

Annatto is the bright yellow-red to red pigment in the aril (seed coat) of an evergreen shrub growing on the fringes of forests in a wide range of tropical countries. The plant has heart-shaped leaves, generally with red-colored veins. It was used as a hedge plant in the gardens of colonial era because of its pink flowers. The fruit capsule is heart-shaped with opposing clefts and reddish-brown prickly spines. When the pods are ripe, it splits open into halves. Inside, 40–50 seeds are covered in a red pulpy skin. The seed is conically shaped with a rough four-sided bottom and appears red because of aril. The red pigments are in the seed coat and not in the inside kernel. The seed coat containing the pigment sometimes separates from the seed on abrasion after steaming.

The seed capsules appear about 30 days after flowering and ripen during the next 1–2 months (Satyanarayana et al. 2003). The color changes from green to red. Harvesting is best done when the seeds split open. This prevents damage in case of rain and prevents scattering of the seeds. The cluster of ripe capsules is cut at the first node. Under normal conditions, the first harvest can be obtained 18 months after planting. The average yield of seed from a hectare is 300–600 kg and in exceptionally good circumstances 750–900 kg. Photo 2 shows unopened and opened annatto pods.

It grows in many countries of South America, Peru being the leading one. It is also grown in Bolivia, Brazil, Ecuador, Guyana, Jamaica, and Suriname. The crop also occurs in lesser amounts in Africa, in Angola, Kenya, Nigeria, and Tanzania.

Annatto is also found in the Asian countries of India, the Philippines, Thailand, and Vietnam. In most places, the shrub grows wild. According to an estimate of the 1990s, the total dry seeds traded in the world are believed to be in excess of 10,000 mt. A large percentage of these are used for extraction of natural colors. The extraction and chemistry of the pigments have been studied by Preston and Rickard (1980).

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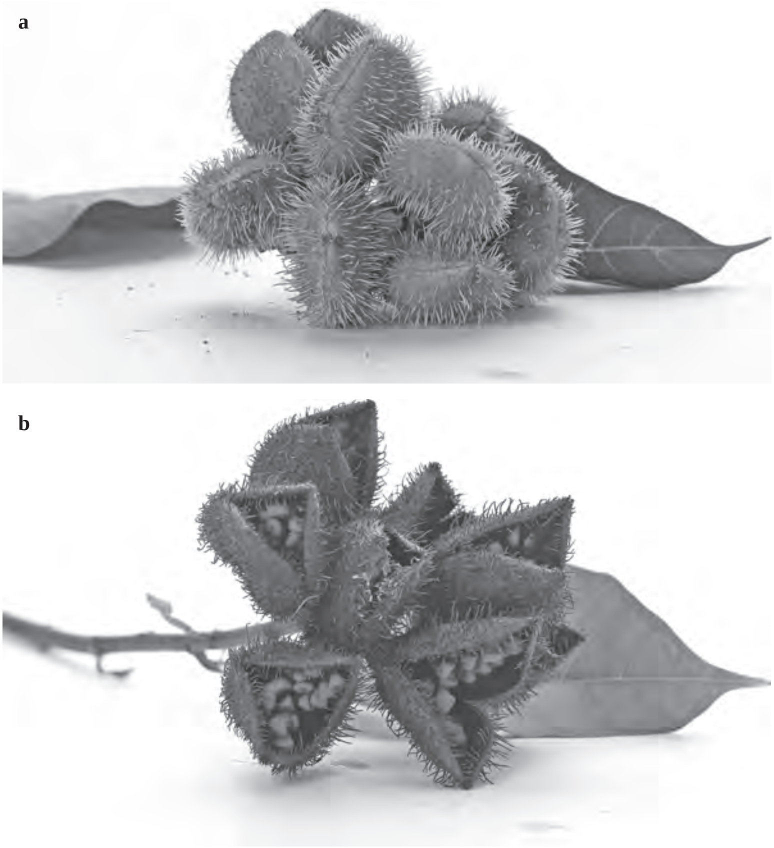

**Photo 2.** (A) Unopened annatto pods. (B) Opened pods with seeds inside. See color insert.

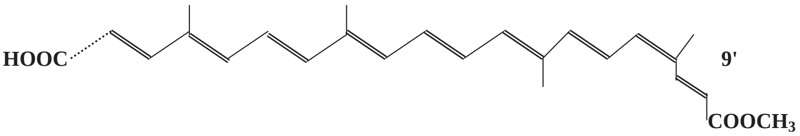

**Figure 17.1.** Bixin.

## Chemistry

The principal coloring compound of annatto is bixin (Fig. 17.1), which is a diapocarotenoid. The numbering of carbon atoms is as in regular carotenes as if carbon rings are at both ends, with middle carbons given 15 and 15′. Carotenoids like *β*-carotene have two rings and therefore have 40 carbon atoms. Bixin is therefore a unique C25 carotenoid.

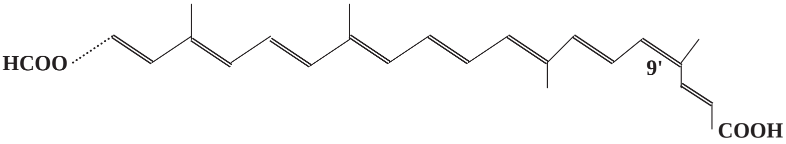

**Figure 17.2.** *nor*-Bixin.

**Table 17.1.** Properties of coloring compounds of annatto

| **Physical Properties** | | | **UV-VIS Spectrophotometric Analysis** | | |
|---|---|---|---|---|---|
| **Compound** | **Physical Description** | **MP (°C)** | **Solvent Used** | **Wavelength Maxima** | **Extinction Coefficient ($E^{1\%}_{1\,cm}$)** |
| *cis*-Bixin | Red-brown crystalline | 189.5–190.5 | Chloroform | 501,470 | 2880,3230 |
| *trans*-Bixin | Red-mauve crystalline | 204–206.8 | Chloroform | 507,476 | 2970,3240 |
| *cis-nor*-Bixin | Orange-red needles | Charred at 290 and did not melt <300 | 0.1 M NaOH | 482,453 | 2550,2850 |
| *trans-nor*-Bixin | Dark red-black granular | Darkened at 250 and did not melt <325 | 0.1 M NaOH | 486,457 | n.d. |

UV-VIS = ultraviolet-visible; n.d. = not determined owing to very low solubility.

Natural bixin is *cis* in 9′ positions with one of the carboxylic acid esterified to methyl group. While the above is orange with melting point of 198°C, all *trans*-bixin has a reddish color and a melting point of 216–217°C. This isomerization can be partially effected by heat. It can also be achieved by the action of iodine in benzene, but naturally this is not an option for food use. *cis*-Bixin is only weakly soluble in fat. It is soluble in most polar organic solvents.

Saponification of bixin extract with warm (less than 70°C) 5% aqueous potassium hydroxide (KOH) or sodium hydroxide will yield corresponding potassium or sodium derivative of *cis*-*nor*-bixin (Fig. 17.2). *nor*-Bixin is isomeric to all *trans* pigment, crocetin, which can be derived from the yellow pigment crocin, which is present in saffron.

The color shade and absorption characteristics of the pigments bixin and *nor*-bixin are presented in Table 17.1 (Satyanarayana et al. 2003).

## Extraction

Dry seed without grinding is fed into a percolator and extracted by gravity percolation at ambient conditions using acetone. Alternatively, an improved extraction can be obtained as follows. An initial wash with *n*-hexane will remove all the fatty impurities from the seed coat. After removal of hexane, annatto can be extracted with acetone to get a cleaner extractive containing bixin. Bixin can be further concentrated by crystallizing from acetone, when even bixin of 95% strength can be obtained. It must be remembered that a large amount of bixin as a natural color is used with a bixin extract of 5%, and so unnecessary concentration is not important in most cases. However, initial washing with hexane will free the extract from interfering impurities which may appear as sediments or floating globules when used in foods.

Because the skin is not separated from the kernel and not size-reduced, some agitation may be needed for extraction by percolation. A more convenient procedure is repeated circulation of percolated solvent for 1 hour using a pump and circulating ducts from bottom to top.

In many cases, especially for coloring fat-based product on a small scale, extraction can be carried out using common fixed oils. Use of stirring and temperature not exceeding 70°C will be beneficial. Among the oils, castor oil is preferred. Then a weak solution of bixin in vegetable oil is obtained, which can be used in butter and other dairy products. Studies on the separation of the dry powder from the seed by using particle attrition and impact have shown a possible extraction method without using solvent (Passos et al. 1998).

Compared with other carotenes, annatto pigments show superior stability to exposure to air, although they are affected by oxidizing chemicals. The dye is stable below 105°C but above 125°C stability is poor. The color in paper chromatography has been determined. Both *cis*-bixin and *trans*-*nor*-bixin are orange, while *trans*-bixin is red. A constituent orellin is found to be yellow. Several thermally formed volatiles originating from bixin, including toluene and xylene, are detected in very minute amounts during processing at high temperature.

Annatto also has an essential oil. The yield is very low (about 0.25%), but has a unique aroma. More than 100 compounds have been reported out of which about half have been identified. Annatto leaf oil has about 54% of a tetracyclic sesquine hydrocarbon, ishwarane. Volatile oils have not yet been utilized as aroma in food.

## Methods of Testing

Unfortunately, the Association of Official Analytical Chemists (AOAC) has not given any testing method for annatto. A very old method of Mckeown and Mark describes extraction of seed with chloroform followed by determination of absorption at 500 nm (A 500) and at 404 nm (A 404) and calculation as follows:

$$\text{Total pigment} = \frac{\text{A } 500 + \text{A } 404 - 0.256\,(\text{A } 500)}{286.6} \times \frac{V}{1000} \times \frac{100}{W}$$

where $V$ is the final volume and $W$ the weight of the seed taken.

Manufacturers of extracts use a method based on spectrophotometric absorption measurement of a cold acetone extract at 487 nm, comparing it to the reading of a standard bixin obtained from any of the supplier of specialized chemicals. For *nor*-bixin content, acetone extract is treated with 0.33 aqueous KOH, before reading at 480 nm. In modern practice, the spectrophotometric method is preferred.

## Uses

In Central and South America, seeds are extensively used as a natural color for food. It is one of the earliest known and safe food colors and therefore is used in meat, fish, and grain-based preparations. It is also believed to add to the flavor and hence is regarded as a spice.

Annatto extract is also used as a natural food color in dairy products. According to the food laws of many countries, only natural colors, especially those of carotenoid nature, are allowed to be used in butter and other dairy products. This gives bixin and *nor*-bixin a virtual monopoly for use in butter, margarine, cheese, and so on. It is also used in a wide range of manufactured foods, from confectionery to savory products, including salad dressings, fruit juice, bakery products, cereals, smoked fish, and sausage.

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Annatto, bixin, *nor*-bixin 2104 | 2104 | – | – | 160 b |
| Annatto extract | 2103 | 8015-67-6 | – | 160 b |

## References

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Preston, H.D.; and Rickard, M.D. 1980. Extraction and chemistry of annatto. *Food Chem.* **5**, 47–56.

Satyanarayana, A.; Prabhakara, Rao P.G.; and Rao, D.G. 2003. Chemistry, processing and toxicology of annatto (*Bixa orellana* L). *J. Food Sci. Technol.* (India) **40** (2), 131–141.

# 18 Asafoetida

## *Ferula assafoetida* L (*Umbelliferae*)

## Introduction

Asafoetida (asafetida), the intense-smelling gummy resin, is so well-liked in India and some nearby Asian countries that some people refer to it as "food of the gods." It is disliked equally by English and European people who gave it names like "devil's dung" and "stinking gum." The important point to be noted is that some flavoring substances at high concentration may appear unpleasant, but at the right dilution and in combination with other materials can be quite attractive.

In the past, it was familiar to the Mediterranean region, having originated in Persia. For some time, it was somewhat popular there. It emerged in Europe from the expeditions of Alexander the Great. Dioscorides in the first century AD spoke favorably about its flavor and curative power. But after the fall of the Roman Empire in the sixteenth century, asafoetida lost its appeal to European consumers. Now, it is almost a forgotten spice in Europe. However, with the popularity of Indian cuisine, there is hope for its revival in Europe for main dishes.

## Plant Material

Asafoetida is the dried exudate of gum oleoresin coming out from a live rhizome or taproot of a few *Ferula* species. Three of them grow in Kashmir and India. Other important growing areas are Afghanistan, Iran, and Pakistan.

The *Ferula* plant has a large taproot (rhizome) which is carrot-shaped with a 12- to 15-cm diameter at the crown, when fully grown at 4–5 years. Just before summer when plants flower, the top of the living rhizome is exposed by cutting the stem close to the crown. Milky latex-like juice exudes from the cut surface. After a few days, the dried gum is scraped off. This process of cutting and collecting the exudate continues for about 3 months. From high yielding plants, the gum collected can weigh as much as 1 kg.

The spice is acrid and bitter to taste. It emits a strong aroma akin to alliaceous odor due to sulfur-containing flavor compounds. The typical piercing aroma is caused by secondary butyl propyl disulfide and other sulfides. To regulate the flavor, it is often compounded with starch or cereals. Because of this, there is very little consistency in the small amount of analytical data available. A typical analysis will show 40–64% resin and 25% gum impurities. But volatile oil is the chief source of aroma. The resin portion consists mainly of asaresinotennol sometimes combined with ferulic acid

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(Pruthi 1976). There is also umbelliferone in the combined state. Disulfides, polysulfides, monoterpenes, $\alpha$- and $\beta$-pinene, some free acids, and traces of vanillin are the major constituents of the volatile oil (Leung and Foster 1996).

## Extractives

Although India is an important market for asafoetida, there is no essential oil or solvent-extracted oleoresin in the market. The spice itself is a gum oleoresin, which is strong in aroma and flavor. Essential oil or solvent extract will be too rich to regulate conveniently. Generally, the spice is diluted by compounding. However, the presence of an identification number by the Flavor Extract Manufacturers Association (FEMA) points to the existence of oil and extract used by flavor houses.

Asafoetida has an essential oil that represents 3–20%. One examination shows optical rotation of –9°0′ to 9°18′, refractive index of 1.493–1.518 at 20°C, specific gravity of 0.906–0.973, and sulfur content of 15.3–29.0% (Pruthi 1976).

With a view to promote solvent-extracted oleoresin in the Indian market, the author's lab carried out extraction. Using compound material available in the market, hexane extraction gives a yield of 11%. The product has 60% volatile oil content. Dilution is carried out with sunflower seed oil and glyceryl monooleate. After hexane extraction, the residue on extraction with ethyl acetate gives a further 25% extract, but the oil content is negligible. Most likely because of the availability of compounded material in different forms, the solvent-extracted product is not a great success.

## Uses

Asafoetida is used extensively in India to flavor savory preparations like vegetable curries, sauces, and pickles. One vegetable preparation with gravy especially popular in vegetarian South Indian cuisine is *sambar*, where the asafoetida flavor stands out distinctly.

Asafoetida is also used in sauces and preparations popular in the Western world, sometimes as oil or fluid extract. It would appear that the taste is an acquired one.

Asafoetida is used for treatment of chronic bronchitis and whooping cough in Ayurvedic therapy. In China, it is used for increasing blood coagulation time. Ferulic acid and sodium ferulate inhibit platelet aggregation. It is applied externally on the stomach to stimulate the digestive system. It also has use in animal medicines.

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Asafoetida oil | 2108 | 9000-04-8 | 182.20 | – |
| Asafoetida fluid extract | 2106 | 9000-04-8 | 182.20 | – |
| Asafoetida gum | 2107 | 9000-04-8 | 182.20 | – |

## References

Leung, Albert Y.; and Foster, Steven. 1996. *Encyclopedia of Common Natural Ingredients*. New York: John Wiley and Sons, pp. 44–45.

Pruthi, J.S. 1976. *Spices and Condiments*. New Delhi: National Book Trust, pp. 22–27.

# 19 Basil

## *Ocimum basilicum* L (*Labiatae*)

### Introduction

Basil, also referred to as sweet basil, is a culinary herb used all over the world. There are many varieties and subspecies that are important in some regions. Basil may have originated in India and Iran but has been cultivated worldwide for over 5000 years. Many varieties are medicinally important. Holy basil (*tulsi*) is revered in India as a symbol of sanctity in Hinduism. It is considered to be sacred and is present at many ceremonies, including funerals.

Many medical benefits, some of them based on myths, are attributed to basil. Even the smell of basil is regarded as curative. Basil is a symbol of love in Italy and a token of acceptance of a young lady by a young man in Romania.

The flavor of fresh basil is attractive in many prepared foods. Basil from different regions has different distinct flavors based on the predominance of different chemical constituents. However, it is the dried herb that is the raw material for extractives. Different varieties of dried herb also show some variation in their flavor characteristics.

### Plant Material

Basil is an annual bush belonging to the mint family. The plant grows to a height of 50–120 cm. It has opposite, dull green velvet leaves with an average length of 7–8 cm and breadth of 3–4 cm. It has small white or light-colored flowers arranged in a terminal spike. The leaves possess dot-like oil glands in which essential oil is stored. The plant emits a light fragrance. When fresh, the herb has a pleasant, minty note. It has a spicy but mildly pungent and bitter taste.

Basil, being a cold-sensitive plant, grows best in warm, dry weather. Therefore, growing basil in cold regions requires careful selection of the area and season.

The dried herb has about 14% protein, 61% carbohydrate, 4% fat, and 18% fiber. It has minerals and vitamins, especially ascorbic acid and vitamin A. But its most significant component is the volatile oil.

### Essential Oil

The yield of essential oil is generally lower than 1%. In one report, the yield from the aerial part is 0.1–0.25%, but the flower top alone gives 0.4%. This indicates that flower

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top has the most oil, but the quantity of herb so obtained will be low. In a recent study in Egypt, hydrodistilled volatile oil of stem, leaf, and inflorescence has been obtained (Islam and Salama 2007). In all three, more than 30 components have been identified. About 70% of these are oxygenated compounds. Linalool, estragole, cardinol, bornyl acetate, ocimene, and 1,8-cineole are prominent. In a study in China, gas chromatography–mass spectrometry (GC-MS) examination of steam-distilled oil shows 54 compounds. The main constituents are anisole, *p*-allylanisole, (+)-epi-bicyclo-sesquiphellandrene, and other compounds (Lu and Li 2006). In oil from the green and purple varieties in Iran, a difference in chemical compositions has been noted (Sajjadi 2006). The variations of four different seasons in composition of essential oil have been studied (Hussain et al. 2008). The yield varies between 0.5% and 0.8%, with the maximum amount being obtained in winter. There is also some difference in the proportions of the various constituents.

Although they are all labeled basil oil, there is significant difference due to regional, seasonal, varietal, and stage of maturity variations. These factors must be carefully considered while standardizing basil oil for flavoring purposes.

European-type oil is obtained by steam distillation of the flowering top or the entire aerial part. Basil oil is pale yellow mobile liquid with a floral, spicy note and is soluble in fatty oils. Comoros-type oil has a more noticeable camphoraceous note.

According to the FCC, Comoros-type basil oil occurs as a light yellow liquid with a spicy odor. It may be distinguished from other types, such as European-type basil oil by its camphoraceous odor and physicochemical constants.

Basil oil dissolves in fatty oils. It is soluble in mineral oil, forming a turbid solution. While it is insoluble in glycerol, it goes into solution in propylene glycol with some haziness.

European-type Basil oil, according to FCC, occurs as a pale yellow liquid with a floral-spicy odor. It may be distinguished from other types like Comoros or Reunion by its more floral odor and its physicochemical constants. It is soluble in most fixed oils and, with turbidity, in mineral oil. One milliliter is soluble in 20 mL of propylene glycol with slight haziness, but it is insoluble in glycerin.

Physical characteristics as defined by the FCC are as follows.

| | **Comoros-type** | **European-type** |
|---|---|---|
| Optical rotation | −2 to +2° | −5 to −15° |
| Refractive index | 1.512–1.520 at 20°C | 1.483–1.493 at 20°C |
| Specific gravity | 0.952–0.973 | 0.900–0.920 |
| Solubility | 1 mL dissolves in 4 mL of 80% alcohol | |

## Oleoresin

There are very few references regarding oleoresin in literature. On commercial level, basil herb, when extracted with a mixture of acetone and hexane (70 : 30), gives 3–3.5% yield with a volatile oil content of 2–6%. When extracted with hexane, the yield comes down to 1.5%–2%, naturally with a higher volatile oil content of 10–15%.

## Uses

Basil leaves are used for flavoring of a variety of dishes. They are particularly useful in vegetarian dishes, although they are also used in meat, seafood, cheese, and soups. When used in processed foods, basil oil or oleoresin will be very convenient as the flavor can be made uniform. Already extractives are used in sauces, salads, croutons, puddings, condiments, liqueurs, and alcoholic beverages. It also finds use in perfume compositions for its distinct fragrance.

## Identification Numbers

| | FEMA No. | CAS | US/CFR | E-No. |
|---|---|---|---|---|
| Basil oil | 2119 | 8015-73-4<br>84775-71-3 | 182.20 | – |
| Basil extract | 2120 | 8015-73-4<br>84775-71-3 | 182.10 | – |

## References

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# 20 Bay Leaf (Laurel)

## *Laurus nobilis* L (*Lauraceae*)

## Introduction

Bay leaves, also called laurel leaves, are produced on an evergreen plant. This plant has a very special place in ancient Rome, as laurel wreaths were placed on winners of chariot races and other competitions. Even kings were crowned with laurel leaves. Ancient medical practitioners like Dioscorides believed that bay could bring relief to pain and aches.

Bay leaves probably originated in Turkey and then moved to Mediterranean countries. The plant will not grow in Northern Europe because of the extreme cold. Bay leaves are very popular as a spice in Europe and North America.

## Plant Material

Laurel grows in Mediterranean countries such as Greece, Spain, Portugal, Cyprus, Italy, and Yugoslavia; in Asia Minor in Turkey; and in Central America in Mexico and Guatemala. The plant is a small evergreen tree, which looks like a bush. The dried leaves are bay leaf proper. Leaves of the "bay rum tree" (*Pimenta racemosa* M) or other trees are sometimes mistaken for bay leaf, but are also used.

The seeds of the laurel plant have a low germination rate and take a long time to germinate. New plants are formed by layering or from cuttings. Once seedlings are produced, the plant can grow into a large tree of 10–13 m in height. If properly pruned, the plant grows into a bush. Growing in pots also limits the size of the plant.

The leaves are 6–7 cm in length and 2–3 cm in breadth. The top surface is green while the underside is pale to yellowish green. The odor of the crushed leaf is mild but fragrant with citrusy and phenolic notes. It has an aromatic taste combined with bitterness. The flavor of laurel leaf is often used in French cooking.

The dried leaf is the raw material for extractives. The full aroma is developed only after slow drying. The dry leaf has 7% protein, 9% fat, 50% carbohydrate, and 25% crude fiber. It has minerals, B vitamins, and some ascorbic acid. The essential oil is its most significant constituent.

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## Essential Oil

On steam distillation, dried bay leaves give 1–3% essential oil. It is a light yellow mobile liquid with characteristic aromatic and spicy aroma. It has a eucalyptus-like odor due to the cineole content. Lawrence (1980) found that the yield of bay leaf oil can be up to 3%. Bay leaf oil from different parts of Turkey shows a high content of 1,8-cineole, sabinene, and $\alpha$-terpinyl acetate. In one case, as much as 60% cineole has been obtained. It also has lower levels of $\alpha$-pinene, $\alpha$-phellandrene, and *trans*-$\beta$-osimen (Sangun et al. 2007). Glycosidically bound volatile compounds have been investigated (Kilic et al. 2005). The aglycones found are benzyl alcohol, linalool diols, 1,8-cineole and its derivatives, sobrerols, and menthadien-8-ols.

Earlier investigations have been well covered by Prakash (1990). Major constituents reported are $\delta$-terpinene, terpinolene, cineole, terpeniol, geraniol, and their acetates. Recent publications of *P. racemosa* are well reviewed by Lawrence (2007). This includes studies wherein 1,8-cineole, terpinen-4-ol, methyl eugenol, thymol, and methyl chavicol have been prominent components in various samples. Lawrence (2008) has also compiled results under laurel leaf oil.

According to the FCC, laurel leaf oil (*Laurus nobilis*) occurs as a light yellow liquid with an aromatic, spicy odor. It is soluble in most fixed oils, and it is soluble with cloudiness in mineral oil and in propylene glycol. It is insoluble in glycerin.

Physical characteristics for laurel leaf oil as defined by the FCC are as follows.

| | |
|---|---|
| Optical rotation | −10 to −19° |
| Refractive index | 1.465–1.470 at 20°C |
| Specific gravity | 0.905–0.929 |
| Solubility | 1 mL dissolves in 1 mL 80% alcohol and remains in solution on dilution to 10 mL |

## Oleoresin

Ground dry bay leaf, on extraction with hexane, gives an oleoresin with a yield between 3% and 4%. The volatile oil content varies between 15% and 20% v/w. It is usual to dilute to a specified volatile oil content, so that it is easier to handle. The product is a dark green viscous liquid with rich aroma dominated by a cineole note. It has spicy flavor with mild bitterness.

## Uses

The bay leaf is used in a wide range of meat, seafood, and vegetable dishes in European and North American cuisine. It is also an ingredient of elite French dishes and Indian *biryani*. In processed foods, extractives like oil and oleoresin will be very convenient to give a standardized flavor. Extractives can be used in soup powders, dressings, and sauces. The oil is useful in beverages, toiletries, scented candles, and as a flavor in medical preparations.

## Identification Numbers

| | FEMA No. | CAS | US/CFR | E-No. |
|---|---|---|---|---|
| *L. nobilis* | | | | |
| Bay leaf oil | 2125 | 8007-48-5<br>84603-73-6 | 182.20 | – |
| Bay leaf oleoresin | 2613 | 84603-73-6 | 182.20 | – |
| *P. racemosa* | | | | |
| Bay leaf oil | 2122 | 91721-75-4 | – | – |
| Bay leaf oleoresin | 2123 | 91721-75-4 | – | – |

## References

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# 21 Beet Root

*Beta vulgaris* L (*Amaranthaceae*)

## Introduction

Beet belongs to a family with many cultivated varieties. The most important is the red tuber known as beet root or garden beet, which is used as a vegetable. Spinach beet is used as an herb. Even the leaves of beet root are consumed. Sugar beet is used as a source of sugar. But for natural color, the deep colored beet root is the raw material.

The sea beet, which grows in the Mediterranean Sea, is regarded as the ancestor of the present-day beet. There is mention of the beet in eighth-century BC, Mesopotamian writings. Theophrastus of Greece describes it as similar to radish. There is reference to it in the writings of Aristotle. Roman and Jewish literature also indicate that in the first century BC, domesticated beet, especially spinach beet, was used in the Mediterranean basin. The use of beet in Medieval Europe is evident in the writings of later years in England and Germany.

Beet root has been considered an aphrodisiac since Roman times. This is mainly because of its rich content of boron, an element that plays an important role in sex hormones. The deep color of the root crops makes it an interesting food item. For this reason, beet root wine is somewhat popular. Consumption of beet root is reported to cause some people to pass pink-tinted urine. Probably because of its resemblance to blood, consumption of the colored vegetable is generally regarded as good for health, particularly cardiovascular.

## Plant Material

The plant is an herbaceous biennial plant with leafy stems 1–2 m in height. The leaves are large, 5–20 cm long, and heart-shaped. Generally, wild varieties have larger leaves than domesticated ones. The flowers appear as dense spikes. The flowers are small, 3–5 cm in diameter, with five petals and colored green though sometimes tinged reddish. They are wind-pollinated to produce fruits, which come as a cluster of hard nutlets. But it is the root tuber that is used as a vegetable and a source for extraction of natural color. The root crop is flattened globularly with leaves originating from the top and a major root tapering from the bottom. The tuber is brightly colored due to the pigment inside.

On fresh weight basis, beet root has 9.6% of carbohydrate, of which 6.8% is sugars and the rest fiber. It has 17% fat and 1.6% proteins. It is rich in B vitamins and

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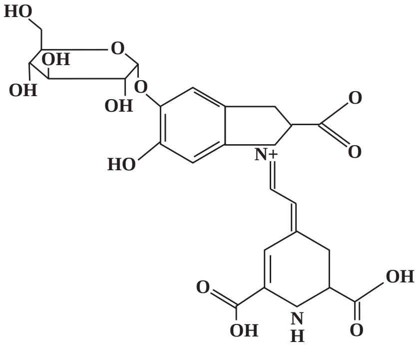

**Figure 21.1.** Betanin.

minerals. Beet pulp is fed to horses during training and conditioning as a healthy food. Beet root is used in folk medicine for a wide range of diseases and hence is a subject of study by modern scientists.

## Chemistry

The coloring components of beet root as a group are called betalains. They generally consist of betacyanins and betaxanthins. The former are red while the latter are yellow. Betanin (Fig. 21.1) represents the most significant and abundant pigment among the betalains. Betanin is a glycoside and the aglycone is betanidin. A small amount of isobetanin is also present. Others present as very minor constituents are probetanin, neobetanin, indicaxanthin, and vulgaxanthin.

## Extractives

Pressed beet juice is generally used for a natural color extract. For this, washed beet roots are pressed using an acidic pH for the stability of the pigment (Emerton 2008). To avoid heat, the concentration is carried out by ultrafiltration. The concentrate is pasteurized to protect against microbial action. The juice concentrate can also be microencapsulated by spray drying using maltodextrin or gum acacia to obtain a water-soluble powder form.

The pigment content in the concentrate is usually below 1% and at best between 1% and 2%. Because of this, a fairly large dosage is required for use as a color, even though the color intensity of betalains is quite high.

A continuous countercurrent diffusion technique was used by Wiley and Lee (1978) to study recovery of the various fractions of the color. The study was further carried out using a continuous solid–liquid extraction system on different varieties of beet roots (Lee and Wiley 1981). The studies on separation of various fractions of color using boiling alcohol followed by chilling of the extract to −25°C have resulted in rapid separation of principal constituents (Bilyk 1979).

Betalain pigments are also found in many plants of *Amaranthaceae* family. Such plants produce high biomass and could be considered as a potential source of pigment (Yi-Zhong et al. 2005).

## Uses

Beet root is used as a food color in foods such as ice cream, beverages, and some fruit products. Because of the sensitivity of the betalains to heat, this color is more suited to frozen or chilled products. It is the natural color equivalent of raspberry or cherry.

Beet root juice is beneficial for reducing blood pressure. Betalain is regarded as good for cardiovascular health. Studies with animals have shown that the dye may give protection to liver disorders, especially higher fat deposits among excessive alcohol users, diabetes sufferers, and people with protein deficiency.

## Analytical Method

There is a method of estimation using spectrophotometric measurement of aqueous solution at pH 4.5–5.

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Beet red | – | – | – | E162 |

## References

Bilyk, Alexander. 1979. Extractive fractionation of betalains. *J. Food Sci.* **44**, 1249–1251.

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# 22 Bergamot Mint

## *Mentha citrata* Ehrh (*Labiatae*)

### Introduction

Bergamot mint is also known as marsh mint, lemon mint, and, in India, *vilayati pudina*. The oil from the ripened fruits is valued as a fragrance in toiletries. The leaves form the herb. Leaves and flowers are used for flavoring iced beverages, teas, desserts, meats, and fish. The brightly colored flowers are very attractive to bees, butterflies, and moths and can also adorn gardens.

### Plant Material

Bergamot plants are adaptable to various agroclimatic conditions. The plant is 30–90 cm in height with branches. The type of soil, amount of sun, and climate will affect the growth to some extent. Moist and well-drained soil is the best for the plant. It can tolerate shade up to a point. Even in temperate weather, the plant can give good yield. It prefers manure and this will be reflected in the yield. The leaves are about 1.25–5 cm in length, thin, bronze-green in color, petiolate, smooth, broadly ovate to elliptical, with apex obtuse (Aktar et al. 1988). Its flowers are purple, appearing in upper axils on short terminal spikes. The calyx is glabrous with subulate teeth.

Root division is the best method for multiplication. The petals of the flowers are used for decorating salads and other edible preparations. The leaves are harvested around the time of flowering.

### Essential Oil

On steam distillation of the aerial parts, the essential oil is obtained. The volatile oil obtained from *Mentha citrata* is analyzed by GC-MS after hydrodistillation (Fathy 2007). The identified compound accounts for 98.66% of the total components of the oil, out of which 84.52% are oxygenated derivatives. The major constituents are linalool (24.69%), linanyl acetate (12.69%), $\alpha$-terpineol (8.51%), and 1,8-cineole (8.39%). Terpene hydrocarbon represents 14.14% of the identified compounds.

Fathy (2007) found on *in vitro* cytotoxicity testing a moderate effect against brain and colon human tumor cells, but no effect against lung, breast, liver, or cervical tumor cells. Oil inhibited *in vivo* antioxidant activity in alloxan-induced diabetic rats using vitamin E as standard.

The aroma of the oil is described as citrusy, fruity, balanced, and warm.

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## Uses

Oil of bergamot mint has the characteristic flavor of the herb. The leaves and flowers are used for flavoring special liqueurs and various beverages. Oils will have a more standardized flavor for the purpose. It can also find use in processed foods like sweetened dishes and meats where the flavor of leaves is desired.

Bergamot mint is a favorite scent of perfumery and fragrance items like soaps, scents for bath, and colognes. It also has value in medical preparations for chest infections, digestive disorders, acne, eczema, and even psoriasis. The oil can reduce fatigue and tension. Because of this, it is a favorite of aromatherapists.

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| M. citrata oil | – | 68917-15-7 | – | – |

## References

Aktar, Husain; Virmani, O.P.; Sharma, Askok; Kumar, Anup; and Mishra, L.N. 1988. *Major Essential Oil-Bearing Plants of India*. Lucknow, India: Central Institute of Medicinal and Aromatic Plants, pp. 167–181.

Fathy, Fify I. 2007. Chemical and biological study of the essential oil of *Mentha citrata* Ehrh. cultivated in Egypt. *Bull. Fac. Pharm. Cairo Univ.* **45** (1), 61–67 (English).

# 23 Black Cumin

## *Nigella sativa* L (*Umbelliferae*)

### Introduction

Black cumin is also called black seed, black caraway, and fennel flower. Sometimes it is mistaken for black sesame seed, but they are quite different.

An ancient Indian medical book regards the spice as a remedy for a wide range of diseases. There is also a report that *Nigella sativa* seeds were found in a number of ancient Egyptian sites including Tutankhamen's tomb. There is also reference to it in the Bible. According to ancient Muslim writings, *Nigella* seed is a remedy for all diseases except death.

### Plant Material

The seeds grow on a small herb with a height around 30–60 cm. Leaves are compound, two to three pinnatisect cut into linear or linear-lanceolate segments (Warrier 1995). It has pale blue flowers, solitary, with long peduncles but without an involucre. The seeds are black, trigonous, and regulose-tubercular. The seeds are acrid and bitter with many medicinal properties.

Black cumin is believed to have originated in the eastern Mediterranean region. It is both cultivated and found as a weed in India. There is some interest in its export both as seed and as essential oil. It has a nonvolatile ether extract value of 35–40%. The volatile oil content is 0.5–1.6%. Solvent-extracted fixed oil is a reddish-brown semidrying oil. Tunisian and Iranian seeds on analysis give 26.7% and 22.6% of protein, 28.5% and 40.4% of fat, 40.0% and 32.7% of total carbohydrates, and 4.9% and 4.4% of ash (Cheikh-Rouhou et al. 2007).

### Essential Oil

On steam distillation, black cumin gives a volatile oil with a yield of about 1%. It has an unpleasant odor because of the acrid constituents.

Physical characteristics of the oil are as follows (Pruthi 1976).

| | |
|---|---|
| Optical rotation | +1.43 to +2.86 |
| Refractive index | 1.4836–1.4844 at 20°C |
| Specific gravity | 0.875–0.886 |

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Besides the usual terpene compounds, oil contains nigellone, which has property to relieve bronchial spasm in guinea pigs. The extract of the oil contains thymoquinone, believed to prevent cancer cell growth. Many physiologically active components such as nigellicine, nigellidine, dithymoquinone, and thymohydroquinone, besides nigellone and thymoquinone, have been reported (Randhawa 2008). These account for the spice's many medicinal properties including anticancer action and immune stimulation. Two samples from Sahara desert regions on hydrodistillation followed by detailed analysis give *p*-cymene 8.9% and 7.2%, 4-terpineol 0.6% and 8.9%, thymohydroquinone 6.1% and 12.2%, thymoquinone 1.6% and 21.8%, carvacrol 12.9% and 12.9%, carvone 4.4% and 0.3%, and thymol 1.5% and 0.7% (Benkaci-Ali et al. 2007). From the southern region of Algeria, most of the above have been noticed in slightly different proportions. But in addition, sabinene, *trans*-sabinene, hydrate, $\gamma$-terpinene, longifolene, and $\alpha$-longipinene have also been noted (Benkaci-Ali et al. 2005).

## Uses

Because of its pungent bitter taste and smell, black cumin and its oil are used in confectionery and liquors. It has great potential in medicinal preparation. In fact, it is surprising that the oil and seeds are so little used in food flavoring. Perhaps the use will increase once its beneficial properties are better understood.

## Identification Numbers

| | FEMA No. | CAS | US/CFR | E-No. |
|---|---|---|---|---|
| Black cumin seed oil | 2337 | 90064-32-7 | 182.10 | – |

## References

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# 24 Black Pepper

## *Piper nigrum* L (*Piperaceae*)

### Introduction

Spices have always evoked thoughts of exotic places in the minds of Western people. Among the spices, it was black pepper that gained the most attention. The conquest of Egypt and the Indus region of India by Alexander the Great made pepper and other spices of the Orient well known in Mediterranean countries even before Christ. In the first century AD, direct sea routes were established between Europe and Egypt, which was a distribution center for pepper. The lure of pepper and other spices of the East was so great that toward end of the fifteenth century, many daring sea expeditions were undertaken mainly to establish a direct sea route between the lands of spices, such as India and the East Indies, and Europe. These included the expeditions of Columbus and Vasco da Gama. The colonization of the East by European powers made the flow of black pepper to Europe easy. It is believed that black pepper was used both for preservation of meat during winter and for masking off-flavor formed due to long storage.

### Plant Material

Black pepper is produced by a perennial climber, which has a woody stem. It needs support which the plant attaches itself using adventitious roots from joints. It has dark green ovate leaves that are somewhat thick. The climber reaches a height of 5–8 m. Flowers are minute. Fruits are grown on a central stalk into an elongated bunch, known as a spike. Each fruit will be dark green and spherical with an average diameter of 4 mm. On drying of the fruit, popularly known as a berry, but botanically a drupe, black pepper is formed. On ripening, the berries turn yellow and red. Photo 3 shows pepper vine and white and black pepper.

Pepper grows well in humid, warm weather such as found in areas near the equator. Rainfall of 1500 mm or above is needed. Temperatures below 10°C are not good for the plant. Propagation of pepper is done vegetatively from cuttings. Small plants are generally grown in nurseries for 3–4 months before they are transplanted to the desired place.

India, Indonesia, Brazil, and Malaysia are the major traditional growers. A recent entrant to pepper production is Vietnam, which has attained the position of top exporter. Unlike in India, they do not have a substantial internal market. Sri Lanka is a producer of extraction-grade pepper with high level of piperine, the constituent responsible for hotness. Cambodia and Madagascar also produce black pepper. By

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**Photo 3.** (A) Pepper vine with pepper berries as spikes. (B) White pepper. (C) Dried black pepper. See color insert.

harvesting at a slightly immature stage, a higher piperine content is obtained. The piperine content of extraction-grade immature pepper, popularly known as “light berries,” will be in the upper range with Sri Lankan material showing 9–11%. Light berries from other major producers show piperine content of 8–9% (India) and 7–8% (Indonesia and Vietnam).

## Chemistry

Piperine is the most significant constituent of dry black pepper and is present to the level of 4–6% (Fig. 24.1). At the immature stage, piperine content may be up to 10%. It, along with its isomers, contributes to the hotness. There are two points of *cis–trans* isomerism. Piperine, which is *trans–trans*, is the most pungent. This is followed in hotness by chavicine (*cis–cis*), isopiperine (*cis–trans*), and isochavicine (*trans–cis*) (Govindarajan 1977).

Starch is the major constituent, accounting for 40% in black and over 50% in white pepper. While starch is mainly in the core, crude fiber is in the skin. The amount of protein has not been investigated, probably because it is not a significant source, particularly since only a very low quantity of pepper is consumed. Piperine accounts for most of the nitrogen in pepper. The volatile oil content of dry pepper is about 4%. As the maturity increases, piperine and the volatile oil content decrease, mainly because of dilution by fast formation of starch and crude fiber (Table 24.1) (Sumathykutty et al. 1979).

The outer skin has essential oil in the inner portion. It also has polyphenols, which by phenolase-induced oxidation, are converted into dark-colored compounds. This is

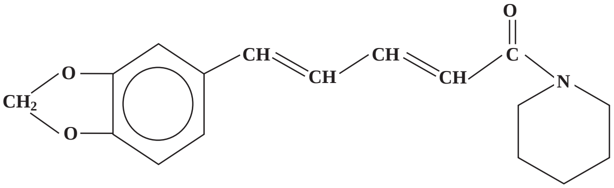

**Figure 24.1.** Piperine.

**Table 24.1.** Changes in chemical composition of pepper at different stages of maturity

| Maturity Stage | Moisture Content (%) (Wet) | Average Berry wt. mg | Content on Moisture Free Basis (%) | | | |
|---|---|---|---|---|---|---|
| | | | Vol. Oil v/w | Piperine w/w | Crude Fiber w/w | Starch w/w |
| Pinhead size | 82.5 | 4 | 2.0 | 0.4 | 18.0 | 15.3 |
| Between pinhead and immature | 77.5 | 15 | 2.0 | 1.9 | 14.7 | 18.5 |
| Immature (light berries) | 75.0 | 25 | 4.8 | 6.8 | 13.0 | 38.4 |
| Under mature | 65.0 | 53 | 4.4 | 6.2 | 11.8 | 38.4 |
| Mature | 60.0 | 62 | 3.7 | 4.2 | 10.5 | 40.9 |
| Ripening | 40.5 | 78 | 2.2 | 4.0 | 8.7 | 46.2 |

the reason for change of the green color of mature pepper (due to chlorophyll) to black on drying. The inner core is rich in starch and piperine.

The use of specific color reagent on microtome sections followed by microscopy has given an insight into the localization of many significant constituents. In the pinhead stage of pepper berries, piperine could not be located. However, estimation showed some piperine. From the immature stage onward, however, piperine cells could be located in the endocarp alone. The number of cells increased gradually, and at maturation, there was a considerable increase in piperine-containing cells. The size of piperine cell varied from 60 to 65 $\mu$m. Again by histochemical method, piperine could not be located in the skin; however, estimation showed 7–8% of total piperine in the skin but more than 90% was in the inner core (Mangalakumari et al. 1983). A cross section of a pepper berry is presented in Fig. 24.2.

Scanning electron microscopy has shown that the essential oil is stored in comparatively large and thin-walled cells, with size ranging from 50 to 55 $\mu$m. Essential oil cells were mainly in the inner portion of the skin. In the inner core, the distribution was restricted to the tip (i.e., stigmatic end) and where the embryo was situated.

Histochemical studies using phenolic reagents showed that polyphenols are present in the epicarp and mesocarp. The pattern of blackening of the pepper on drying coincides with the distribution of polyphenols. The substrate is identified as 3,4-dihydroxy-6-(*N*-ethyl amino) benzamide (Bandyopadhyay et al. 1990). It is a case of enzymatic browning wherein the enzyme phenolase is contributed by the spores of the fungus *Glomerella cingulata*, which is invariably present in the berries (Mangalakumari et al. 1983).

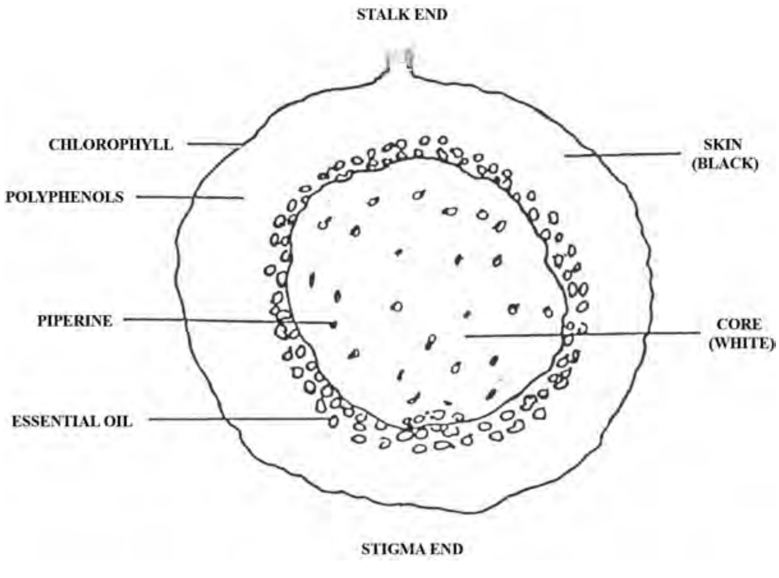

**Figure 24.2.** Cross section of pepper.

## White and Green Pepper

If the fibrous outer skin is removed from berries by retting and abrasion, especially when they are ripe or overmature, the hard core emerges as white pepper. White pepper has a typical putrid smell in addition to a hot taste. Steaming of green pepper or black pepper followed by efficient abrasion peeling using a mechanical pulper is suggested as a quick method. However, the absence of the slightly putrid note from retting is seen as a disadvantage.

At a very immature stage, pepper has a special "green" flavor, which is retained by inhibiting enzyme action to produce products such as green pepper in brine, dehydrated green pepper, and canned green pepper. The method employed in retaining the green color is inactivation of the phenolase enzyme. In dehydrated green pepper and canned green pepper, heat inactivation does this. In pepper in brine, continued steeping in acidified brine inactivates the enzyme.

## Essential Oil

Dried black pepper is made into flakes by roller grinding. On steam distillation of this, pepper oil can be obtained with a yield of 2–4%. It is customary to obtain it in two fractions, so that the second fraction will have more of the heavier compounds such as caryophyllene and less of monoterpene hydrocarbons such as pinenes and limonene. The second fraction, therefore, will have a desirable mellow aroma, whereas the first fraction will have a harsher note due to the higher content of monoterpene hydrocarbons. The first fraction is used for blending in oleoresin and the second as salable pepper oil.

Major constituents of pepper oil are $\alpha$- and $\beta$-pinene, sabinene, limonene, $\delta$-careen, $\alpha$-phellandrene, and $\beta$-caryophyllene (Govindarajan 1977). GC-MS study has shown 39 terpene compounds, which account for 99.51% of volatile oil. *trans*-Caryophyllene is the major constituent (Dong and Pan 2007).

According to the FCC, black pepper oil occurs as an almost colorless to slightly green liquid with characteristic odor of black pepper. It is soluble in most fixed oil and in propylene glycol but sparingly soluble in glycerin.

Physical characteristics of black pepper as defined by the FCC are as follows.

| | |
|---|---|
| Optical rotation | −1° to −23° |
| Refractive index | 1.479–1.488 at 20°C |
| Specific gravity | 0.864–0.884 |
| Solubility in alcohol | 1 mL in 3 mL of 95% alcohol |

## Oleoresin

When flattened, black pepper is extracted with solvents such as ethylene dichloride, a mixture of acetone and hexane, or ethyl acetate; miscella contains both aroma and pungent fractions. On removal of solvent, oleoresin is obtained. In recent years, it has become customary to produce oleoresin by a two-stage operation. As explained earlier, oil is distilled off as the first step. The deoiled pepper is freed of moisture and extracted with solvent. The resin rich in piperine will emerge on desolventization. This is then blended with pepper oil, usually the first fraction, so that the mellow-flavored second fraction can be sold as high-quality pepper oil.

Most international quality standards specify a solvent residue of less than 30 ppm. This level is obtained by use of open steam, efficient stirring during evaporation, and vacuum.

Black pepper oleoresin is generally sold in the specification of 40 : 20, which means 40% piperine and 20% volatile oil. Oleoresins with lower or higher content of either constituent are also traded. For use in light-colored products, decolorized oleoresin is made by using carbon as adsorbent. For special flavors, both oil and oleoresin are prepared from white pepper and green pepper. A new product that has emerged recently is 95% piperine in crystal form. This is obtained by repeated crystallization from piperine-rich resin obtained from deoiled pepper, which is rich in piperine. Piperine is used as a bioactive material as it aids in better absorption of other drugs taken along with it. Piperine is the major hot component of oleoresin.

## Method of Testing

Piperine determination is by UV spectrophotometric reading at 342–345 nm (ASTA, AOAC). The pure standard is supplied by Sigma-Aldrich Chemical Company.

## Uses

Black pepper is one of the most well-liked spice flavors in the world. No savory preparation can go without black pepper. It is used in meats, seafood, vegetable preparations, snacks, soups, sauces, and salad dressing. Pepper powder is sprinkled on egg preparations, salads, and cheese.

Pepper oil is used in food as a flavor when aroma and not hotness is valued. A small quantity is used as fragrance material, especially in men's cosmetics. Pepper oil is believed to give an oriental note to perfumes.

When both aroma and taste are required, oleoresin black pepper should be used. It is widely used in processed foods of meat, seafood, vegetables, snacks, and soups. Piperine crystals with 95% purity are used as a bioactive agent, which helps the body to absorb other drugs taken along with it.

## Identification Numbers

| | FEMA No. | CAS | US/CFR | E-No. |
|---|---|---|---|---|
| Pepper oil (black) | 2845 | 8006-82-4<br>84929-41-9 | 182.20 | – |
| Pepper oil (white) | 2851 | 8006-82-4 | 182.20 | – |
| Pepper oleoresin (black) | 2846 | 84929-41-9 | 182.20 | – |
| Pepper oleoresin (white) | 2852 | 84929-41-9 | 182.20 | – |

## References

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Dong, Dong; and Pan, Shengli. 2007. Analysis of chemical constituents of volatile oils from *Piper laetispicum* and *Piper nigrum* by GC-MS. *Zhongguo Zhongyao Zazhi* **32** (7), 647–650 (Chinese) (*Chem. Abstr.* **149**:252615).

Govindarajan, V.S. 1977. Pepper-chemistry, technology and quality evaluation. *CRC Crit. Rev. Food Sci. Nutr.* **9**, 115–225.

Mangalakumari, C.K.; Sreedharan, V.P.; and Mathew, A.G. 1983. Studies on blackening of pepper (*Piper nigrum* L), during dehydration. *J. Food Sci. (IFT)* **48** (2), 604–606.

Sumathykutty, M.A.; Rajaraman, K.; Sankarikutty, B.; and Mathew, A.G. 1979. Chemical composition of pepper grades and products. *J. Food Sci. Technol.* **16**, 249–252.

# 25 Capsicum

## *Capsicum annuum* L; *C. frutescens* L (*Solanaceae*)

### Introduction

Capsicum, or chili, is sometimes referred to as cayenne pepper or red pepper. It has a very hot taste or pungency. Asians in general and Indians in particular love this hot taste, and their food contains a fair amount of this spice. But about 500 years ago, it was not available in the Old World. Chili is thus a gift from the New World, as are tobacco, cassava, sapota, rubber, and cashew nuts.

Spanish explorers discovered this crop in South and Central America and the Caribbean islands. From there, it was transplanted to Europe where in the cold weather, less pungent varieties thrived. The Portuguese introduced chili to India, where only the hot variety thrived and became a favorite food seasoning.

Chili is probably a native of Mexico from where it spread to the rest of Latin America. Use of this hot spice in Mexico is recorded as early as 7000 BC. There is historical evidence of the Aztecs having used this spice. It was also used in the Caribbean islands both for food flavoring and as a medicine. The specialists who accompanied Columbus's expedition made important observations about the plant and its usage in food and medicines.

Because of differences in agro-climatic conditions and natural hybridization, chilis differing in size, shape, color, and intensity of hotness appeared. Chili or red pepper is one of the most colorful spices. The presence of whole dried red chili in a prepared dish and fresh green chili in salads has great display value. (See Photo 4.)

### Plant Material

Chili is an annual plant, attaining a height of 0.5–1.4 m and has a branched stem. The flower is white in color and bears a single fruit, which is the chili. It is green before ripening, but changes to red on ripening. The intensity and color vary with cultivars. Exotic varieties have white, yellow, purple, and orange colors, but they do not form raw material for extractives (Govindarajan 1985).

Commercially significant chilis are red in color. There are rows of seeds inside, attached to a sheath-like dissepiment (Fig. 25.1). While seeds come free of hotness, dissepiment is rich in capsaicin, the chemical constituent that causes hot taste. Separated seeds usually contain small pieces of dissepiment, giving an impression that seeds are indeed hot. Pericarp contains most of the color and capsaicin. The

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**Photo 4.** (A) Harvesting of ripe chilis. (B) Dried *Byadege* chili. (C) Fresh green chili. See color insert.

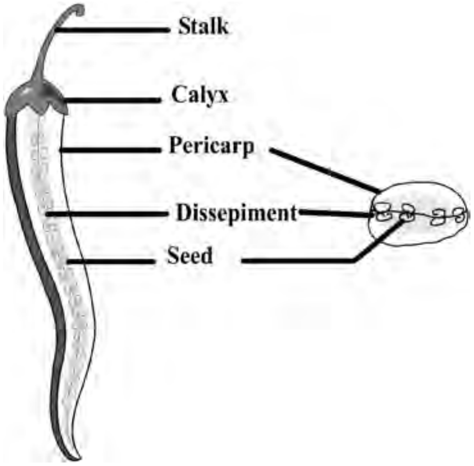

**Figure 25.1.** Section of chili and distribution of constituents.

**Table 25.1.** Distribution of active constituents in different parts of dried chili

| | | Whole | Pericarp | Seed | Stalk |
|---|---|---|---|---|---|
| Total dry weight | % of whole | 100 | 40.0 | 54.0 | 6.0 |
| Capsaicinoid | % distribution | 100 | 94.6 | 4.9 | Trace |
| Color (as β-carotene) | % distribution | 100 | 94.6 | 4.9 | 0.5 |

percentages of different parts of a chili pod and distribution of active constituents are given in Table 25.1.

The dissepiment has to be considered as a part of pericarp and accounts for 2% of the total chili pod. Compared with the total pericarp, dissepiment carefully separated shows about four times the capsaicin contents but only one-third of the color value. The success of capsaicin extraction is dependent on not losing the dissepiment, especially when only the pericarp separated from the seed is used for extraction.

Dried capsicum is the raw material for extraction. Barring some extraction in the United States and China, almost all extraction for capsaicin-rich oleoresin is carried out in India. Originally, Sanam and, to a lesser extent, Mundu varieties were abundantly available as the raw material. About 20 years ago, an intensely high pungent variety called Jwala was introduced. In recent year, the varieties Teja and Namdhari are used as the main raw material, because of good color and hotness.

Manipur in Northeast India has a very pungent chili (also known as Nagaland chili). The hotness and color were recently analyzed in the oleoresin that is obtainable when extracted with ethylene dichloride (Table 25.2) (Naidu et al. 2007).

It can be seen that Teja in particular and Namdhari to a lesser extent give oleoresin with a high capsaicin content. Manipur is high in hotness, but this has not yet become a commercial crop. In color value, Byadegi is the highest. This after deheating is now the raw material for oleoresin paprika in India.

**Table 25.2.** Chili oleoresin: color and pungency levels for selected varieties in India

| Variety/Cultivar | Color Value (EOA Units) |  | Total Capsaicinoids (% w/w) |  |
|---|---|---|---|---|
|  | Whole Chili Oleoresin | Pericarp Oleoresin | Whole Chili Oleoresin | Pericarp Oleoresin |
| Sannam | 17,700 ± 260 | 40,550 ± 350 | 1.83 ± 0.06 | 3.46 ± 0.15 |
| Mundu | 11,660 ± 400 | 32,500 ± 400 | 1.70 ± 0.10 | 4.10 ± 0.12 |
| Namdhari | 23,060 ± 585 | 51,350 ± 200 | 3.30 ± 0.25 | 6.73 ± 0.10 |
| Teja | 13,100 ± 200 | 22,700 ± 200 | 4.26 ± 0.15 | 7.33 ± 0.21 |
| Byadgi | 49,600 ± 250 | 1,15,000 ± 480 | 0.76 ± 0.05 | 1.30 ± 0.10 |
| Manipur | 10,900 ± 200 | 16,400 ± 100 | 22.20 ± 0.72 | 29.26 ± 0.15 |

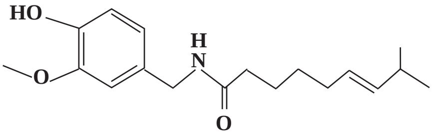

**Figure 25.2.** Capsaicin.

Bird's eye chili, very small in size but high in heat, belongs to *C. frutescens*. They are primarily grown in kitchen gardens and very little commercially.

Capsaicin is also recovered from mildly hot paprika in India during production of oleoresin paprika. Generally, such capsaicin-containing fraction, recovered to make paprika oleoresin free of hotness, has limited solubility in fatty oil. Therefore, it is generally used in small proportions in regular capsicum oleoresin.

Sometimes due to cloudy or rainy conditions, a small percentage of dry chili never attains the red color. This is called "white chili" and is usually cheaper. When color is not essential, this could be a cheap raw material, provided any problems caused by mycotoxin are addressed. Top extraction companies do not use white chili due to this problem.

In the Americas, special mild to hot chilis are cultivated, such as Jalapeño. There are also very hot chilis cultivated for extraction purpose. Because of their high capsaicin content, it is advantageous to use these chilis. Cultivation is mainly in warm southern states. Although China is basically a cold country, in the southern provinces, there is some cultivation of hot chilis. The main Chinese variety is Yidu. While paprika oleoresin is a major item in China, capsicum oleoresin is mostly imported from India.

## Chemistry

Chili contains about 12% protein, 17% fat, 57% carbohydrates, and 25% crude fiber. It is rich in vitamin A and contains water-soluble vitamins and minerals. The bulk of the fat is contributed by seeds. Chili has no essential oil.

It is valued mainly for hot chemical constituents, notably capsaicin and allied compounds. The capsaicin, which accounts for 69%, is *N*-vanillyl-8-methyl-6-nonenamide (Fig. 25.2). Other compounds present are dihydrocapsaicin (22%), nordihydrocapsaicin (7%), homodihydrocapsaicin (1%), and homocapsaicin (1%). A few more analogues are present at very low levels. The active pungent components are capsaicin and two isomeric compounds, dihydrocapsaicin and nordihydrocapsaicin, wherein the double bond on the side chain is saturated with two hydrogen atoms. All these together are called total capsaicin.

A study using GC-MS in China showed that the most prominent compound noted is capsaicin, followed by ethyl linolenate, palmitic acid, dihydrocapsaicin, bis (2-ethyl hexyl) phthalate, and stearic acid (Zhu et al. 2003).

## Oleoresin

Capsaicin oleoresin is an important natural flavor. Since it has no essential oil, solvent extraction of dry size-reduced material is the accepted process. Preparation of the raw material is very important for efficient extraction.

Seeds and stalks contain neither pungency nor color. They are removed by a series of operations including cutting, sieving, and air classification. The seed has a good market in the grinding industry and therefore it has to be recovered efficiently taking care that the fine powder of pericarp, which has both hot components and coloring compounds, is not lost.

Extraction is more efficient (with a higher yield of active components) if the particle size is low. But with fine powder, passage of solvent through the bed is difficult in batch processing. To avoid this problem, the powder is made into pellets.

The pelletized powder of pericarp is fed into percolators, and extraction is carried out using ethylene dichloride or a mixture of hexane and acetone. From the miscella, the oleoresin is obtained by removing the solvent.

Chili has a gummy material, which must be avoided. When extracted with methanol or ethanol, the oleoresin comes as a thick mass, generally with a capsaicin content of less than 5%. In the early days of oleoresin, ethyl alcohol extracted product was used. The thickness of the oleoresin is due to the gummy matter, which is slightly lipophobic.

A free-flowing oleoresin free of sediments is currently preferred. It is easier to work with such products. Additionally, when increasing the concentration of capsaicin and decolorizing, the free-flowing quality is essential. When capsicum is extracted with acetone or ethyl acetate, the oleoresin contains a large amount of gummy sediments. The way to avoid this is to use a less polar solvent such as ethylene dichloride or acetone–hexane mixture with a hexane content greater than 50%.

It is likely that a perfectly dry ethyl acetate may yield an oleoresin without gummy sediments, but on subsequent reuse, moisture absorbed by ethyl acetate increases the polarity of the solvent system, resulting in an oleoresin with gummy sediments.

Extraction of capsicum oleoresin with aqueous ethanol or methanol (alcohol : water = 70 : 30) results in a fraction of higher content of capsaicin. Aqueous alcohol preferentially extracts capsaicin fraction, leaving behind a fraction with low capsaicin content and higher color value. Extraction using alcohol with 20% water results in an enrichment from about 5% to a level between 10% and 20%, while with 30% water, enrichment can be more than 30% of capsaicin content. There will be a proportionate reduction in color value. In fact, if a two-liquid partitioning system of 70% aqueous methanol or ethanol and hexane is used, the aqueous methanol fraction can yield an oleoresin of above 50% capsaicin content. The hexane fraction, if repeatedly freed of capsaicin by washing with aqueous methanol or ethanol, can give a highly colored oleoresin.

Liquid–liquid partitioning using heptane, instead of hexane, in combination with aqueous methanol or aqueous ethanol gives excellent enrichment of capsaicin. Of the two alcohols, methanol (70%) is more effective. However, there are restrictions on the presence of residual methanol. Similarly, heptane may also be regulated.

Oleoresin capsicum is a red to red-brown oily liquid with the very high pungency characteristic of hot chili. Humans feel hot taste by experiencing pain when pungent compounds come in contact with pain receptors. In the mouth, along with other sensoric factors, capsaicins at optimum level are felt as a desirable savory flavor. Generally, when the capsaicin content is higher, the color is browner. Using the above methods, capsaicin content can be adjusted from 1% to 40%. For pharmaceutical use, a capsaicin content of 60–65% may be required, and for this, two-liquid partitioning is needed.

Specification for color value can also vary between 1000 and 20,000 cv although the usual range is between 4000 and 8000 cv. There is demand for decolorized capsicum oleoresin for use in colorless or white products. Processors treat the oleoresin with benzyl peroxide to reduce the color value to below 1000 cv. Excessive treatment with benzyl peroxide may leave a residue of benzoic acid, a chemical restricted in some countries. Hydrogen peroxide may not leave this residue.

If the color value has to be reduced to around 100 cv, then absorption of color with carbon is the only way this can be accomplished. Good grade activated carbon can be mixed with the capsicum powder before solvent percolation when miscella with low color is obtained. On removal of solvent, oleoresin with low color is obtained.

## Analytical Methods

Capsaicin is estimated using high-performance liquid chromatography (HPLC) as described in ASTA or AOAC. The area peaks of the sample extracted are compared with a pure standard of capsaicin, obtainable from Sigma. The column used is $C_{18}$ and the mobile phase a mixture of acetonitrile (40%) and 1% aqueous acetic acid (60%). Detection is at 280 nm. The industry, however, still uses the Essential Oil Association (USA) (EOA) method for color value.

In the past, Scoville heat units (SHU) were used to describe hotness. But because of the subjective nature of the test, HPLC results are used to compare with SHU as described in AOAC.

The color of chili is caused by xanthophylls. The red pigments are capsanthin and capsorubin. For details of the structure of pigments and estimation of color value, see Chapter 82 on paprika.

## Uses

Hot chili is widely used to make food items hot. Generally, Asians like their food to taste hot. But in recent years, the Western world is also beginning to appreciate some hot taste in their food rather than a bland one. However, excessive and high doses may cause stomach irritation.

Oleoresin capsicum can replace hot chili in processed food. In China, it is used in meat and in noodles. In Indian curries, use of oleoresin ensures uniform flavor. Even in Western dishes, oleoresin capsicum gives an underlying hotness, which, even if not perceived, will bring out a desirable effect. Oleoresin can replace ground chili in meat, seafood, vegetable curries, soups, dressing, sauces, and savory snacks.

Hot chili stimulates secretion of gastric hormones in saliva. It increases peristaltic movement and helps in reducing retention time of fecal matter in the rectum.

Oleoresin is used as a counterirritant in pain balms, liniments, foundation cosmetics, prickly heat powder, and special sticking plaster. Because it is highly irritating, capsaicin is added to sprays that are used by the police and others who want to ward off attackers. Studies have indicated that capsaicin can retard different types of cancer growth and reduce postsurgical pain (Pushpakumari and Pramod 2009).

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Capsicum extract | 2233 | 8023-77-6 | 182.20 | – |
| Capsicum oleoresin | 2234 | 8023-77-6<br>84603-55-4 | 182.20 | – |
| Capsaicin | 3404 | 404-86-4 | – | – |

## References

Govindarajan, V.S. 1985. Capsicum—production, technology, chemistry and quality. *CRC Crit. Rev. Food Sci. Nutr.* **22** (2), 109–176.

Naidu, Madhava M.; Sowbhagya, H.B.; Sulochanamma, G.; and Sampathu, S.R. 2007. Comparative study of chilli constituents in six commercially grown varieties of *Capsicum annuum* L. *J. Plant. Crops* **35** (3), 181–187.

Pushpakumari, K.N.; and Pramod, S. 2009. Health benefits of spices. *Spice India* (Indian Spices Board, Cochin) **22** (12), 13–19.

Zhu, Xiaolan; Liu, Baizhan; Zong, Ruowen; and Gao, Yun. 2003. Analysis of chemical constituents of capsicum by GC-MS. *Fenxi Ceshi Xuebao* **22** (1), 67–70 (*Chem. Abstr.* **139**:275875).

# 26 Caramel

## Introduction

Caramel is obtained by heating any kind of sugar until the color changes to a shade between brown and nearly black. Caramel accounts for a major share of the color substance used in processed food. The product is generally an amorphous brown solid or a thick liquid. Caramelization also develops some flavor, including a bitter note. Caramel from burned sugar is poured over custard pudding to make the well-known caramel custard. It is used as a color in a wide range of alcoholic beverages, cola-based soft drinks, and baked products where the browning coloration is found to be inadequate. Many candies, including milk-based candies and chocolate bars, are called caramel if caramel is used for flavoring and color.

## Production Aspects

Caramel is produced by controlled heating of food-grade carbohydrate to about 190°C. Dextrose, invert sugar, lactose, malt syrup, molasses, cane sugar, starch hydrolysates, and its fractions can be made into caramel (Reineccius 1994). A large amount of commercial caramel is produced from liquid corn syrup or glucose syrup. By modifying the conditions, many different grades of caramel for different applications can be made. In India, cane sugar is used as the raw material.

To promote caramelization and greater color intensity, food-grade acids, alkali salt, sulfite, and ammonia are added, ensuring that there is no violation of good manufacturing practice and food laws. Ammonium sulfate is a catalyst often used.

The chemical reactions that take place are complex. Two sets of reactions that occur are a pure charring reaction, caused by burning of sugar, and the Maillard reaction. A carbohydrate such as sugar without any additives, when subject to heating, undergoes changes to produce caramel or burned sugar. The product so obtained is regarded as a food ingredient and falls beyond the scope of the colors directive (Emerton 2008). When other substances are added, the aldehydes and ketones of the sugars react with naturally occurring nitrogenous compounds. These changes, initiated by the Maillard reaction, generally bring about the formation of pyrazines, lactones, and other heterocyclic compounds, which contribute toward formation of flavor beyond just the bitter note of burned sugar. However, unlike the normal Maillard reaction, caramel making is not always an amine-catalyzed reaction, and the process also requires a high

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temperature. Heating to above 150°C is required for a complete reaction. At high pH, the reaction goes faster. Therefore, alkali is used in the manufacture of caramel flavorings.

Caramel colors are totally miscible with water. Besides soluble materials, there are colloidal aggregates that account for the coloring quality and the characteristic properties in food. Depending on the method of production, the caramel may be positively or negatively charged. The isoelectric point determines the category of food which the caramel will be used. At a pH above the isoelectric point, the caramel is negatively charged, and below that pH, it is positively charged. Reineccius (1994) offers three classifications: acid proof, bakers, and spirit, with isoelectric points below 2, 4 or above, and below 1, respectively.

Another important quality is the intensity of color, which can be determined using a tinctometer. Caramel is usually sold as a thick viscous liquid, with total soluble solids sufficiently high to prevent microbial attack. The thick material is diluted for use; it is best to dilute only what is required for immediate use, as the diluted material is liable to be attacked by fermenting and spoilage microbes.

Since caramels carry electrical charges, they have to be used where oppositely charged particles are absent. Meat products, sauces, and gravies contain a high salt content, and therefore positively charged products are suitable. Caramels are heat- and light-stable.

## Classification

There are different types of caramel.

*Class I.* Plain caramel produced by heat with or without acid or alkali. No ammonium or sulfite compounds can be used.

*Class II.* Caustic sulfite caramel prepared by heat with or without acids or alkali. No ammonium salt compounds can be used but sulfite compounds can be present.

*Class III.* Ammonia caramel is prepared by heat with or without acid or alkali. No sulfite compounds are used but ammonium compounds can be present.

*Class IV.* Sulfite ammonia caramel is prepared by heat with or without acid or alkali. Both sulfite and ammonium compounds can be present.

The details of the characteristics and testing are given in the FCC. The details of properties are also presented by Smith and Hong-Shum (2003).

## Uses

Caramels are used extensively in wide variety of foods such as baked goods, cereals, and dairy and meat products. It is a commonly used color in candies. Its widest use is in soft drinks and alcoholic beverages. Whiskey, brandy, rum, and sometimes even beer are given a dark tint usually with plain caramel, which is referred to as spirit caramel. In a popular sense, ammonia caramel is referred to as beer caramel, sulfite caramel as brandy caramel, and sulfite ammonia caramel as soft drink caramel.

Plain caramel has high stability in alcohol. Beer has positively charged proteins, while soft drinks are negatively charged with acid. Sometimes caramel is used to intensify the color of cocoa-based food items such as ice cream, cake, pastries, and icing.

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Caramel color | 2235 | 8028-89-5 | 182.1235 | E150 |
| Plain (Class I) | – | – | – | E150 a |
| Caustic sulfite (Class II) | – | – | – | E150 b |
| Ammonia (Class III) | – | – | – | E150 c |
| Sulfite ammonia (Class IV) | – | – | – | E150 d (1) |

## References

Emerton, Victoria, ed. 2008. *Food Colours*. Oxford, UK: Leatherhead Publishing and Blackwell Publishing, pp. 39–41.

Reineccius, Gary, ed. 1994. *Source Book of Flavours*, 2nd ed. New York: Chapman and Hall; New Delhi: CBS Publishers and Distributors, pp. 807–808.

Smith, Jim; and Hong-Shum, Lily. 2003. *Food Additives Data Book*. Oxford, UK: Blackwell Science, pp. 168–182.

# 27 Caraway

## *Carum carvi* L (*Umbelliferae*)

### Introduction

Caraway seed has been used in Europe since ancient times. It could have its origin in the Near or Middle East, as the name is believed to have originated from Caria, which was a region in Asia Minor. Caraway has probably been cultivated in Europe since medieval times. Seeds are found in debris in the lakes of Switzerland, making it a spice most likely used longer than many other spices.

Caraway seeds are popularly used to mask bad breath, especially alcoholic breath. In ancient times, many virtues were attributed to the seed. They include controlling gas formation, fighting anemia, as an antidote to biting by venomous beasts, and even as protection from witchcraft.

### Plant Material

Caraway seed is the dried fruit of a biennial herb that belongs to the parsley family. The plant resembles a carrot plant with finely divided leaves produced on a flower stem of 40–60 cm in height. The seeds are small but elongated and slightly curved with a length of 2–5 mm. It has five or six ridges longitudinally on the outside.

The seeds have a pungent, mildly medicinal aroma caused by the essential oil. Holland is the world's major producer, but it is also grown in Germany, Russia, Morocco, Scandinavian countries, Canada, and the United States.

### Chemistry

The major constituent is carvone, which demonstrates stereoisomerism. It forms two mirror image enantiomers: S-(+)-carvone and R-(−) carvone (Fig. 27.1). The typical smell of caraway is caused by the former. The latter gives an aroma resembling spearmint. Carvone enantiomers are special in that each of them is perceived differently by the human olfactory system. Not all similar asymmetric isomers are perceived differently. While S and R forms are modern ways of describing isomerism of this nature, older books refer to these respectively as dextro- or *d*- (for S) and as levo- or *l*- (for R) forms. *d* and *l* are based merely on polarimetric readings, while S and R forms are based on the order of distribution of radicals at an optically active carbon.

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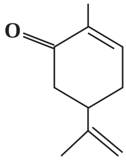

**Figure 27.1.** Carvone.

## Essential Oil

The drying and size reduction of seeds are important processes in producing the corresponding essential oil. On steam distillation, dry spice yields 7–8% volatile oil.

S-(+)-carvone is present to the extent of 50–70% of caraway oil. Besides carvone, the oil contains a significant amount of limonene. Composition of essential oils from caraway by supercritical fluid (SCF) extraction and steam distillation has been compared from the point of view of efficiency, reproducibility, and accuracy (Sedlakova et al. 2001).

Caraway seed oils from Austria reveal that major components are carvone and limonene (Bailer et al. 2001). A similar trend in carvone is noted by Iacobellis et al. (2005) but with noticeable quantities of dihydrocarveol, $\beta$-caryophyllene, germacrene, and limonene.

According to the FCC, caraway oil occurs as a colorless to pale yellow liquid with the characteristic odor and taste of caraway.

Physical characteristics as defined by the FCC are as follows.

| | |
|---|---|
| Optical rotation | +70° to +80° |
| Refractive index | 1.484–1.488 at 20°C |
| Specific gravity | 0.900–0.910 |
| Solubility | 1 mL dissolves in 8 mL of 80% alcohol |

Very little oleoresin is made from caraway seed. For flavoring purpose, either the seed or the oil is used.

## Uses

Caraway seeds are used for the flavoring of bakery products, especially rye bread. Sausages, cheese, soups, and sauerkraut are also flavored by it. Caraway is used in meat, seafood, dips, and bakery items. Oil can be a substitute if similar items are made as processed foods. The oil is used in liqueurs, chewing gum, toothpaste, and mouthwashes.

Oil of carvone is used as a room freshener and in aromatherapy. Because of the phenolic nature of carvone, the oil is used in soaps, lotions, and even in perfumes.

An infusion of seeds is used as a remedy for colic and digestive disorder, and to counter worms.

## Identification Numbers

| | FEMA No. | CAS | US/CFR | E-No. |
|---|---|---|---|---|
| Caraway seed oil | 2238- | 8000-42-8<br>85940-31-4 | 182.20 | – |
| Caraway seed extract | – | 8000-42-8<br>85940-31-4 | | – |

## References

Bailer, J.; Aichinger, T.; Hackl, G.; de Huber, K.; and Dachler, M. 2001. Essential oil contents and composition of commercially available dill cultivars in comparison with caraway. *Ind. Crops Prod.* **14**, 229–239. Cf. Lawrence, B.M. Progress in essential oils. *Perfumer Flavorists* **31** (1), 54–57.

Iacobellis, N.S.; Lo Cantore, P.; Capasso, F.; and Senatore, F. 2005. Antibacterial activity of *Cuminum cyminum* L and *Carum carvi* L essential oils. *J. Agric. Food Chem.* **53**, 57–61.

Sedlakova, Jitka; Kocourkova, Blanka; and Kuban, Vlastimil. 2001. Determination of essential oil content and composition in caraway (*Carum carvi*). *Czech J. Food Sci.* **19** (1), 31–36 (English).

# 28 Cardamom

## *Elettaria cardamom* M (*Zingiberaceae*)

### Introduction

In early historical records, there is reference to two types of cardamom, small and large. There is mention of cardamom in ancient Greek literature before Christ, but it is not clear whether it refers to small cardamom belonging to the *Elettaria* family or large cardamom belonging to the *Amomum* family. However, there has been clear differentiation in Europe, since the second century AD, in the list of spices from Asia, which were subjected to collection of duty at the Roman customs office in Alexandria. Among the different spices imported from the East, there was confusion in the identity of some spices. However, by the sixteenth century with definite sea routes being established, there was a clear difference in small cardamom from Malabar and large cardamom from Nepal.

In historical writings, there was confusion about its use in cookery. *Ela* was mentioned, which is the cardamom described in a medical treatise attributed to early Ayurveda masters, Charaka and Sasruta, of the first century AD (the Hindi name for cardamom is *elachi*).

Greeks and Romans are believed to have used cardamom in food, fragrant preparations, and medicines about 2000 years ago. In fact, the people of Babylon cultivated cardamom in their gardens around 700 BC. The Vikings entered into its trade in Constantinople over 1000 years ago, so there is no wonder that cardamom is a special ingredient in Danish pastries and Swedish cakes. Due to sun drying and prolonged storage, bleached cardamom was used in Scandinavian countries until very recently.

Arabs promoted the use of green-colored cardamom, as they preferred the fresh green color. To achieve the maximum green color, special cultivars are chosen and drying is done in ovens, to prevent the removal of chlorophyll by sun drying. Small cardamom is generally regarded as the third costliest spice after saffron and vanilla.

### Plant Material

Zingiberaceae plants are distributed throughout the tropical forests of the world. The plant that is the source of small cardamom originally evolved by natural cross-pollination; today, considerable variation in size and shape is seen in cultivars. Until recent times, two cultivars, Mysore and Malabar, have been propagated. Oddly, the one cultivated in Kerala State is known as Mysore and the one in Karnataka State (until recently known as Mysore State) is called Malabar.

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**Photo 5.** (A) Cardamom plant with capsules growing from the base. (B) Dried green capsules. See color insert.

The Mysore cultivar, grown in Kerala and in the Western Ghats slopes in adjoining states, has slightly elongated capsules with greater green color. The other variety is more rounded and has a poor green color. This rounded variety is made into the bleached grade. Because of the preference for dry green capsules in international trade, most of the cultivation is changing to the more greenish, elongated cultivar (Mysore). This system ended the custom of using chlorine-containing chemicals or sulfur dioxide for lightening the color. There were also reports of using metanyl yellow solution in some places for a uniform and appealing bleached color.

The small cardamom bearing plant is a 1.5- to 4-m-high herbaceous perennial plant. From the subterranean roots stock arise a number of upright leafy shoots. The leaves are alternate and elliptical. Flowers are born in panicles about a meter long coming from the base of vegetative shoots. Fruits are trilocular capsules, fusiform or ovoid in shape, and have a green color. Inside, 15–20 hard, brownish seeds covered with a thin mucilaginous membrane are formed. Photo 5 shows the cardamom plant and the dried green capsules.

Cardamom plants thrive in rich loamy soil. They are shade-loving and require some rainfall. Multiplication can be carried out vegetatively by dividing the rhizome or through seeding raised from specially selected seeds.

Plants mature in about 3 years. The life of a cardamom plant is 10–15 years. A well-maintained estate can yield of 110–170 kg of dry capsules when the plants are in excellent conditions. Otherwise, 50–75 kg is considered satisfactory.

Cardamom capsules are dried using artificial ovens. A well-designed cross-flow or through-flow electrical dryer is satisfactory. Where electricity is not available, a room heated by tin pipes through which hot flue from a firewood furnace just outside can be used for drying. Systematic opening of small vents periodically and interchange of trays depending on the different heat zones will be required for satisfactory results.

Generally, a temperature of above 60°C with high humidity can destroy some amount of chlorophyll on the outside of the capsule. Besides India, Guatemala is the most important producer of cardamom. There the holdings are small in the northern areas, which has humus-rich soil and heavy but uniformly distributed rainfall. However, the cultivated area lacks in shade trees. In southern areas, large holdings are available and scientifically planned cultivation is possible. The cultivar used is Mysore, with vegetative propagation using rhizome suckers. Replantation is generally carried out after 10 years.

There is some cultivation in Sri Lanka, where the variety used was *Elettaria cardamomum* L Maton var major Thwaites, but it has been replaced by the Indian cultivar Mysore.

## Chemistry

Cardamom capsules on a dry basis contain about 10% crude protein, 42% carbohydrate, and 20% crude fiber, with B vitamins, ascorbic acid, and minerals. Since its value is mainly as flavoring substance, the most important constituent is the essential oil, which is present to the extent of 5–11% depending on the region and grade.

The chief constituent of the volatile oil is 1,8-cineole (Fig. 28.1). The component is noted for its camphoraceous and cool odor. Alcohols such as linalool and terpineol are present both in free and acetate forms.

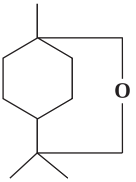

**Figure 28.1.** 1,8-Cineole.

## Essential Oil

Cardamom oil is a highly valued spice oil. In the early days, steam distillation was carried out by Western user countries. More recently, distillation is mostly done in producing countries.

The seeds on a dry basis represent about 65% of the capsule. The husk accounts for 35%. There can be variation based on region and grade. Almost all the essential oil is present in the seeds. If the capsule is ground and distilled, the full yield of the oil can be obtained in 2–4 hours. Since the husk and deoiled seeds are in demand for grinding, in recent times, large manufacturers carry out distillation in different steps.

The first step is breaking the capsule by passing it through a loosely adjusted plate mill. The husk will be opened and be ready for separation without damaging the seeds. From this, seeds are carefully separated by combination of vibrating screens and, if necessary, by manual winnowing.

The collected seeds are fed into a stainless steel distillation unit. The steam is adjusted at a slow rate without pressure. Distillation is continued for several hours, even as much as 48–64 hours. Emphasis is also placed on obtaining undamaged seeds. Oil is collected in two or more fractions. The early fraction will have more of the terpene hydrocarbons and so is regarded as slightly cheaper. The later fraction has a more desirable rounded aroma required for food flavoring.

Deoiled whole seeds are used for blending and for curry powder. Even though most of the volatiles are removed, it will still contribute to the overall flavor. Even the husk has a value; it is used for solvent extraction.

Chemical analysis using GC has been carried out by a number of workers. The composition of total oil in Indian cardamom is as given in Table 28.1. It can be seen that 1,8-cineole with 32–35% and terpinyl acetate with 38–40% are the major constituents. However, when fractional steam distillation is carried out, the second fraction will show a higher content of terpinyl acetate, that is, 40–43% with corresponding decrease of 1,8-cineole to 28–33%. Higher contents of 1,8-cineole and $\alpha$-terpinyl acetate as well as presence of linalool, linalyl acetate, and geraniol are reported by Lawrence and Shu (1993).

Higher levels of alcohols and esters give more value to the oil as a food flavor. Too much cineole gives an unwanted camphoraceous aroma. The oil from Malabar cultivar with rounded shape and less green color gives higher cineole content than the above. That is another reason why such cardamom is considered inferior, apart from the poor green color. It may be noted that upgradation of oil quality for use as a flavor can be achieved to a level by fractional steam distillation.

**Table 28.1.** Composition of total cardamom oil (GC area percentage)

| Constituent | % Range |
|---|---|
| α-Pinene | 1.0–3.0 |
| β-Pinene | 3.0–5.0 |
| Myrcene | 2.0–3.0 |
| Limonene | 3.0–4.0 |
| 1,8-Cineole | 32.0–35.0 |
| Linalool | 0.5–1.5 |
| Linalyl acetate | 1.0–2.0 |
| Geraniol | 0.5–1.5 |
| Terpinyl acetate | 38.0–40.0 |

For further details about cardamom and its processing, refer to the excellent reviews by Govindarajan et al. (1982) and Krishnamurthy and Sampathu (2002).

According to the FCC, cardamom oil occurs as a colorless or very pale yellow liquid with the aromatic, penetrating, and somewhat camphoraceous odor of cardamom and a pungent, strongly aromatic taste. It is affected by light and is miscible with alcohol.

Physical characteristics as defined by FCC are as follows.

| | |
|---|---|
| Optical rotation | +22 to +44 |
| Refractive index | 1.462–1.466 at 20°C |
| Specific gravity | 1.917–0.947 |
| Solubility | 1 mL dissolves in 5 mL of 70% alcohol. The solution can be clear or hazy. |

## Oleoresin

Cardamom is more valued for its aroma, and this quality is obtained by using cardamom oil. All the same, there is demand for oleoresin, especially for a water-dispersible type. Oleoresin gives a more rounded true flavor of the spice. Additionally, the resinous portion acts as a good fixative.

The resin is contributed by the husk. Husk on cold extraction using ethylene dichloride, ethyl acetate, or a mixture of acetone and hexane gives a yield of 2–3% of resinous material. Generally, this is blended with polysorbate and propylene glycol before oil is added. Oleoresin can be made with a volatile oil content of 5–80%, depending on customers' demands. Such oleoresin will disperse in watery food blends. A typical oleoresin will be a dark greenish liquid with the warm, spicy, pleasing flavor characteristic of cardamom.

## Uses

Cardamom oil is highly valued as a food flavor. It blends well in baked products, dairy products, ice cream, sweet preparations, confectionery, and a variety of food products.

It is very convenient for making cardamom-flavored tea and coffee. Where heating is involved, care should be taken that addition of oil is done toward the end of processing; otherwise, oil may evaporate. Thus, for cream biscuits, oil is mixed with the cream portion since that is not subjected to baking. For tea bags, it is better to use microencapsulated cardamom oil.

Oleoresin will be easier to use in ice cream, candies, and some confectionery, where water dispersibility is helpful. It should be kept in mind that oleoresin will impart a slight dark color if used in greater proportions.

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Cardamom oil | 2240 | 85940-32-5 | 182.10 | – |
| Cardamom oleoresin/extract (FEMA has given 2241 for cardamom seed oil) | – | 8000-86-6 | 182.20 | – |

## References

Govindarajan, V.S.; Narasimhan, S.; Raghuveer, K.G.; and Lewis, Y.S. 1982. Cardamom—production, technology, chemistry and quality. *CRC Crit. Rev. Food Sci. Technol.* **17**, 229–326.

Krishnamurthy, N.; and Sampathu, S.R. 2002. *Industrial Processing and Products of Cardamom. Cardamom: Genus Elettaria*. London and New York: Taylor and Francis, pp. 223–244.

Lawrence, Brian M.; and Shu, C.K. 1993. Essential oils as components of mixtures, analysis and differentiation. In C.T. Ho and C.H. Manley, eds., *Flavor Measurement*, 267–325. (See Lawrence, Brian M., Progress in essential oils. *Perfumer Flavorist* 2007, **328**, 32–45.)

# 29 Carob Pod

## *Ceratonia seliqua* L (*Leguminosae* or *Fabaceae*)

### Introduction

Carob pods grow on a tree. The pods when ripened are somewhat sweet. It is believed that St. John the Baptist ate them for survival during his life in the wilderness, hence its alternate name "St. John's Bread."

The term "karat," the unit of weight of diamonds, is derived from the Greek word *keratin*. This alludes to the ancient practice of weighing gold and precious stones against the seeds of the carob tree, before "karat" was standardized as 0.2 g. In Roman times, a pure gold coin weighed 24 "karat" seeds. The species name of the carob plant is thus derived. The seed of the fruit is referred to as locust seed.

The carob tree is resilient in harsh climate and drought and hence carob has a reputation as a last source of food in bad times. St. Luke mentioned that in bad times the Prodigal Son dreamed of eating pods that he used to feed to the pig, in order to escape starvation.

In ancient Egypt, it was common to eat the fleshy part of the carob pod. Carob juice-based drinks are traditionally used during the holy month of Ramadan. Dried carob pods were traditionally eaten during Jewish holidays. Before cane sugar and beet sugar became commonly available items, ripened carob pods were an important ingredient in sweetening food products.

In times of famine, peasants have survived on carob pods. The pods also form feed for livestock. Spanish missionaries introduced carob to Mexico and California in the mid-nineteenth century. The United States tried to promote carob in the early twentieth century as a part of development of arid land in the western region and as a promotion of natural health food.

### Plant Material

The tree grows to a height of 10–15 m and, when it has grown for over 15 years, the bottom portion of the trunk will have a diameter of 25 cm. The crown is wide and semispherical. The tree has sturdy branches and rough, brown-colored bark. The leaves are evergreen and are pinnate with 6–10 opposite leaflets. The leaves, which are frost-tolerant, are oval, dark green in color, and somewhat leathery. They are 3–6 cm in length.

The tree is dioecious, with male, female, or hermaphrodite separate trees. The flowers are tiny, red, and numerous. They are arranged spirally along the inflorescence

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axis. Male flowers produce a characteristic semen-like odor. The pollination is carried out by wind and insects. The pod is light to dark brown in color, long, flattened, and either straight or slightly curved. The pods take a year to mature and ripen. The unripe pod is green but on ripening assumes a brown color. The pods have 10–12 flattened hard seeds. Because the seeds are loose in their cells when fully ripened, they make a rattling noise when shaken. At the green stage, the inside is moist and astringent but on ripening assumes a sweet fruity taste, somewhat resembling a date fruit. The tree, being a *Leguminosae*, has nitrogen-fixing bacteria in nodules.

Currently, carob is produced in Spain and Portugal. It grows well in warm regions near the coast. Carob is grown in Cyprus, Crete, Sicily, Sardinia, and Majorca. It is exported from Italy to Russia and Central Europe. Although the tree is cultivated for the pods and seeds, many still grow in the wild, especially in the Mediterranean region.

Carob pods are rich in sugars, being present to a level of 40–50%. Sucrose is present at 26% and fructose at 13% (Leung and Foster 1996). In addition, carob has other sugars such as xylose, maltose, and glucose. The presence of reducing sugars prevents the crystallization of sucrose. Analysis shows that carob pod meal has carbohydrate, (45%), some proteins (3%), and low levels of fat (0.6%) (Plessi et al. 1997). Pods have polyphenols, both proanthocyanidin condensed and hydrolyzable tannins. The pulp has proteins, fats, and starch, as well as some free amino acids, gallic acid, and abscisic acid, which is a plant-growth inhibitor.

The seeds of carob, often referred to as the locust bean, give a good hydrocolloid, which is available for commercial use as locust bean gum. The gum is a neutral galactomannan where mannose is joined by 1,4-linkage to the side chain of galactose and, in every fourth and fifth unit, by 1,6-linkage. It has limited solubility in cold water, but at 80°C, full hydration occurs. At 3%, it forms a thick gel with some turbidity. The gum is pseudoplastic with apparent viscosity decreasing when the rate of shear is increased.

## Extractive

Kibbled (cut into pieces) dried carob pods are extracted and mildly roasted to make into a valuable industrial product for use as a flavor in many foods and tobacco products. A general process for this can be given as follows.

Kibbled carob pods dried to a low moisture level are extracted using 50% aqueous ethyl alcohol as the solvent. About 100 kg of carob is extracted with 200 L of the solvent and heated to 40°C for about 3 hours. The extract is decanted out. The partially extracted cut carobs are further extracted three or four times, while the temperature is kept at 40°C. The combined extract is freed of the ethanol at a low temperature, making sure that temperature does not rise above 70°C. When the volume is reduced by the evaporation of ethanol and some of the water, the concentrated extract is given a roasting treatment to develop the required flavor. The total soluble solids at this stage will be 70–75° Brix in Abbes refractometer. For this, it is heated at 57–60°C for 3–4 hours. One must take care that excess heated flavor is avoided. It is necessary to stick to optimum conditions based on the roasted note desired. Unroasted extract is also used for its flavor.

## Uses

Carob pods are used for making flour and syrups; roasted extracts are used in a wide range of products, as well as for chewing because of the sweet fruity flavor. The pods are sometimes processed into a cocoa-like flour and used in various preparations and milk drinks as a chocolate substitute. In Central Europe, roasted seeds are used as a coffee substitute. Locust bean gum is used as a stabilizer in ice cream, cheese, sauces, salad dressings, canned pet food, and some dairy products.

The pods with seeds are ground and used as cattle feed. Because of its high polyphenol content and tanning property, it is usually restricted to a level of 10% of the feed. Carob flour is added to dog biscuit recipes. The high tannin content makes carob a valuable major ingredient in weight-regulating formulations.

Roasted and unroasted carob extracts are used primarily for flavoring the tobacco used in cigarettes. The extract usually comes in different strengths of roasted flavor and fruity sweetness based on the specifications of the users. The extract has use in confectionery, as a chocolate substitute, and in some beverages.

Production of dextran and fructose from carob pod has been explored using microbial techniques (Santos et al. 2005). This will improve further industrial utilization.

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Carob bean extract | 2243 | 9000-40-2 | 182.20 | – |
| | | 84961-45-5 | | – |

## References

Leung, Albert Y.; and Foster, Steven. 1996. *Encyclopedia of Common Natural Ingredients*. New York: John Wiley and Sons, pp. 123–124.

Plessi, M.; Baraldi, M.; and Monzani, A. 1997. Determination of chemical composition of carob (*Ceratonia siliqua*). *J. Food Compos. Anal.* **10** (2), 166–172.

Santos, Mariana; Rodrigues, Alirio; and Tiexeira, Jose. 2005. Production of dextran and fructose from carab pods. *Biochem. Eng. J.* **25** (1), 1–6.

# 30 Carrot

## *Daucus carota* L (*Apiaceae*)

### Introduction

Carrots are primarily cultivated as a vegetable. However, the carrot remains the symbol of carotenes, especially *β*-carotene, which has value as a food color. *β*-Carotene is also a provitamin A. There are other sources of carotenes, such as green leaves, fish liver oil, and, more recently, oil palm fruit. But carotenes were named after their prime source, the carrot.

Wild carrots probably came from Afghanistan. Selective breeding over centuries has helped to reduce bitterness, increase sweetness, and almost eliminate the woody core. Early cultivation of the crops was for their aromatic leaves and seeds. Some related crop of the family such as parsley, cumin, fennel, and dill are grown for this purpose. Perhaps carrots came to Europe in the period between the eighth and tenth centuries. Arab scholars have described red and yellow carrots in the twelfth century. In the seventeenth century, orange-colored carrots appeared in the Netherlands, and at around the same time, England started growing the vegetable.

Association of poor vision especially night vision with lack of vitamin A brought the carrot to the forefront as recently as during World War II. There are stories of British military and Royal Air Force pilots eating carrots to improve their vision to be more efficient in combat. Germans also had similar ideas about carrot consumption and the improvement of vision.

The city of Holtville in California prides itself as the carrot capital of the world and holds a festival devoted to the carrot every year. Some of the well-known dishes based on this vegetable are carrot julienne, carrot cake, carrot pudding, and the Indian sweet dish carrot *halva*.

### Plant Material

The carrot plant is biennial. The edible part rich in carotene is the taproot. The flowering stem grows to about 1 m in height. The plant grows a rosette of leaves. It has an umbel of white-colored flowers that produce fruit, which can be described botanically as mericarp. Carrot flowers are usually pollinated by bees. What is now cultivated is the domesticated cultivar of the wild carrot with considerable modifications having been effected to improve the taste and texture for use as a popular vegetable. The normal carrot has an elongated conical shape with a bright orange color due to the presence of carotene.

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While carrots can be harvested early to produce more tender baby carrots, there are also varieties that produce small carrots. It is also common for supermarkets to slice and shape large carrots into small uniform carrots for use as a cooking vegetable and for salads.

While other colors like purple, pink, yellow, and white are common for carrots, orange is regarded as the norm for carrot color. Apart from a plentiful supply for nutraceutical carotenoid pigments, orange also stands for the color of the Netherlands in its struggle for independence. The Western carrot emerged in the Netherlands from the Eastern variety from Central Asia, which are purple or yellow. In the seventeenth century the orange color became quite popular for the vegetable. Anthocyanin pigments give the purple color to some Eastern carrots.

## Chemistry

The main pigment of the carrot is $\beta$-carotene. It also has $\alpha$- and $\gamma$- carotenes. $\beta$-Carotene is a provitamin A, which is extremely important for the health of the eye. Although Nobel laureate Paul Karrer discovered carotenes in Hungarian paprika, it is the carrot that is symbolic of carotenes. Carotenes are hydrocarbons, and when oxygenated, they are called xanthophylls. Oxygenated derivatives usually have a more intense color (see Chapter 82 on paprika for structure).

Among the different cultivars of the carrot, the proportion of $\beta$-carotene ranged between 46 and 103 $\mu$g/g and $\alpha$-carotene from 22 to 49 $\mu$g/g (Heinonen 1990). Analysis of different varieties reveals that some of them have no *cis* isomer, some 9-*cis* isomers, and some 13-*cis* isomers. Some cultivars of the sweet potato showed even slightly higher provitamin A content while some fruits have a moderate quantity. A source of $\beta$-carotene that has become important in recent years is oil palm fruit and unrefined palm oil.

## Extractives

$\beta$-Carotene and other carotenes are highly oil-soluble, so an extract in oil is a very convenient form for use as color in oil-based food products. Solvents such as ethanol and propanol are used for extraction. Prior freezing followed by extraction at 60°C gives a good extract in 2–4 hours (Fikselova et al. 2008). The author's experience of similar products indicates that disintegration of the carrot, followed by some shade drying and extraction by gravity percolation at ambient temperature using a mixture of acetone and *n*-hexane, will yield a good miscella. This on careful removal of solvent at controlled temperature using some vacuum will give an oily suspension of carotenes.

Extraction using supercritical carbon dioxide of freeze-dried carrots has given a satisfactory extract (Barth et al. 1995). Comparing supercritical carbon dioxide extraction and liquid extraction using ethanol–pentane shows that the former gives 23% higher $\beta$-carotenes and that extraction time is considerably shorter (Marsili and Callahan 1993).

The carotenes are hydrocarbons and therefore they are highly oil-soluble and insoluble in water. Such extracts disperse very well in oil-based food products to give the right color. For water-based application, carrot extract has to be made water-soluble by using appropriate emulsifying agents such as polysorbate, mono- and diglycerides, lecithin, or even some solid hydrocolloids such as starch derivatives or gelatin.

The European Commission has given an E-number to $\beta$-carotene, but with a stipulation that only the required quantity should be used for the intended purpose.

According to the FCC, $\beta$-carotene occurs as a red crystal. It is sparingly soluble in ether, hexane, and vegetable oil and is practically insoluble in methanol and ethanol. Its melting point is between 176 and 182°C with decomposition.

## Carrot Seed Oil

On steam distillation of the crushed seeds of the carrot, a light yellow to reddish-brown mobile essential oil is obtained. It has a pleasing aroma and is sometimes used as a flavor.

## Uses

Carotene extract of carrot can be used to give orange color to fatty foods. In many countries, only carotenoid natural color is allowed in butter and other dairy products. Although annatto extract gives a more intense color, carrot extract can give an effective color with vitamin A.

Carrot extract of carotene after introducing water dispersibility can be used in a wide range of confectionary, beverage, ice cream, and even fruit products. Because of its heat stability, it is useful as a natural color in baked products.

As a nutraceutical, this natural color has great value. It is provitamin A and an effective antioxidant. It is therefore a scavenger of free radicals and a protectant against cardiovascular and cancer-related disorders.

## Analytical Method

The FCC describes a method of determination using cyclohexane solution using an atomic absorption spectrophotometer set at 445 nm. A simple and rapid method for $\beta$-carotene extraction from the carrot has been developed using spectrophotometric measurement at 436 nm of petroleum ether extract (Zaraik and Yariwake 2008).

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Carrot extract | – | 8015-88-1 | – | – |
| | | 84929-61-3 | | – |
| Carrot seed oil | 2244 | 8015-88-1 | 182.20 | – |
| | | 84929-61-3 | | – |
| Carotenes | – | – | – | 160 a |
| β-Carotene (synthetic) | – | – | – | 160 a (i) |
| Natural extracts | – | – | – | 160 a (ii) |

## References

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Heinonen, M.I. 1990. Carotenoids and provitamin activity of carrot (*Daucus carota* L.) cultivars. *J. Food Chem.* **38**, 609–612.

Marsili, R.; and Callahan, D. 1993. Comparison of a liquid solvent extraction technique and supercritical fluid extraction for the determination of alpha- and beta-carotene in vegetable. *J. Chromatogr. Sci.* **31** (10), 422–428.

Zaraik, Maria Luiza; and Yariwake, Jenete Harumi. 2008. Extraction of β-carotene from carrots. A proposal for experimental courses in chemistry. *Quimica Nova* **31** (5), 1259–1262.

# 31 Cassia

*Cinnamomum aromaticum* or
*C. cassia Blume* (*Lauraceae*)

## Introduction

There are reports that cassia was known to the ancient Egyptians as early as 2000 BC. It was probably used in embalming. In ancient China, cassia was worshipped as the "Tree of Paradise." It was believed that fruits of the tree would enable people to enjoy everlasting happiness and even immortality.

In the past, cassia was confused with true cinnamon; as both were grown mainly in Sri Lanka, many of the historical references to cinnamon could be to either spice. In the United States and Canada, cassia is referred to as cinnamon, perhaps because true cinnamon is not as widely available in North America. It would be more convenient to call this spice cassia to distinguish it from what is known as true cinnamon in many other parts of the world.

## Plant Material

Cassia is the dried bark of an evergreen tree. It is from the relatively thicker outer skin, whose outside is rough. In most cases, the trees grow wild and are not subjected to systematic agricultural practice. They grow in China, Indonesia, and Vietnam, as well as grown in Laos and Cambodia. Indonesia's *Kurintji* grade is highly valued in trade. Photo 6 shows dried cassia bark pieces.

The bark is peeled twice a year. Chinese cassia has a thick but brittle bark. Although there are grades called whole quill or China roll, and broken grades called Canton roll, a large quantity is traded as broken pieces. Similar, though with some variation, is the processing in Indonesia and Vietnam. Broken bits are used for extraction.

India and the United States are two major importers of cassia. In India, cassia is used mostly in savory preparations such as meat, vegetable curries, and *biryani*. In the United States, cassia is used in sweet bakery products like rolls, buns, pastries, cakes, and doughnuts.

In India, there is a related spice like *tejpat* (*Cinnamomum tamala* Ness), which is the thick bark of an evergreen tree that grows to a height of 8 m and a girth of 1.4 m. A recent study reports high levels of linalool and $\alpha$-terpineol in *C. tamala* bark oil (Baruah 2010).

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**Photo 6.** Cassia. See color insert.

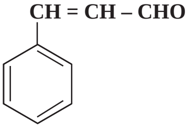

**Figure 31.1.** Cinnamaldehyde.

## Chemistry

The composition of the bark will vary from species to species. On average, the bark contains 7–32% carbohydrate, 3–3.5% protein, about 2% fixed oil, 12–28% crude fiber, and 0.5–5% essential oil.

The volatile oil is the most important constituent because of its aroma and flavor. The major component is cinnamic aldehyde or cinnamaldehyde (Fig. 31.1). Cinnamaldehyde was first isolated in 1834 by Dumas and Peligot. Naturally occurring cinnamaldehyde is *trans* isomer.

## Essential Oil

On prolonged steam distillation, ground cassia gives cassia oil. The oil consists of a high boiling fraction like cinnamaldehyde and has a specific gravity higher than 1.0.

To facilitate steam distillation, it is better to use a side arm connected to the water condenser above the packed material, instead of an upward gooseneck. The collected oil tends to diffuse, making its separation from water very difficult. Salting may not help, as the oil is heavier than water and so will sink. Separation requires the solution to stand for some time. The commercial yield will be about 2%. The cinnamaldehyde content will be around 75%. Other compounds present are $\alpha$-pinene 1.2%, limonene 2%, coumarin 2.5%, benzaldehyde, cinnamic acetate, and chavicol.

Cassia oil is extremely difficult to produce. Cassia leaf oil is used as the essential oil.

According to the FCC, cassia leaf oil is a yellow to brown liquid with the characteristic odor and taste of cassia cinnamon. On aging or exposure to air it darkens and thickens. It is soluble in glacial acetic acid and in alcohol.

Physical characteristics as defined by the FCC are as follows.

| | |
|---|---|
| Optical rotation | −1° to +1° |
| Refractive index | 1.602–1.614 at 20°C |
| Specific gravity | 1.045–1.063 |
| Solubility | 1 mL dissolves in 2 mL of 70% alcohol |

Cassia bark is found to have significant quantities of cinnamaldehyde. The highest level is noticed in the debarked cortex (He et al. 2005). By establishing markers based on major components and coumarin, scientists are able to distinguish genuine cassia bark from adulterants. In another study, *trans* cinnamaldehyde is determined by 1 H-NMR spectrometry. The amount of cinnamaldehyde extracted is highest with ethyl acetate, followed by chloroform and *n*-hexane (Song et al. 2005). By extracting with supercritical carbon dioxide, 3.75% cinnamon bark oil is obtained with a pressure of 120 bar (Cai et al. 2008). Compounds identified in the tender stem of cassia include 2-methoxy cinnamic acid, 1,4-diphenylbutanedione, ergosterol-5a-, 8a-peroxide, 2-methoxybenzoic acid, and syringaldehyde, which have not been reported earlier (Liu et al. 2002).

## Oleoresin

Because of the long duration of distillation and for separation of oil, cassia bark is generally extracted directly to make oleoresin. For this, the raw material is pulverized coarsely in a hammer mill, followed by passing through a roller mill. It is then extracted using solvents such as ethylene dichloride or acetone–hexane mixture.

The yield of oleoresin in the case of ethylene dichloride is around 5% with a volatile oil content of 60–70% v/w. If the solvent is an acetone–hexane mixture, the yield is slightly lower, with about 4.8% with oil content of 60–70% v/w. The oleoresin so obtained with either solvent will be a thick reddish-brown liquid with a sharp, medicinal aroma and a spicy burning taste. Suitable diluents can give a relatively free-flowing product. Generally, acetone extraction gives a reddish tint and ethylene dichloride a brownish tint. This will be reflected in the extraction using the acetone–hexane mixture.

## Uses

Cassia is a spice that gives a strong flavor generally referred to as “cinnamon flavor.” Sri Lankan cinnamon (*Cinnamomum verum*) is generally regarded as tree cinnamon, but it is very mild. In the United States, cassia is a popular flavor in meat, vegetable, and bakery products. The well-known cinnamon rolls are flavored using cassia. For such processed food products, oleoresin is very convenient to use. Oil is rarely used. The cassia leaf oil is used in cleaning lotions and other cheaper toiletries where the phenolic constituents of the oil serve as a mild antiseptic.

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Cassia oil | 2258 | 8007-80-5<br>84961-46-6 | 182.20 | – |
| Cassia oleoresin/extract | 2257 | 84961-46-6 | – | – |
| Cassia absolute (*Acacia farnesiana*) | 2260 | 8023-82-3<br>89958-31-6 | 172.510 | – |

## References

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Song, Myoung-Chong; Yoo, Jong-Su; and Back, Nam-in. 2005. Quantitative analysis of *t*-cinnamaldehyde of *Cinnamomum cassia* by 1H NMR spectrometry. 2005. *Han’guk Eungyong Sangmyong Hwahakhoeji* **48** (3), 267–272 (Korean) (*Chem. Abstr.* **144**:398470).

# 32 Celery Seed

## *Apium graveolens* L (*Umbelliferae*)

### Introduction

The celery plant was known to the ancient world. There is mention of celery in archeological reports covering of the ninth century BC. In Homer's *Odyssey*, there is mention of wild celery, and in the *Iliad*, there is description of horses grazing on wild celery, which grows in the marshy outskirts of Troy. Celery leaves and inflorescence were part of the garland discovered in the tomb of Tutankhamen, a pharaoh of Egypt.

The plant is closely related to parsley and carrots. Celery's leaf stalk and fleshy taproot are used as a vegetable in colder climates of Europe and America. However, in temperate climates, celery is cultivated for the seeds, which give valuable extractives used for flavoring. Generally, the cultivar used in producing essential oil and oleoresin from seeds, and cultivated in a temperate climate may not be the best suited for use of its leaf stalk and taproot as a vegetable; similarly, the cultivar used as a vegetable is not suitable for producing essential oil and oleoresin.

### Plant Material

Celery seed is the seed of a perennial herbaceous plant, which grows to a height of 0.5–1.5 m. The plant has succulent and numerous roots. Stems are branched and produce leaves that are radical, pinnate, and large, divided into three segments. Flowers are small and white in color. Fruits are small with 1-mm diameter and 1.5-mm length and, on drying, produce very small seeds, which are brown in color and bitter in taste (see Photo 7).

The plant is cultivated in various countries including France, Holland, Hungary, China, and the United States. But the cultivation of the seed-yielding cultivar is most prevalent in India, especially in the Punjab State around Amritsar. Here, in relatively cooler, hilly climatic conditions, the plant is biennial, producing seeds only in the second year; in the plains, it is an annual, producing seeds in the first year. In the plains, where the bulk of cultivation is carried out, seeds are sown in September, transplanted in January and harvested during May and June. Being bitter, celery seed was primarily used for therapeutic purposes. Various medicinal properties, such as the lowering of blood pressure, relief from joint pains, antiseptic properties for the urinary tract, diuretic action, and promotion of the onset of menstruation are attributed to the seed. But the main use of the seed is to produce extractives useful in food flavoring.

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**Photo 7.** Dried celery seeds. See color insert.

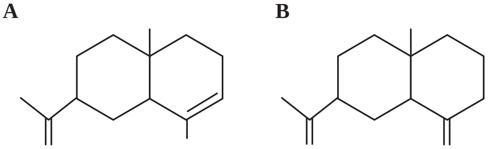

**Figure 32.1.** Selinenes of celery seed oil. (A) $\alpha$-Selinene. (B) $\beta$-Selinene.

## Chemistry

The seed on analysis shows about 23% fat, 41% carbohydrate, and 18% protein. It is rich in minerals and water-soluble vitamins. However, since the seed is used for extracting oil and oleoresin, its nutritional quality is of no significance. Seeds contain 1.5–2% of essential oil, which needs prolonged steam distillation. While the main constituent is limonene, the value of the oil is determined by two isomers of a cyclic sesquiterpene hydrocarbon, $\alpha$-selinene and $\beta$-selinene (Fig. 32.1). Bitterness of oleoresin is caused by phthalides, of which sedanolide is the most prominent (Fig. 32.2). This is lactone of sedonolic acid. Another phthalide present is sedonic anhydride or tetrahydro-*N*-butlidene phthalide.

## Essential Oil

For release of oil, treatment with water is recommended. For this, dry seeds and about 40% of water are mixed well in a mechanical screw mixer. This is then fed into a

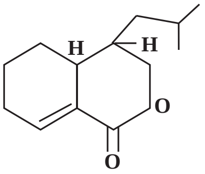

**Figure 32.2.** Sedanolide.

stainless steel distillation unit, and steam is admitted from the bottom at normal pressure. Steam distillation of celery seed is a slow process. The value of the oil is more in its sesquiterpene constituents. Full distillation takes 40 hours, giving a yield of 1.8–2.2%.

The main constituents of celery seed oil are *d*-limonene and selinene. The former (1-methyl-4-isopropenyl-1-cyclo-hexene) is present in the amount of 69–75%. Selinene, which is cyclic sesquiterpene, is present in levels of 10–15%. High boiling selinene is actually a mixture of $\alpha$- and $\beta$-isomers. The $\beta$-isomer is more abundant than the $\alpha$-isomer.

Celery seed oil is a yellow to yellowish-brown mobile liquid with a curry-like, pleasant aroma. According to the description given by the FCC, celery seed oil occurs as a yellow to greenish-brown liquid with a pleasant aromatic odor. It is soluble in most fixed oils with the formation of flocculent precipitate and in mineral oil with turbidity. It is partially soluble in propylene glycol, but it is insoluble in glycerin.

Physical characteristics as defined by the FCC are as follows.

| | |
|---|---|
| Optical rotation | Not given |
| Refractive index | 1.480–1.490 at 20°C |
| Specific gravity | 0.870–0.910 |
| Solubility | 1 mL dissolves in 8 mL of 90% alcohol usually with turbidity |

(Author's data for optical rotation is +48 to +78°.)

## Oleoresin

The best way to obtain a good yield is to extract the deoiled residue and blend the resin that is obtained with the essential oil. For this, the deoiled material after steam distillation is dried. To get maximum yield of nonvolatile constituents, mainly triglycerides and other lipids, the dried material is passed through an expeller in which cells will be broken for combination with a solvent. If the powder is overdried, slight moisturizing with about 5% of water on the basis of weight of the extractable deoiled material may be needed. If completely dry, heat will be formed during the passage through the expeller. During the process, no oil is actually taken out since the purpose is to break up the cells. If any fatty oil oozes out, that is taken into the percolator along with disintegrated deoiled material.

Solvent extraction is carried out by batch countercurrent method. Usually, the quantities handled may not justify a continuous extraction plant. The rich miscella is distilled free of the solvent to obtain the resin fraction. The weaker miscella that comes out after the withdrawal for distillation is passed on to the next percolator. The final wash will be with pure solvent. The yield of resin fraction will be 17–18% on the basis of original dry raw material.

An appropriate quantity of oil obtained earlier is added to form oleoresin of required specification. Commercial requirement is from 7% to 10% of volatile oil content. The resin fraction will have some oil that escapes steam distillation. Considering this, only a smaller quantity of oil will need to be added. This will leave some salable celery seed oil. Celery seed oleoresin is a greenish-brown oily liquid with typical warm aroma and bitter taste.

Bitterness of the oleoresin is caused by phthalides, which are present to the extent of 2.5–3%. While sedanolide is the most important, sedonic anhydride and tetrahydro-*N*-butlidene phthalide present to a level of 0.5% also contribute toward bitterness.

Phthalides are mostly present in the nonvolatile hexane-extracted fraction. However, small quantities can be present in the high boiling fraction of the volatile oil as recent research shows.

Sedanolide is used as an herbal remedy to treat inflammatory conditions such as gout and rheumatism. It is relatively nontoxic to cells in culture but the protection it affords against hydrogen peroxide and tertiary butyl hydroperoxide-induced toxicity was not statistically significant (Woods et al. 2004). It can be washed out from resin with methanol or ethanol, as they are relatively polar. Alternatively, concentrated phthalide fraction can be obtained by extraction of deoiled material with methanol or ethanol. After the removal of solvent, the resin can be freed of nonpolar lipid constituents by washing with hexane. The residual, near solid material has intense bitterness used in special flavoring and for medicinal use.

Direct single-stage extraction with hexane results in a lower yield of extractives. During the step of passing through the expeller to break up the cells, there is loss of essential oil. Two-stage extraction, first steam distillation to separate oil and then solvent extraction to obtain the nonvolatile resin (followed by appropriate blending), therefore has merit.

GC-MS studies of Indian celery seed oil has been carried out by Rao et al. (2000). It shows 44 constituents, out of which limonene (50.90%), $\beta$-selinene (19.53%), 3-*n*-butyl phthalide (6.92%), nerolidol (2.29%), and $\alpha$-selinene 1.63% are the most prominent. On hydrodistillation, celery seed volatile oil reveals several terpene hydrocarbons and oxygenated derivatives including limonene, $\beta$-selinene, and butyl phthalide (Chowdhury and Kapoor 2000). In the study of Chinese oil, the compounds noted are terpenes, phenolic compounds, and some phthalides (Liu and Liao 2004).

## Uses

Celery seed essential oil is used in food flavoring to give a pleasant aroma to a range of products such as soup, beverages, confectionery, and baked goods. The oleoresin with a bitter taste is used in various savory preparations of meat and vegetables.

The solid extract rich in phthalides finds use in some special foods that need a bitter note and also for medicinal purposes.

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Celery seed oil | 2271 | 8015-90-5 | 182.20 | – |
| Celery seed extract (including $CO_2$ extract) | 2270 | 89997-35-3 | 182.20 | – |
| Celery seed extract solid | 2269 | 89997-35-3 | 182.20 | – |

## References

Chowdhury, A.R.; and Kapoor, V.P. 2000. Essential oil from the fruit of *Apium graveolens*. *J. Med. Aromat. Plant Sci.* **22** (1B), 621–623.

Liu, Li; and Liao, Lixin. 2004. Study on chemical constituents in essential oil from celery seed. *Tianran Chanwu Yanjiu Yu Kaifa* **16** (1), 36–37 (Chinese) (*Chem. Abstr.* **143**:474910).

Rao, L.; Jagan, Mohan; Nagalakshmi, S.; Puranaik, J.; and Shankaracharya, N.B. 2000. Studies on chemical and technological aspects of celery (*Apium graveolens* L) seed. *J. Food Sci. Technol.* **37** (6), 631–635.

Woods, J.A.; Jewell, C.; and O'Brien, N.M. 2004. Sedanolide, a natural phthalide from celery seed oil: effect on hydrogen peroxide and tert-butyl hydroperoxide-induced toxicity in HepG2 and CaCo-2 human cell lines. *In Vitr. Mol. Toxicol.* **14** (3), 233–240.

# 33 Chicory

## *Chichorium intylus* L (*Compositae* or *Asteraceae*)

## Introduction

Chicory root is a well-known coffee substitute. It is also known as “blue sailors” or “coffee weed.” The cultivated forms are grown also for the leaves, which are eaten raw as salad. But the main use of chicory is for the root, which after roasting and grinding becomes a coffee substitute or additive.

Chicory has a long history in France, cultivated as a potherb. In Napoleon’s time, it became important as an adulterant or substitute for coffee. This is a practice that was later followed in the United States, England, and India. Coffee containing more than 50% of chicory powder is referred to as “French coffee” in the English-speaking world. In Roman cuisine, chicory root is used after frying with garlic and chili to give a welcome bitter and spicy flavor to meat dishes.

## Plant Material

Chicory is a bushy perennial herb, which is commonly seen growing on the roadside in Europe, the United States, and Australia. The plant, when it starts flowering, attains a height of 30–100 cm. The leaves are stalked, lanceolate, and unlobed. It generally has bright blue and, in a few cases, white, flowers whose heads will be 2–4 cm in diameter. There will be two rows of involucral bracts, the inner being longer and erect and the outer shorter and spreading. It has spindle-shaped taproot, which is used as raw material for flavor.

The root has a polysaccharide, inulin, which is similar to starch. It is a storage carbohydrate that may be present from 20% to over 50% according to cultivar. On hydrolysis, inulin yields mostly fructose and some glucose. It is sometimes used as a mild sweetener in the food industry and as a prebiotic in yogurt. It is also becoming popular as a source of soluble dietary fiber.

Chicory root has an aroma fraction made up of pyrazines, benzothiozoles, carbonyl compounds, furans, phenol, and organic acids (Leung and Foster 1996). It has also bitter components, small amounts of indole alkaloids, phenolics, pectin, and some fixed oil. Volatiles isolated from roasted chicory by simultaneous steam distillation and solvent extraction on headspace analysis have been investigated by GC-MS (Baek and Cadwallader 1997). They include some pyrazines and *N*-furfuryl pyrroles as well as some minor aroma-contributing chemicals. Five known (and one unknown)

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sesquiterpene lactones are reported in fresh chicory root (Van Beek et al. 1990). The threshold values of these bitter substances have been determined.

## Extractives

Roasted chicory roots are extracted with hot water at 60°C. This, on concentration, becomes a valuable flavor. Like tea, the extract can also be made by 50% aqueous ethyl alcohol, which results in an extract with more of the organic molecules, including bitter substances.

## Uses

Roasted chicory is used as an additive to roasted coffee. Its extractives are also added to instant coffee. Chicory generally improves the body of coffee decoction but reduces the aroma. The use of chicory naturally reduces the caffeine content of coffee, which is seen as an advantage by some. Chicory has value as a source of soluble fiber and as a prebiotic.

Chicory extract is used in bakery items, frozen dairy desserts, and alcoholic drinks to provide bitterness; it is also used in herbal tea. Chicory extract has some pharmaceutical properties and therefore finds use in digestive and diuretic preparations.

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Chicory extract | 2280 | 68650-43-1 | 182.20 | – |

## References

Baek, H.H.; and Cadwallader, K.R. 1997. Roasted chicory aroma evaluation by gas chromatography/mass spectrometry/olfactometry *J. Food Sci.* **63** (2), 234–237.

Leung, Albert Y.; and Foster, Steven. 1996. *Encyclopedia of Common Natural Ingredients*, 2nd edition. New York: John Wiley and Sons, pp. 161–163.

Van Beek, Teris A.; Maas, Paul; King, Bonnie M.; Leclercq, Edith; Voragen, Alphons G.J.; and De Groot, Aede. 1990. Bitter sesquiterpene lactone from chicory roots. *J. Agric. Food Chem.* **38** (4), 1035–1038.

# 34 Cinnamon

## *Cinnamomum verum* Presl; *C. zeylanicum* Nees (*Lauraceae*)

### Introduction

Cinnamon was used in the embalming and religious ceremonies of Egypt. It is possible that in ancient literature, true cinnamon was confused with Chinese cassia. Cinnamon is mentioned in the Old Testament where Moses is commanded to use it; its value is described in the songs of Solomon; and it finds mention in the classical writings of Herodotus and others. It was considered too expensive for ordinary funerals of ancient Rome, but it is believed that Nero commanded a huge quantity to be burned at the funeral of his wife.

Arab traders used to deal in this costly spice for Europe. Later, European forces landed in Ceylon (Sri Lanka) where the Portuguese, the Dutch, and finally the English took control. Slowly, cultivation spread to other tropical colonies. While there was confusion between cassia and cinnamon in early literature, in recent times, true cinnamon bark is recognized as a thin inner layer of bark that has smoother surface and originates from a different tree. The Greek word for tube or pipe is *kinnamon*, a reference to the dried barks that are produced as tube-like rolls.

### Plant Material

Cinnamon is a bushy evergreen tree with a height of 10–15 m. The stem is covered with thick, brown-colored bark, while young branches are covered with green-colored bark. While young leaves are reddish in color, mature ones are smooth and dark green. Flowers are formed on auxiliary panicles and are of about 3 mm in diameter and pale yellow in color.

Cinnamon grows at sea level in humid conditions with much rainfall. Vegetative propagation is carried out through cuttings, layering, or by division of old rootstock. Early harvest brings about 50 kg of quills per hectare/year. But when the tree is fully mature at 10 years, harvest increases to around 200 kg of dry quills.

Sri Lanka is the major producer of cinnamon; it is also cultivated in Southwest India, Sumatra, Borneo, Java, Madagascar, Seychelles, and Brazil.

Commercial cinnamon is made by cutting branches and scraping the rough outer skin. Then the inner bark is removed to make into recognized grades. The long rolls of inner bank of 1-m length become the best grade, known as “quills.” Due to breakage during the processing, small pieces are obtained; rolls of this grade are known as “quillings.” Although also of good quality, because they are pieces, this grade is

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**Photo 8.** Cinnamon quills. See color insert.

mostly used for grinding. Other lower grades are “feathering,” which are inner barks or twigs that cannot give straight quills or quillings, and “chips,” which are pieces obtained from thick branches. Photo 8 shows cinnamon quills.

## Chemistry

Cinnamon contains 16–23% carbohydrates, 3–5% proteins, below 2% fixed oil, 25–30% crude fiber, and 1.5–2.5% essential oil. It has vitamins, but since it is mainly used for flavor, they are not significant.

The most important constituent is cinnamon oil. The major component of the oil is cinnamic aldehyde or cinnamaldehyde (for the structure, see Chapter 31 on cassia). Cinnamaldehyde was isolated in 1834 by Dumas and Peligot. The naturally occurring one is *trans*-cinnamaldehyde.

## Essential Oil

Steam distillation is carried out from ground cinnamon of lower grades. Distillation takes a long time as the oil is heavy, with a density higher than that of water. To facilitate movement of vapors, generally a side arm is connected to a condenser just above the packed spice instead of an upward projecting gooseneck. The collected oil tends to diffuse, and separation from water takes some time. Salting will not help as the oil is heavier than water. A small portion of lighter fraction collects at the top. This is added to the stock. Generally, the commercial yield will be around 1%.

The oil contains 65–75% cinnamaldehyde, though a higher content is also reported. The other components are l-linalool, furfural, methyl amyl ketone, some aldehyde, terpene, and sesquiterpene hydrocarbons. Cinnamon of Sri Lankan origin was historically regarded as true cinnamon. Now based on analysis, especially of coumarin, it is possible to distinguish true cinnamon from others including cassia (Lungarini et al. 2008).

An analysis carried out with a sample of *Cinnamomum zeylanicum* purchased from a local market in Italy shows cinnamic acid content at 32.7% and eugenol content at

46.5% (Chericoni et al. 2005). The cinnamic aldehyde contents of two samples collected from the Bangalore and Mysore areas in India are 59.30% and 60.49%, respectively (Mallaverappu and Rajeswara 2007). In the case of the Bangalore sample, the linalool content is 13.78%, *p*-cymene 4.71%, $\beta$-caryophyllene 1.54%, and benzyl benzoate 1.51%. In the Mysore sample, the cinnamyl acetate content is 13.58%, but the $\beta$-caryophyllene content is 5.56%. By supercritical carbon dioxide extraction of a Sri Lankan sample, cinnamyl aldehyde accounts for 72.6–79.0% and $\beta$-caryophyllene 5.1–7.6% of the extract (Marongiu et al. 2007).

Cinnamon bark oil is a brownish-yellow liquid with a sweet and spicy aroma. The taste is sweet and mildly burning, typical of cinnamon bark.

Physical characteristics as defined by the FCC are as follows.

| | |
|---|---|
| Optical rotation | –2 to 0° |
| Refractive index | 1.573–1.591 at 20°C |
| Specific gravity | 1.010–1.030 |
| Solubility | 1 mL dissolves in 3 mL of 70% alcohol |

## Uses

Cinnamon is widely used in baked goods, confectionery, meat, and other food products. The extractive can give a delicate flavor to processed foods. Small quantities of the essential oil are used in cosmetics.

## Identification Numbers

| | FEMA No. | CAS | US/CFR | E-No. |
|---|---|---|---|---|
| Cinnamon bark oil | 2291 | 8015-91-6<br>84649-98-9 | 182.20 | – |
| Cinnamon bark oleoresin | 2290 | 8015-91-6<br>84961-46-6 | 182.20 | – |

## References

Chericoni, S.; Prieto, J.M.; Iacopini, P.; Cioni, P.; and Morelli, I. 2005. *In vitro* activity of the essential oil of *Cinnamomum zeylanicum* and eugenol in peroxynitrite-induced oxidative process. *J. Agric. Food Chem.* **53**, 4762–4765.

Lungarini, S.; Aureli, F.; and Coni, E. 2008. Coumarin and cinnamaldehyde in cinnamon marketed in Italy. A natural chemical hazard? *Food Addit. Contam. Part A Anal. Control Exposure Risk Assess.* **25** (11), 1297–1305.

Mallaverappu, G.R.; and Rajeswara Rao, B.R. 2007. Chemical constituents and uses of *Cinnamomum zylanicum* Blume. In I. Jirovetz, N.X. Dung, and V.K. Varshney, eds., *Aromatic Plants from Asia: Their Chemistry and Application in Food Therapy*. Dehra Dun, India: H.K. Bhalla and Sons, pp. 49–75.

Marongiu, B.; Piras, A.; Porcedda, S.; Tuveri, E.; Sanjust, E.; Meli, M.; Sollai, F.; Zucca, P.; and Rescigno, A. 2007. Supercritical $CO_2$ extract of *Cinnamomum zeylanicum*. Chemical characterization and antityrosinase activity. *J. Agric. Food Chem.* **55**, 10022–10027.

# 35 Cinnamon Leaf

## *Cinnamomum verum* Presl. *C. zeylanicum* Nees (*Lauraceae*)

### Introduction

In addition to the bark, the cinnamon tree yields leaves from which essential oil can be produced by steam distillation. The history of cinnamon has already been given in Chapter 34. The cinnamon leaf's essential oil resembles clove bud oil both in flavor quality and use.

### Plant Material

The tree has shiny green leaves when mature. In the immature stage, leaves have a reddish color. It is not practical to pluck fresh leaves for the distillation of oil. Generally, the leaves that fall and dry on the ground are collected for steam distillation.

### Essential Oil

On steam distillation, dry leaves give a yield of 1.5–2% cinnamon leaf oil. The principal component is eugenol, which along with eugenyl acetate accounts for as much as 90%. Typical analysis of Sri Lankan and Indian leaf oils based on several samples is given in Table 35.1.

It can be seen that Indian oil has a higher level of eugenol and its acetate. As could be expected, Sri Lankan oil has other constituents at higher levels. Sri Lankan cinnamon leaf oil on analysis showed 74.9% eugenol. Other compounds present in noticeable amounts are $\alpha$-pinene, linanol, cinnamaldehyde, safrole, $\beta$-caryophyllene, cinnamyl acetate, $\alpha$-farnasene, eugenyl acetate, and benzyl benzoate (Schmidt et al. 2006). Indian oil obtained from the Hyderabad region showed 79–91% eugenol. Other constituents are $\alpha$-pinene, limonene, eugenol acetate, benzyl benzoate, safrole, cinnamyl acetate, and cinnamic aldehyde (Rajeswara et al. 2006). Cinnamon leaf oil from Fiji has 86% of eugenol and most of the above constituents at low levels, but $\beta$-caryophyllene at 5.7% and linalool at 2.3% (Patel et al. 2007).

One analysis of fresh leaves from India gave only 0.25% yield (dry basis) when fresh leaves with a moisture level of 47% were steam distilled. Oils with higher boiling components need distillation over a long period of time. It was not surprising that the oil from fresh leaves as above showed a specific gravity of only 0.9223 (Shintre and Rao 1932).

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**Table 35.1.** Analysis of cinnamon leaf oils from Sri Lanka and India

| Chemical Constituents | Sri Lankan (%) | Indian (%) |
|---|---|---|
| α-Pinene | 0.7–1.3 | 0.1–0.5 |
| β-Pinene | 0.2–0.5 | 0.1–0.3 |
| δ-3-Carene | 1.0–1.5 | 0.4–0.8 |
| Limonene | 0.2–0.5 | 0.1–0.3 |
| Safrole | 0.8–1.2 | 0.2–0.5 |
| Cinnamic aldehyde | 1.0–2.0 | 0.2–0.6 |
| β-Caryophyllene | 3.0–4.0 | 2.0–3.0 |
| Eugenol | 75.0–79.0 | 85.0–89.0 |
| Eugenyl acetate | 1.5–2.5 | 2.0–3.0 |
| Benzyl benzoate | 2.5–3.5 | 0.5–1.5 |

Collection of fallen and sun-dried leaves is an expensive process. It is therefore not uncommon to see that primary distillation is carried out locally in crude stills. Such lots are then consolidated. Distillation carried out in primitive iron stills yields an oil that has a black color, because of interaction of phenolic eugenol with iron.

As per the FCC, cinnamon leaf oil occurs as a light to dark-brown liquid, with a spicy cinnamon–clove odor and taste. It is soluble in most fixed oils and in propylene glycol. It is soluble with cloudiness in mineral oil but is insoluble in glycerin.

Physical characteristics of Ceylon and Seychelles cinnamon leaf oils are defined by the FCC as follows.

| | Sri Lanka type | Seychelles type |
|---|---|---|
| Optical rotation | –2 to +1° | –2 to 0° |
| Refractive index | 1.529–1.537 | 1.533–1.540 at 20°C |
| Specific gravity | 1.030–1.050 | 1.040–1.060 |
| Solubility in alcohol | 1 mL in 1.5 mL of 70% alcohol | 1 mL in 1 mL of 70% alcohol |

As far as is known, no oleoresin is made from cinnamon leaves on commercial basis.

In a laboratory study done with oil and oleoresin of cinnamon leaf, eugenol is found to account for over 87% of the volatiles. Leaf volatiles are found to be effective against most fungi (Singh et al. 2007).

## Uses

The main value of cinnamon leaf oil is due to the high content of eugenol and its consequent antiseptic property. It is therefore used in toothpaste, mouthwash, and other dental preparations. It is often added to similar preparations of clove oil, as cinnamon leaf oil is less costly than clove oil.

Cinnamon leaf oil can even replace clove oil in processed food since it is cheaper. It is also used in cosmetics and toiletries.

## Identification Numbers

| | FEMA No. | CAS | US/CFR | E-No. |
|---|---|---|---|---|
| Cinnamon leaf oil | 2292 | 8007-80-5<br>8015-91-6 | 182.20 | – |
| Cinnamic aldehyde | 2286 | 104-55-2 | 182.60 | – |

## References

Patel, K.; Ali, S.; Sotheeswarn, S.; and Dufor, J.P. 2007. Composition of the leaf essential oil of *Cinnamomum verum* (*Lauraceae*) from Fiji islands. *J. Essent. Oil-Bearing Plants* **10**, 374–377.

Rajeswara, Rao; Rajput, D.K.; Sastry, K.P.; Kothari, S.K.; and Bhattacharya, A.K. 2006. Leaf essential oil profiles of *Cinnamomum zeylanicum* Blume. *Indian Perfumer* **50** (4), 44–46.

Schmidt, E.; Jerovetz, I.; Buchbauer, G.; Eller, G.A.; Stoilova, I; Karstanov, A.; Stoyanova, A.; and Geissler, M. 2006. Composition and antioxidant activities of the essential oil of cinnamon (*Cinnamomum zeylanicum* Blume) leaves from Sri Lanka. *J. Essent. Oil-Bearing Plants* **9**, 170–182.

Shintre, V.P.; and Rao, Sanjeva, B. 1932. Essential oil from leaves of *Cinnamomum zylanicum* Breyn. *J. Indian Institute Sci.* **15a**, 84–87.

Singh, Gurdip; Maurya, Sumitra; de Lampasona, M.P.; and Catalan, Cesar A.R. 2007. A comparison of chemical, antioxidant and antimicrobial studies of cinnamon leaf and bark volatile oils, oleoresins and their constituents. *Food Chem. Toxicol.* **45** (9), 1650–1661.

# 36 Clove

## *Syzygium aromaticum* L (*Myrtaceae*)

### Introduction

Clove has been an important spice since ancient times. There are reports that in China around 200 BC, during the Han period, it was used as a mouth freshener while speaking to important people like the Emperor. For the same reason, it is also believed to have been important in ancient Rome and medieval England.

After black pepper and paprika, clove may be the most traded spice in the world. Clove is indigenous to Moluccas, which is now a part of Indonesia. Zanzibar, which is now a part of Tanzania, was at one time a major supplier of clove bud. The island of Pamba is known as the "Island of Cloves." But today, Indonesia, Sri Lanka, and Madagascar are suppliers to the world. Cloves are also cultivated in India, but its huge demand is met mostly by import.

### Plant Material

Clove is the unopened flower bud of an evergreen tree of 10–15 m in height. The tree is an attractive one, with two or three erect branches and smaller side branches with simple, green leaves. Inflorescence is terminal, corymbose, trichotomous panicle, shortly peduculate, and branched from the base. The number of flowers varies between three and 50 and in some cases even more.

The plant requires a tropical climate with 150–300 cm of rainfall per year as in Indonesia, Zanzibar, Madagascar, Sri Lanka, and Southwest India. The tree prefers rich loamy soil with high humus. The crop is propagated by seeds that are obtained from fully ripe fruits. The tree is ready for harvesting in 4–5 years. The buds are harvested when pink in color, with petals intact. Individual buds are then separated and dried in the sun. Harvesting is done manually. A good average yield per tree is 3.5–7 kg of dried buds. Photo 9 shows (A) cloves on the plant and (B) dried cloves and the resulting oil.

### Chemistry

The main constituent is eugenol (Fig. 36.1); being phenolic, it lends a medicinal smell to spice and extractives. It has good antiseptic properties. Eugenol acetate, $\beta$-caryophyllene, linalool, and $\alpha$-pinene are also present. Some of the sesquiterpenes identified are $\alpha$-cubebene, $\alpha$-copaene, $\beta$-caryophyllene, $\alpha$-humulene, and cadinenes.

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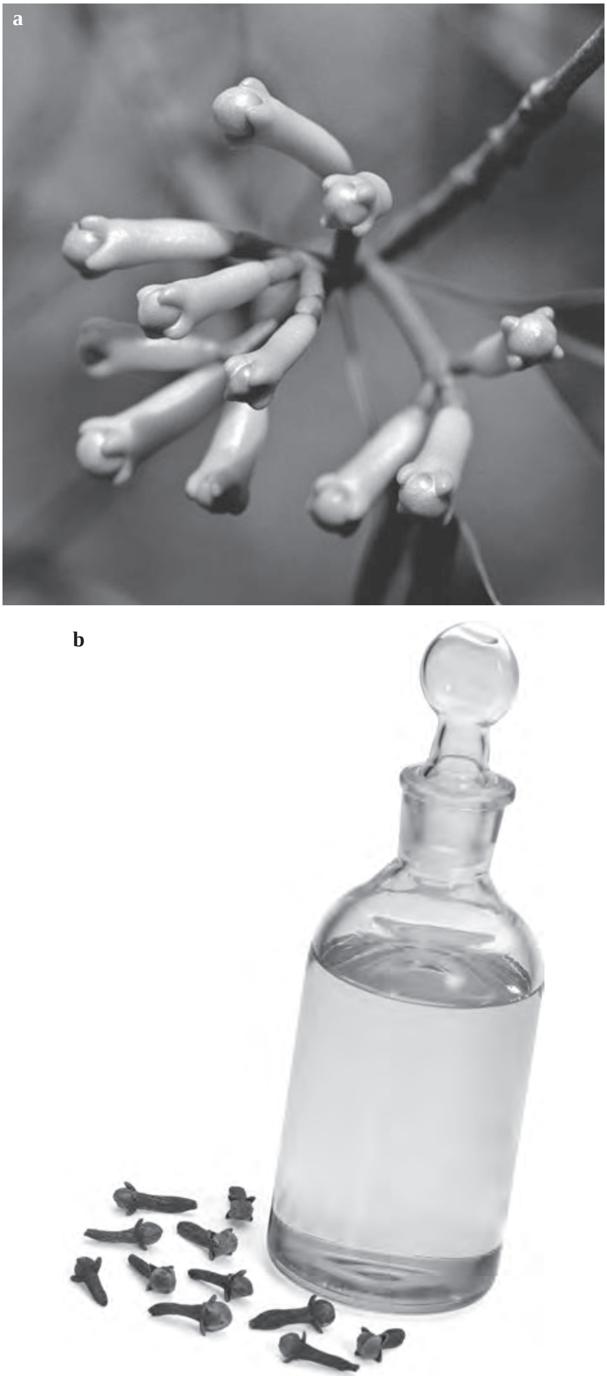

**Photo 9.** (A) Clove on the plant. (B) Dried clove and clove oil. See color insert.

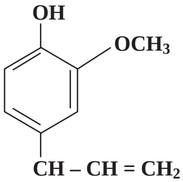

**Figure 36.1.** Eugenol.

## Essential Oil

Clove bud oil has fractions which are both lighter and heavier than water. It is rich in the phenolic constituent eugenol. Because of this, steel equipment is not suitable since the combination of eugenol and iron gives a dark color. In England in earlier years, glass distillation equipment was used. Today, stainless steel units are used.

Commercial steam distillation is carried out in stainless steel distillation units fitted with a water-cooled condenser and Florentine flask arrangement meant for heavier-than-water oils. Generally, clove buds need no disintegration. Histochemical studies using a microscope have clearly shown that oil cells are on the periphery of the buds, with a slightly higher concentration at the flower head than on the stem. Indian cloves without disintegration yield 15–16% of volatile oil with a distillation time of 20–24 hours. Disintegration yields about 1% more. This procedure will not result in whole deoiled buds. Whole deoiled buds are in demand and therefore steam distillation without disintegration gives a better return. In many dishes, whole cloves have display value, and thus deoiled whole bud has a demand. It is also possible that some deoiled cloves are used for mixing with normal buds. Water distillation also gives slightly higher yield but the deoiled material will be cooked and therefore will have no value. During distillation, almost all of the oil is heavier than water and will be collected from the bottom of the water trap. Only about 1% may be collected from the top, which is added to the oil.

In general, when compared with a yield of 15–16% oil when distilled whole with external steam for Indian cloves, Madagascar cloves will yield 14–15% and Sri Lankan cloves a slightly higher yield of 15–17%.

Clove bud oil has a mild golden yellow color. It is a mobile liquid with warm spicy and medicinal aroma and a flavor characteristic of the clove bud. The chief chemical constituent is eugenol, which is present to the extent of over 70%. Other major constituents are $\beta$-caryophyllene and eugenol acetate (Table 36.1). A large number of other terpenes, sesquiterpenes, and oxygenative derivatives are reported in small quantities.

In recent years, volatile oils obtained by different methods have been subjected to analytical studies. Extraction by supercritical carbon dioxide reveals eugenol (70.91%) as the major component, followed by $\beta$-caryophyllene (11.92%), eugenyl acetate (10.92%), methyl pentyl ketone, methyl salicylate, humulene, and other components (Liu et al. 2003). The volatile oil of clove, usually employed as a flavor for tobacco, also shows eugenol, caryophyllene, and caryophyllene oxide (Dong et al. 2004). Clove buds, after headspace hanging drop liquid phase microextraction, are examined by

**Table 36.1.** Major components of clove bud oil (Sri Lankan)

| Component | Content (%) |
|---|---|
| Eugenol | 72–80 |
| Eugenyl acetate | 7–9 |
| $\beta$-Caryophyllene | 8–12 |

GC-MS. This shows eugenol, $\beta$-caryophyllene, and eugenol acetate (Jung et al. 2006). Essential oils from both the fruit and bud have a high content of eugenol and caryophyllene, but recently 2,3,4-trimethoxy acetophenone and 2-methoxy-4-(2-propenyl) phenol acetate have been reported in clove (Zhao et al. 2006). Turkish clove shows 87.0% eugenol, 8.01% eugenyl acetate, and 3.56% $\beta$-caryophyllene (Alma et al. 2007).

According to the FCC, clove oil occurs as a colorless to pale yellow liquid with a sharp, spicy odor and taste. It darkens and thickens on aging or exposure to air.

Physical characteristics of the oil as defined by the FCC are as follows.

| | |
|---|---|
| Optical rotation | –1.5 to 0 |
| Refractive index | 1.527–1.535 at 20°C |
| Specific gravity | 1.038–1.060 |
| Solubility | 1 mL dissolves in 2 mL 70% alcohol |

## Oleoresin

Deoiled buds are dried and disintegrated by passing through a roller mill. This is packed in a stainless steel percolation vessel and the nonvolatile portion is extracted with a suitable solvent. A mixture of acetone and hexane will be a good solvent as it combines polar and nonpolar properties. After removal of solvent, a yield of about 15% can be obtained. This is then blended with clove oil as per customer specification. Usually, food additives such as propylene glycol and soya lecithin are added to get proper homogeneity, clarity, and flow characteristics.

A typical clove bud oleoresin will be a dark brown, thick, viscous liquid with warm spicy and medicinal aroma and a flavor characteristic of clove bud. Because of the presence of fixed oil and resinous matter of clove, oleoresin will show a more mellow, rounded flavor. The volatile oil level is adjusted between 10% and 75% as per customer demand.

Clove bud absolute is an alcohol extract capable of dissolving in alcoholic fragrance preparations. It can also be made by extracting alcohol solubles from the oleoresin.

## Uses

Clove is a valuable ingredient in many sweet and savory food items. In many Asian dishes, a clove note is important. In processed foods of this type, clove extractives can replace a clove bud. Oleoresin has a more mellow flavor than the oil, and therefore its use in processed food is beneficial. Clove absolute is used in expensive perfumery preparations and in certain cigarettes.

Because of the presence of phenolic eugenol, clove bud oil is used in many dental preparations and mouth fresheners, such as toothpaste, dentrifuge, mouthwash, and antiseptic mouth preparations. It is also used in medicinal preparations for asthma, arthritis, rheumatism, sprains, and toothache.

## Identification Numbers

| | FEMA No. | CAS | US/CFR | E-No. |
|---|---|---|---|---|
| Clove bud oil | 2323 | 8000-34-8 | 184.1257 | – |
| Clove bud extract | 2322 | 84961-50-2 | 184.1257 | – |
| Clove bud oleoresin | 2324 | 84961-50-2 | 184.1257 | – |
| Clove bud absolute | – | 8000-34-8 | – | – |

## References

Alma, M. Hakki; Ertas, Murat; Nitz, Siegfrie; and Kollmansberger, Hubert. 2007. Chemical composition and content of essential oil from the bud of cultivated clove (*Syzygium aromaticum* L). *Bioresources* **2** (2), 265–269.

Dong, Li; Zhu, Shu-kui; Su, Xue-li; Xing, Jun; and Wu, Cai-ying. 2004. Analysis of volatile compounds of clove oil by GC-MS. *Fenxi Kexue Xuebao* **20** (4), 394–396 (Chinese) (*Chem. Abstr.* 143:83160).

Jung, Mi-Jin; Shin, Yeon-Jae; Oh, Se-Yeon; Kim, Nam-Sun; Kim, Kun; and Lee, Dong-Sun. 2006. Headspace hanging drop liquid phase microextraction and gas chromatography-mass spectrometry for the analysis of flavours from clove buds. *Bull. Korean Chem. Soc.* **27** (2), 231–236 (English).

Liu, Bo; Chen, Kaixun; Chen, Weiping; and Chang, Qing. 2003. Study of extraction of clove bud by supercritical carbon dioxide and its GC-MS analysis. *Xiangliao Xiangjing Huazhuangpin* (3), 3–4, 26 (Chinese) (*Chem. Abstr.* 141:137005).

Zhao, Chenxi; Liang, Yizeng; and Li, Xiaoning. 2006. Chemical constituents and antimicrobial activity of the essential oils from clove. *Tianran Chanwu Yanjiu Yu Kaifa* **18** (3), 381–385 (Chinese) (*Chem. Abstr.* 147:230706).

# 37 Clove Leaf

## *Syzygium aromaticum* L (*Myrtaceae*)

### Introduction

When dried, clove leaves that fall to the ground yield an essential oil with many of the characteristics of the bud oil. This is often used as a cheaper substitute.

### Plant Material

The source of the leaves is the same tree that produces the clove bud. The leaves of clove are simple, opposite, coriaceous, exstipulate, and glabrous. It is aromatic with a smell similar to that of the buds.

When leaves fall to the ground and dry out, they are collected for steam distillation of the oil in the leaf. Because of the cost of collection and transportation, it is customary to water-distill the oil locally in crude stills. Oil from such sources is then mixed, and great quantities are made. Because of iron contamination, a dark color is generally present. But if distilled in a stainless steel or glass unit, oil has a golden yellow color and a warm spicy and medicinal aroma and flavor characteristic of clove bud oil. Chelation of iron by treatment with citric acid has been suggested, but, it is unknown whether this is a practical solution.

Eugenol is the main constituent, being present at levels over 80% (for the structure, see Chapter 36). $\beta$-Caryophyllene accounts for about 10%. Generally, Indonesian oil has slightly less eugenol and more $\beta$-caryophyllene than Indian oil (Table 37.1). Sri Lankan oil is closer to Indian oil.

In a recent analysis, the compounds identified in clove leaf oil include eugenol (76.8%), $\beta$-caryophyllene (17.4%), $\alpha$-humulene (2.1%), and eugenyl acetate (1.2%) (Jirovetz et al. 2006).

Clove leaf oil, according to the FCC, is a pale yellow liquid with a sharp, spicy, peppery odor and taste. It is soluble in propylene glycol and in most fixed oils with slight opalescence, and it is relatively insoluble in glycerin and in mineral oil.

Physical characteristics as defined by the FCC are as follows.

| | |
|---|---|
| Optical rotation | −2 to 0° |
| Refractive index | 1.531–1.535 at 20°C |
| Specific gravity | 1.036–1.046 |
| Solubility | 1 mL dissolves in 2 mL of 70% alcohol (slight opalescence may occur when additional solvent is added) |

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**Table 37.1.** GC analysis of clove leaf oil

| | **Indonesian (%)** | **Indian (%)** |
|---|---|---|
| $\alpha$-Pinene | <0.1 | <0.1 |
| $\beta$-Pinene | <0.1 | <0.1 |
| $\beta$-Caryophyllene | 11–15 | 10–13 |
| Eugenol | 80–85 | 85–88 |
| Eugenyl acetate | 0.5–1 | 0.1–0.5 |

## Uses

Clove leaf oil is used as a cheaper substitute for bud oil. In some dental preparations, leaf oil with or without admixture with bud oil is used. It is also used in such products as massage oils, lotions, room fresheners, and aromatherapy.

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Clove leaf oil | 2325 | 8000-34-8<br>8015-97-2 | 184.1257 | – |

## Reference

Jirovetz, Leopold; Buchbauer, Gerhard; Stoilova, Ivanka; Stoyanova, Albena; Krastanova, Albert; and Schmidt, Erich. 2006. Chemical composition and antioxidant properties of clove leaf essential oil. *J. Agric. Food Chem.* **54** (17), 6303–6307.

# 38 Coca Leaf

## *Erythroxylum coca* Lam (*Erythroxylaceae*)

## Introduction

Coca is a plant whose leaves are valued as a source of stimulant. It plays an important role in the culture of the Andes region. In this region, the plant is considered to have a divine influence. Archeological evidence from South American mummies pointed to its use even in the sixth century AD. While it is used as a masticatory, at the time of the Inca empire, its use was restricted to nobles and the powerful of the society. As the Inca lost control, the leaf became more widely available.

Coca leaf might be useful as a remedy for gastrointestinal diseases, for motion sickness, and as a substitute for antidepressant medicines (Well 1978). It is a substitute stimulant for coffee and adjunct in slimming and physical fitness programs. According to Well (1978), the effect of whole leaf is quite distinct from that of the extract, thus the leaf can be considered safe for use in chewing gum and other products. However, food and pharmaceutical laws of many countries do not take such a liberal view. Coca, like cocaine, is controlled by the U.S. federal narcotics agency. The Bolivian government argues that coca leaf should be legalized for international trade.

## Plant Material

The plant is an evergreen shrub or small-sized tree. It resembles a black thorn bush with a height of 3–5 m. Generally, plants grown in higher altitudes are smaller than those grown in lower altitudes. The leaf is thin and leathery, shaped as an elongated elliptical that tapers at both ends. It has small flowers growing as a small cluster with a short stalk. Each flower has five pale yellow petals, a heart-shaped anther, and pistil consisting of three carpels to form a three-chambered ovary. The fruit is a red-colored berry. Propagation is through seeds.

The leaves are the important and useful plant part. Fresh leaves, when carefully dried, have a green color on top and are gray-green on the lower surface. When the leaf is chewed, a pleasurable numbness is felt in the mouth with an agreeable pungent taste.

The chief constituent is cocaine, which is an alkaloid. There are many derivatives of cocaine and some related alkaloids in small proportion. The concentration of the alkaloids varies with region, age of the plant, and so on. Cocaine accounts for 70–80% in Bolivian leaf, while it is only 50% in Peruvian leaf (Leung and Foster 1996). The leaf has carbohydrates, protein, a small amount of volatile oil, and flavones.

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## Extractives

Because of its stimulant action, coca leaf extract was used in earlier formulations of cola-based soft drinks. Today, extracts from which cocaine has been removed are used. Various companies have their own confidential procedures, and very little information about the exact conditions of methods of extraction is published.

## Uses

Coca leaf is a popular and invigorating masticatory used by the people of South America. Cocaine is used as a mild local anesthetic for minor operations of the face and its organs.

Extract freed of cocaine is heavily used in many soft drinks. It is also used in some alcoholic beverages and confectionery items. There are many people who feel that while extracts rich in cocaine may be injurious, the leaf itself is safe. Presently, governments of growing regions argue that the leaf should be made legal for international trade and should be removed from the United Nations' list of illegal drugs. Recently, a liquor containing coca leaf extract was introduced in the Netherlands.

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Coca leaf extract (undecocainized) | 2329 | 84775-48-4 | 182.20 | – |

## References

Leung, Albert Y.; and Foster, Steven. 1996. *Encyclopedia of Common Natural Ingredients*, 2nd edition. New York: John Wiley and Sons, pp. 179–180.

Well, A.T. 1978. Coca leaf as a therapeutic agent. *Am. J. Drug Alcohol Abuse* **5** (1), 75–86.

# 39 Cochineal

## *Dactylopins coccus* Costa (*Coccoidea*)

## Introduction

Cochineal insects produce a crimson-colored pigment known as carmine. The insect is a parasite of cacti from the genus *Opuntia*. The insect is a member of suborder *Sternorrhyncha*. There are other insects belonging to *Dactylopins* that are very similar to *Dactylopins coccus* and produce a similar dye. Therefore, the insects are referred to as cochineal insects. While it is probable that majority are *D. coccus*, other members of the genus could be present.

The pigment was in use in early American history by the Aztecs and Mayans. Cochineal was considered to be of high value, and various communities used it to pay yearly tribute to the Emperor. Spaniards who traveled to America saw its potential, as the dye was more brilliant and produced better color than those used in Europe at that time. The dye became very popular in Europe before the present synthetic dyes came into existence. Cochineal became a valuable item of commerce and was traded in major commodity exchange centers such as London and Amsterdam. The newly found, superior pigment was used by the British military for their jackets and Roman cardinals for their robes.

In the nineteenth century, Mexico's monopoly of carmine ended when the insects were brought to the Canary Islands. In 1862, the Canary Islands sold 6 million pounds (2.73 million kilograms) of cochineal, which represents over 400 billion insects.

While its use as a textile dye was most prominent in the presynthetic dye era, cochineal also found use in foods and cosmetics. It made a spectacular entry in various fruit products, beverages, confectionery, and animal products. Cosmetic rouge was a great success; cochineal is still popular in cosmetics.

In the middle of the nineteenth century, with the appearance of alizarin-based crimson pigment, use of cochineal fell dramatically and amounted to near nothing by the twentieth century. However, with the present trend of using natural food additives rather than synthetic items, it has made a comeback. However, its producers try to hide the fact that it is of insect origin. Naturally, it is not permitted in foods for vegetarians, and some religious people would not use a dye made by killing live insects. The European Commission has recognized the color with an E-number.

## Living Material

The insects that produce the carmine color are soft-bodied and flat oval in shape. The females are important in producing the dye. Females are slightly larger than males,

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with a length of 5 mm, but have no wings. They suck into the host cactus with the beak-like part of their mouth. While sucking nutrients, they are immobile. After fertilization by slightly smaller males which have wings, the females grow in size and give birth to very small nymphs. The nymphs produce the dye, which colors the inside of their bodies dark purple. The nymphs secrete a white waxy material to cover their bodies to prevent water loss and damage due to sunlight. Thus, the insect appears white or gray even though the inside is full of the pigment.

The young insects inside the waxy coating move around for feeding. When they move to the edge of the cactus, wind sometimes carries them to a new host cactus. This way, a new site for production of natural pigment is formed with a new generation of cochineal after fertilization with males. Male nymphs feed on cactus until they attain sexual maturity. Then they live just enough to fertilize the female eggs. Being small and with a short lifespan, the male is hardly observed. Generally, the females outnumber the males, which naturally increases the efficiency of dye production.

*D. coccus* is native to South America and Central America, especially Mexico where the host cacti thrive. There are about 200 species of cacti belonging to *Opuntia*, the best one for cochineal insects being *Opuntia ficus-indica*. Such cacti have been introduced in Spain, the Canary Islands, Algiers, and Australia for the production of cochineal. Eritrea already had the correct type of cactus. Continuous feeding by insects can weaken and even completely destroy the host cactus. But with several varieties of *Opuntia* cacti available, this is not a major problem. The farming of cacti with cochineal insects are carried out by the traditional method by planting cactus pads infected with insects. In the improved method, clean fertile females are allowed to settle on cacti and are then fertilized by males. There is a need to protect them from predator insects, cold, and rain. A cycle of growth is about 90 days, during which time temperature is maintained at 27°C. The dye is extracted after drying the insects, making sure that some are used for starting a new cycle.

Peru is the major supplier of dried cochineal insects. In 2005, Peru produced about 400 tonnes of dried insects, representing nearly 85% of the world production. Other producing countries are Mexico and the Canary Islands. Production began in Australia mainly because of the need for British authorities to control it. However, cochineal production and cacti specially grown for the purpose were allowed to die in the twentieth century.

While cochineal dye lost its former importance with the introduction of artificial pigments, presently there is some interest because of the importance of natural colorants especially in food and cosmetics.

## Extractives

The dye is extracted from the female insects. Depending on the method of extraction, cochineal dye comes in different shades such as scarlet, orange, and red. The color is caused by carminic acid (Fig. 39.1).

For simple extraction, the insects are killed by immersion in hot water, by exposure to sunlight, by treatment with steam, or by heat toasting in a hot dryer. These different methods give slightly different shades. So for commercial purposes, the processing has to be standardized to get the reliable shade required. The insects are dried to less

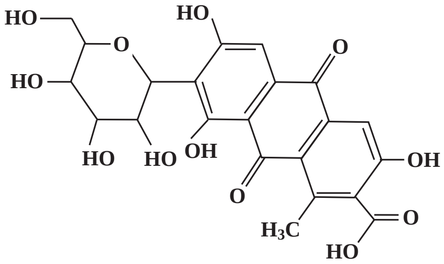

**Figure 39.1.** Carminic acid.

than one-third of their weight for safe storage. The carminic acid content is 19–22% of the dry weight of the insects. Over 150,000 insects are required to make 1 kg of dry cochineal.

To produce carmine, a more purified dye, the ground dead insects are treated with a base such as ammonia or sodium carbonate solution. The insoluble materials represent the debris from dead insects. Alum is then added to clear the carminic acid as a precipitate of aluminum salt. Freedom from iron ensures pure, clear dye. To get a shade of purple, lime is added with the alum. To regulate the formation of the precipitate, chemicals such as stannous chloride, citric acid, borax, or gelatin are added.

Carminic acid is responsible for the color. Carmine is the finished aluminum/calcium lake of carminic acid, and is the commercial dye used to impart color to food or textiles.

Both carminic acid and carmine are water-soluble, light, and heat-stable. Carminic acid is orange at a pH lower than 5 and bluish-red over 8. A variety of shades from yellow-red to near blue is possible (Delgado-Varghas and Paredes-Lopez 2003). In the early days of production, extraction of the pigment was carried out with water, but today, by using alcohol and distilling off alcohol, a concentrated solution with as high as 4% clear carminic acid without unwanted residues can be produced.

## General Aspects

Cochineal is a water-soluble natural dye that is reasonably stable against light, heat, and oxidation. Because of the use of aluminum from alum for complexing, carmine can be described as a “semisynthetic” dye (Dapson 2007). Amino carminic acid is used in acidic foods; a somewhat insoluble calcium carmine is used in many solid foods.

The European Commission has assigned an E-number of E120 (I) for purified carmine, while the number given for raw dye from ground insects with a carminic acid content of about 20% is E120 (II). A new U.S. Food and Drug Administration (FDA) regulation will require all foods and cosmetics containing cochineal to declare it in the ingredient list beginning January 5, 2011.

There is an azo dye E124 that is close to cochineal called “cochineal red.” The color is similar but E124 is synthetic.

According to the FCC, carmine comes as bright red, friable pieces or as a dark red powder. It is the aluminum or calcium–aluminum lake on an aluminum hydroxide substrate. Carmine acid crystallizes from water as bright red crystals that darken at 130°C and decompose at 250°C. It is freely soluble in water, alcohol, and ether but insoluble in petroleum ether and chloroform.

## Uses

Traditionally, cochineal dye was used for fabric. Now that synthetic dyes have been developed, this has decreased dramatically.

With the demand for natural food additives on the increase, however, carmine color is being used as food coloring. A water-soluble form is used in alcoholic beverages and water-based drinks. The calcium derivative finds use in a wide range of meat products, bakery items, toppings, dessert, icing, fruit products, and some cheese and dairy products.

The FDA has a regulation that it should be declared in the list of ingredients. A small number of people have an allergy to and a few others get an asthma reaction from cochineal. The Hyperactive Children's Support Group recommends that the dye be eliminated from children's diets. Many religious groups, such as Muslims and Jews, do not use this product as it is from an animal and not processed according to standard religious practices. It is also not acceptable to vegetarians and vegans. Likewise, Jains cannot use an item produced by the killing of insects.

## Analytical Method

The FCC describes a method of assay measuring absorption at 494 nm after acidification.

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Carmine | 2242 | 1390-65-4 | – | E-120 |

## References

Dapson, R.W. 2007. The history, chemistry and modes of action of carmine and related dyes. *Biotech. Histochem.* **82** (4–5), 173–187.

Delgado-Varghas, Francisco; and Paredes-Lopez, Octavio. 2003. *Natural Colorants for Food and Nutraceutical Uses*. Boca Raton, FL: CRC Press, pp. 221–255.

# 40 Cocoa

## *Theabroma cacao* L (*Sterculiaceae*)

### Introduction

Cocoa is the dried and processed seed of the cocoa tree. Chocolate is made from the processed seeds. Like many other important crops, cocoa also has its origin in the Americas. It is possible that the plant has its origin in the foothills of the Andes in the Amazon and Orinoco basins of South America. It spread to Central America by enterprising tribes well before the Spanish arrived on the scene. The precise history of the crop before the Europeans arrived is shrouded in mystery. However, it is clear that rulers of the pre-Columbian era considered it to be extremely tasty and valuable.

Cocoa and chocolate were introduced to Europe by the Spaniards by the mid-seventeenth century. It became quite popular, and European nations tried to cultivate the tree in the colonies under their control. It was soon understood that cocoa thrives well in a narrow tropical land approximately 15–20° north and south of the Equator. The Spanish introduced it in the Caribbean islands and the Philippines. English and French authorities grew the crop in Africa. Around 70% of the world's production is in West Africa. In recent years, South Asian countries developed cocoa through their own initiative. While the chocolate industry is huge and is the main outlet of the crop, the present discussion concentrates on the use of this product as a flavor and, to a limited extent, as a color in other products.

### Plant Material

The cocoa tree grows to a height of 15–20 m. It is common to refer to the tree as "cacao" and the beans as "cocoa." When young, it needs good shade and therefore cacao trees are produced under the shade of taller trees. Shade-protected trees can grow to an age of nearly 100 years.

The tree has small flowers usually colored pink or white. Tiny flies pollinate the trees, which is essential for the development of the fruit. To encourage pollination, the ground is mulched heavily with fallen leaves and other agricultural waste. It is also possible to pollinate by hand.

The tree produces fruits called pods in 3–5 years. The pods have the shape of a rugby football. It has a rough, leathery rind 3 cm thick, the inside of which is filled with sweetish muscilaginous pulp. The pulp has 30–50 almond-like seeds, called beans, which are somewhat soft and lightly colored pink- or purple-brown.

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Of the three varieties of cocoa now cultivated—Forastero, Criollo, and Trinitario—the first one is the most cultivated due to its higher yield. Criollo, however, gives the best quality chocolate. The world's largest producer of cocoa beans is the Ivory Coast with 1.3 million tonnes, followed by Ghana with 720,000 tonnes and Indonesia with 440,000 tonnes. Other producers are Cameroon, Nigeria, Brazil, Ecuador, the Dominican Republic, and Malaysia. In 2006–2007, the total quantity produced in the world was 3.5 million tonnes of beans.

## Processing

Cocoa pods are harvested when they are mature but still green in outside color, rather than after they change to red or orange. After the pods are opened, the pulp and seeds are made into a heap or put in bins to start the important step of fermentation. During this process, sweating takes place and after a series of biochemical changes, the beans are ready for drying. The beans are trodden and shuffled about so that they are all separated. Drying is done either in the sun or in ovens. Generally, producing countries ship out dried beans. Around 300–600 beans are required to make 1 kg of chocolate.

The next step of processing is roasting, followed by deshelling using a winnower. Deshelled roasted beans are called "nibs" which when ground will yield a product rich in fats and having all the flavor. This is called "cocoa mass" or "cacao paste." This is then separated into chocolate powder and cocoa butter through the use of a hydraulic press. The chocolate powder will have 10–12% fat. Both cocoa mass and chocolate powder can be used as flavor. Cocoa butter, which accounts for 50% of the cocoa mass, is mostly triglycerides. Because of even distribution of the fatty acids, cocoa butter melts within a narrow temperature range, just below human body temperature. This property makes it a valuable fat usable in specialty foods and cosmetics.

Cocoa nibs have alkaloids such as theobromine, present at a level of 1–1.5%, and some caffeine present at a level of 0.7%. Theobromine is a metabolite of caffeine in the liver. It has a structure similar to that of caffeine, though with the $CH_3$ group at 7 position absent (see Chapter 41 on coffee for the structure of caffeine). Leung and Foster (1996) have summarized the compounds present in cocoa. The major flavor components are aliphatic esters, polyphenols, unsaturated aromatic carbonyls, pyrazines, diketopiperazines, and theobromine. The bitter taste is contributed by diketopiperazines, which react with alkaloid theobromine during the crucial roasting step.

## Extractives

Two types of extractives of cocoa can be made for use as a flavor, one from cocoa powder and another from the shell.

For extraction from the cocoa powder, the powder is first freed of all fat by extraction with hexane to obtain extracted cocoa butter, which has value. The spent material obtained after this process is extracted with ethanol or methanol. After the removal of solvent from the combined miscella, the yield will be 2.5–3%. Generally, propylene glycol is added to a level of 25% to get a homogeneous, water-dispersible, and free-flowing flavor extract. The extract will also contribute the typical cocoa color to food products in which it is used.

The shell that is removed to obtain nibs has a good characteristic cocoa flavor that can be extracted either by methanol or ethanol. The coarsely ground shell is first roasted at 110°C to develop the flavor. This is then extracted by percolation using about one and a half to two times the amount of methanol. The miscella is then reduced to about 70% of the original volume by distillation. Water is then added, about eight times the volume of concentrated miscella. This is then kept at 5°C in a refrigerator, at which point the waxes will separate as a solid. The clear liquid obtained on filtration is then freed of methanol and concentrated by boiling to a total soluble solid strength of above 60° Brix. Addition of about 5% propylene glycol will result in a free-flowing, homogenous shell extract, which can be used as a cocoa flavor.

## Uses

The chocolate industry, based on cocoa, is one of the major food industries. Cocoa powder is used in many varieties of chocolate. It is also used in malted beverages. Cocoa butter with its short range of melting point below human body temperature is a valuable fat in chocolate manufacture. It has value in cosmetics and some toiletries. It is used as an ointment base and skin softener, in lotions, lipsticks, and massage creams.

Cocoa flavor in the form of extractives or powder is used in bakery products, candies, malted beverages, and dairy products. In baked items, beverages, ice cream, and cake icing, it also contributes a desirable color. Extractives are used in liqueurs and candies. The shell extract is used as a cocoa aroma booster.

Cocoa and cocoa butter contain antioxidants. Theobromine, being an alkaloid, increases action of the central nervous system and is therefore a stimulant.

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Cocoa extract/absolute | – | 84649-99-0 | – | – |

## Reference

Leung, Albert Y.; and Foster, Steven. 1996. Cocoa. In A.Y. Leung and S. Foster, eds., *Encyclopedia of Common Natural Ingredients*. New York: John Wiley and Sons, pp. 181–185.

# 41 Coffee

## *Coffea arabica* L; *C. robusta* Lindeu (*Rubiaceae*)

## Introduction

The attraction of coffee is so great that the dawn breaks for many people with the stimulating aroma of fresh, hot coffee. The taste for coffee seems to be universal and it is consumed almost all over the world. To facilitate coffee production, many types of soluble coffee are prepared. In recent years, cold coffee has also gained popularity. While coffee is an important food item, in only some cases has it become a flavor in other food products. It is this aspect that will be mainly highlighted in this chapter.

In 2004, the Food and Agriculture Organization (FAO) estimated that coffee was the top agricultural export commodity in 12 countries. In 2005, it was considered to be the seventh largest agricultural export item in the world by value. Over a hundred million people in the developing world have become dependent on coffee as their primary source of income.

The term “coffee” is believed to have been introduced from the Turkish word *kahve*, which in turn is probably from the Arab *quahwah*. The source of the Arabic word may have come from the Kaffa region of Ethiopia, which is believed to be the country where coffee originated. The English word “coffee” was first used in the mid-1600s.

There is a story that coffee was first noticed by a goatherd in Ethiopia, but there is some evidence to show that the stimulating effect of coffee was first recognized in Yemen. From the Arab world, coffee spread to Italy and from there to Europe, Indonesia, India, and Americas. The world’s biggest producer is Brazil with 2.25 million tonnes annually as per data of 2007. This is followed by Vietnam (961,200 tonnes), Colombia (697,377 tonnes), Indonesia, and India. Several South and Central American countries are also significant producers. Vietnam is a relatively new entrant and has pushed Colombia to third place. The United States imports coffee mainly from Colombia.

## Plant Material

There are two species that produce coffee, *Coffea arabica* and *Coffea robusta*, also known as *Coffea canephora*. There are many similarities in the nature of these plants. With a height of 6 m, Arabica plants are shorter than robusta plants, which may reach 8 m. Arabica plants yield coffee that is regarded as superior, and the following description is based primarily on this variety.

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**Photo 10.** Coffee fruits on the tree. See color insert.

The coffee plant is a glabrous large shrub with spreading branches (Warrier 1994). Its leaves are simple and opposite with interpetiolar stipules. The surface is shiny, oblong, and acuminate, with six to 10 pairs of main lateral nerves connected by intramarginal veins. The flowers are white and numerous. The fruits are fleshy, obovoid berries, which are purple when fully ripe. The seeds, the most important part, are concave and grooved vertically. Photo 10 represents the top portion of the coffee plant with fruits.

## Processing

It is important that only fully ripened fruits are picked. Picking of unripe or overripe fruits must be avoided. There are two ways of processing coffee: the wet process to produce "plantation," "parchment," or "washed coffee"; and the dry method to produce "cherry" or "unwashed coffee." Wet processing involves pulping, natural fermentation, washing to remove mucilage and other debris, and drying. Processing for plantation coffee requires pulping and an adequate supply of water for washing. The water requirement of 1 tonne of arabica is about 80,000 L, but for 1 tonne of robusta, it is 93,000 L. Cherry coffee requires hullers to remove the matter outside the seeds (Coffee Board, India).

Drying is very important. Depending on the processing, variety, and size, there are many grades, including "bits." Generally, arabica is more expensive than robusta. Similarly in each, plantation or parchment grades obtained through the washing method are regarded as superior to the cherry grade. In making extractives, these aspects must be taken into consideration. While making extractives, appearance, especially that of broken pieces, is not important.

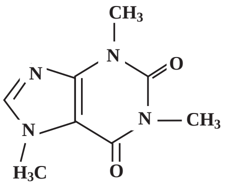

**Figure 41.1.** Caffeine.

The green beans do not have any aroma. Aroma is developed by roasting beans to a temperature of 220°C. The temperature and duration of roasting depends on the grade, size, market, and so on.

## Chemistry

Coffee beans contain up to 3% caffeine (Fig. 41.1). Other related compounds are trigonelline and chlorogenic acid. Caffeine is responsible for physiological activities resulting in powerful stimulation of the central nervous system, which affects many functions. It has over 50% carbohydrates, over 10% protein, and about 2% free amino acids and polyphenols. Polyphenols contribute toward astringency.

The aroma of roasted coffee is a result of hundreds of compounds. They include alicyclic compounds, aromatic compounds, and heterocyclic compounds. Heterocyclic compounds are very important for aroma and include furans, pyrazines, pyrroles, thiophenes, and thiazoles.

## Extractives

Instant coffee or soluble coffee is indeed an extractive. It is produced from roasted coffee after grinding and extraction by percolation. Sometimes pressure is also used. The combined water extract, after removal of sediments by gravity centrifugation, is made into a water-soluble solid powder by spray drying. The fine powder that results is sometimes agglomerated to avoid lumping while redissolving. For the same purpose, granular instant coffee is made after freeze-drying the hot water extract. To reduce the cost and increase body, chicory can be added to coffee.

Decaffeinated coffee is made by using ethyl acetate and supercritical carbon dioxide to remove most of the caffeine. The caffeine that is removed is used as a source of natural caffeine.

To be used as a flavor, coffee extract is made by extraction with cold 50% aqueous ethyl alcohol. After removal of alcohol and water, the extract is a dark brown or nearly black thick liquid with bitter taste and the fine invigorating aroma of brewed coffee. The product will be water-soluble.

If the alcohol content is increased to 70%, then the extract will contain more caffeine. Alternatively, if the alcohol content is decreased below 70%, then the caffeine content will be lower and an astringent taste due to polyphenol will be higher. An innovation that is successfully carried out is as follows. First, the ground roasted coffee is extracted with hexane. Most of the aroma will come into the hexane with very little body contributed by polyphenols, carbohydrates, and so on. The aroma fraction is made after carefully distilling out the hexane. After this, the residual coffee powder is freed of hexane by steaming.

The residual coffee powder is then extracted with 50% aqueous ethanol to obtain coffee extract. To this, the hexane-extracted aroma fraction is added and mixed thoroughly. This extract will have the stimulating aroma of freshly brewed coffee.

## Uses

Coffee is widely used as an invigorating warm beverage. But apart from this, coffee extract also finds use as a flavor.

Cold coffee itself is one such case, with or without other flavors. Citrus flavor is often added.

Coffee flavor is used in boiled sweets, candies, ice cream, malted beverages, liqueurs, and frozen dairy preparations. The caffeine separated from decaffeinated coffee is used in cola soft drinks. Caffeine has medical properties and is therefore used in many pharmaceutical preparations.

## Analytical Method

Analysis of coffee for various constituents including caffeine is well covered by the AOAC.

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Coffee extract | – | 84650-00-0 | 182.20 | – |
| Caffeine (natural) | 2224 | 58-08-2 | 182.1180 | – |

## References

Coffee Board, India. Undated. *A Guide to Coffee Quality*. Bangalore: Coffee Board.
Warrier, P.K. 1994. *Indian Medical Plants*. Madras: Orient Longman, vol. 8, pp. 155–156.

# 42 Coriander

## *Coriandrum sativum* L (*Umbelliferae*)

### Introduction

Coriander seed was used as early as 5000 BC, according to Indian Vedic literature. It finds reference in the Bible, in Exodus. It was used in Egyptian burials in 1000 BC and possibly even before. The great Arabian classic *A Thousand and One Nights* refers to this spice as an aphrodisiac. Coriander is thought to have originated in the Mediterranean and in the southwest area of Europe.

Coriander's name is derived from the Greek word *kopis*, meaning insects. When macerated at an immature stage, the plant emits a strong and unwelcome odor associated with insects. But when the plant reaches maturity, the bad odor is lost and the ripe fruit, on drying, becomes the spice.

### Plant Material

Coriander seed is the dried fruit of an annual plant that is a glabrous, aromatic, herbaceous annual with a height of 30–90 cm. The leaves are decompound; lower ones are long-petioled, the upper ones short-petioled or subsessile. The flowers are small and colored white or pinkish-purple in compound terminal umbels. Fruits are yellowish-brown, globular, and ribbed, separating into two halves of mesocarps each containing a seed (Warrier 1994). The dried fruit is commercially called a seed and will have a diameter of 3–4 mm.

Dried coriander is valued for the essential oil it contains (see Photo 11B). It has some fixed oil, some malic acid, and a relatively high ash content. India, Russia, and Morocco are the major producers of coriander. The Russian variety has about 1.7% of volatile oil as compared with 0.3% in the Indian variety.

Some medicinal properties are attributed to coriander, such as it being a stimulant and carminative. It is also used as a disguise for the unwelcome taste of some purgatives and, in ancient times, to mask spoilage in food items.

### Essential Oil

Dry coriander is crushed using a roller mill and steam-distilled in a suitably sized stainless steel unit. Steam at normal pressure enters from the bottom. The distillation time is about 16 hours. The vapors of oil and water are condensed and collected in a three-stage Florentine flask arrangement for lighter-than-water oils.

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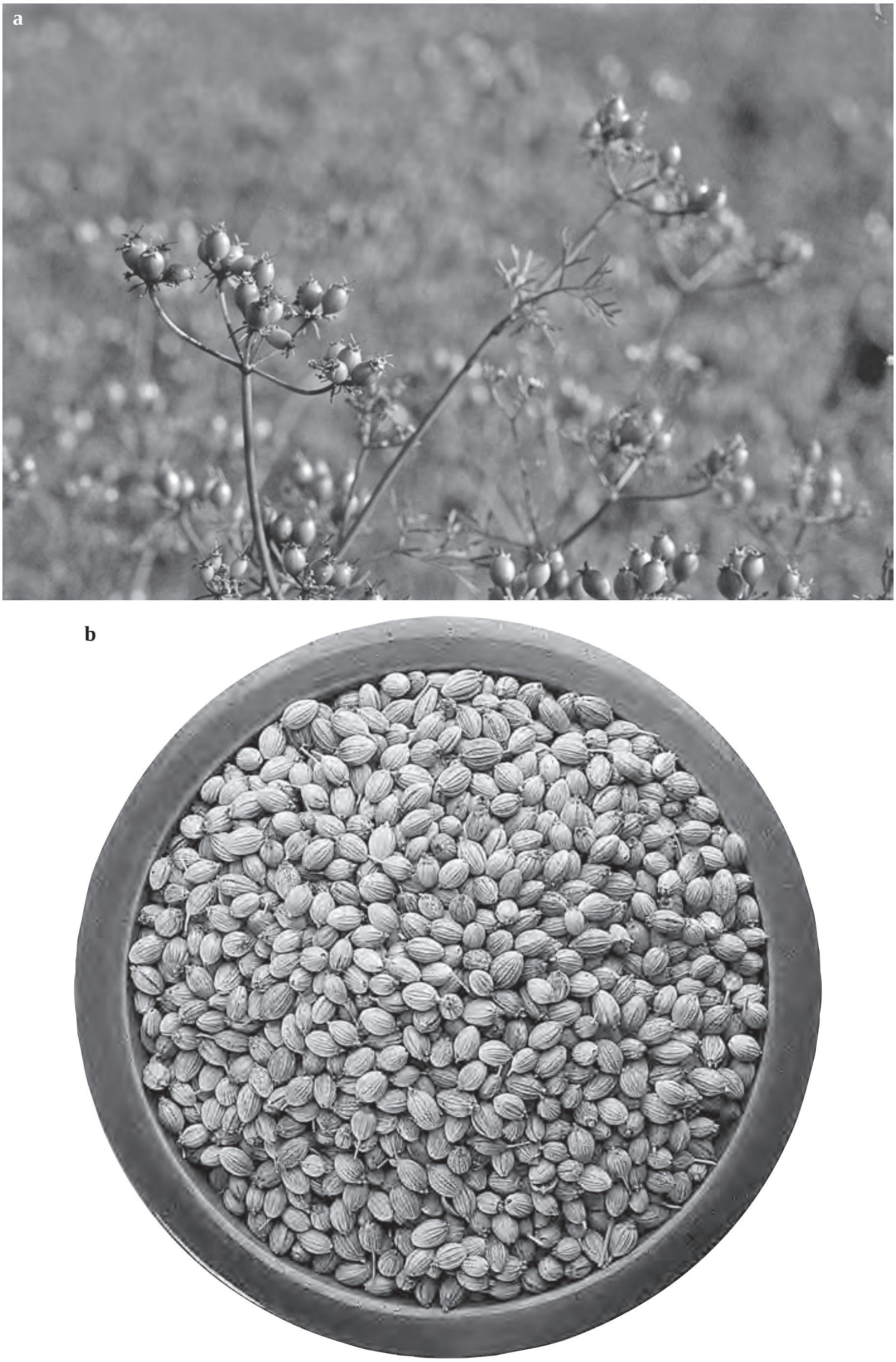

**Photo 11.** (A) Coriander on the plant. (B) Dried coriander seeds. See color insert.

Coriander oil is a pale yellow, mobile liquid with the characteristic aroma of the spice. Because of the presence of linalool, the aroma has a lemony note. The aroma can be described as warm, spicy, nutty, and citrus-like.

The main constituent of the oil is linalool, present at 67–70%. It also has $\alpha$-pinene (4–7%), limonene (2–4%), $\delta$-terpinene (3–7%), geranyl acetate (2–6%), and camphor (4–7%).

A recent analysis done in China revealed that seed oil shows 35 constituents, which account for 96.5% of the oil (Li et al. 2001). In this, the prominent ones are linalool (56.82%), linalool oxide (13.32%), and dihydro-2-camphenol (7.12%). In another investigation, 21 compounds were found, including linalool, endo-borneol, and $\alpha$-fenchene (Li et al. 2005). Linalool (73.61%) is the predominant constituent in every analysis. The oil in this case exhibits powerful inhibitory action on *Aspergillus niger* as well as on some bacteria (Li et al. 2008). In an analysis carried out in India, the major compounds noted are linalool (52.26%), myrcene (1.71%), citronellol (4.64%), geraniol (9.29%), safrole (2.67%), $\alpha$-terpenyl acetate (1.07%), and geranyl acetate (18.07%) (Bhattacharya et al. 1998). Steam distillation of Algerian seeds shows linalool (70.2%) as the prominent component (Benyoussef et al. 1999).

According to the description given by the FCC, coriander oil occurs as a colorless or pale yellow liquid with the characteristic odor and taste of coriander.

Physical characteristics as defined by the FCC are as follows.

| | |
|---|---|
| Optical rotation | +8° to +15° |
| Refractive index | 1.462–1.472 at 20°C |
| Specific gravity | 0.863–0.875 |
| Solubility | 1 mL dissolves in 3 mL 70% alcohol |

## Oleoresin

Coarsely ground powder is packed in a stainless steel percolator and extracted using hexane. The major contributor to the flavor is essential oil, and therefore other reasonably nonpolar solvents may give similar results. The fixed oil and resinous material act as fixatives. It is customary to specify volatile oil content; pricing is determined by the percentage of oil.

The oleoresin is a dark yellowish-brown oily liquid with the aroma and flavor typical of the essential oil. The volatile oil content is usually adjusted at 1–2%.

## Uses

Coriander is used in a wide variety of foods, notably in meat preparations. It is also used in condiments, seasonings, curry powder, baked goods, confectionery, chewing gum, and alcoholic beverages.

A recent review has highlighted animal studies that demonstrate a hyperglycemic effect on carbohydrates, hypolipidemic action on lipids, and anticancer properties (Ilaiyaraja et al. 2010). While these are of great interest, further studies, especially with humans, are required.

Coriander oil and oleoresins are used in processed foods corresponding to fresh foods where coriander seeds are used as a spice. In Indian meat preparations and curries, coriander flavor is very valuable. It is useful in condiments, seasonings, baked goods, and confectionery. Coriander oil is used for flavoring alcoholic beverages, such as gin.

## Identification Numbers

| | FEMA No. | CAS | US/CFR | E-No. |
|---|---|---|---|---|
| Coriander seed oil | 2334 | 8008-52-4 | 182.20 | – |
| Coriander extract | – | 84775-50-8 | – | – |
| Coriander seed oleoresin | 2334 | 8008-52-4 | 182.20 | – |
| Coriander absolute | – | 8008-52-4 | – | – |

## References

Bhattacharya, A.K.; Kaul, P.N.; and Rao, B.R. Rajeswara. 1998. Chemical profile of the essential oil of coriander (*Coriandrum sativum* L) seeds produced in Andhra Pradesh. *J. Essent. Oil-Bearing Plants* **1** (1), 45–49.

Benyoussef, E.H.; Beddek, N.; Belabbes, R.; and Bessiere, J.M. 1999. Analysis of extracts of Algerian coriander seeds. *Rivista Italiana Eppos* **28**, 27–32 (French) (*Chem. Abstr.* 134:21262).

Ilaiyaraja, N.; Farhath, Khanum; Anilkumar, K.R.; and Bawa, A.S. 2010. Therapeutic properties of coriander seeds. *Spice India* **23** (2), 23–31.

Li, Congmin; Shang, Jun; Ren, Yunhui; and Xu, Chunming. 2001. Analysis of chemical constituents of coriander seed oil from Laifeng county. *Xiangliao Xiangjing Huazhuangpin* (**6**), 1–2 (Chinese) (*Chem. Abstr.* 136:284135).

Li, Feng; Xie, Cheng-xi; Fan, Wei-gang; and Fu, Ji-hong. 2005. Analysis of volatile chemical components of *Coriandrum sativum* L seed by gas chromatography–mass spectrophotometry. *Zhipu Xuebao* **26** (2), 105–107 (Chinese) (*Chem. Abstr.* 144:75010).

Li, Wei; Feng, Dan; and Lu, Zhanguo. 2008. Chemical components and antibacterial activity of the essential oil of coriander seeds grown in Heilongjiang. *Zhongguo Tiaoweipin* (1), 42–45 (Chinese) (*Chem. Abstr.* 149:127086).

Warrier, P.K. 1994. *Indian Medicinal Plants*. Madras: Orient Longman, vol. 2, pp. 184–188.

# 43 Coriander Leaf

## *Coriandrum sativum* L (*Umbelliferae*)

## Introduction

The leaf of coriander, also called cilantro, is used in cooking in fresh form. In Peru, it is used in a large number of dishes, sometimes to such an extent that those not used to the flavor may dislike it.

## Plant Material

The coriander plant (see Chapter 42 on coriander) is an odoriferous, hardy, annual plant of the parsley family. Coriander herb has an excellent flavor. It is used in soups and salads and also as a floating small branch with leaves in some alcoholic cocktails. In India, it is popular in vegetarian cooking. It finds application in Russia and East European countries, Guatemala, Mexico, and the United States.

The fresh leaves have 86–88% moisture, 3.3% protein, 0.6% fat, and 6.5% carbohydrate. They are rich in minerals and some vitamins. However, these have no importance in extractives.

## Essential Oil

Coriander herb gives an essential oil with yield of 0.1–0.6%. There is no major commercial production. Small quantities can be prepared by water distilling fresh or partially shade-dried herbs.

The essential oil obtained from the aerial part of the coriander plant by water distillation is examined by GC-MS (Lu et al. 2006). Of the 86 components, 49 have been identified, which represent 87.90% of the oil. They include alcohols (39.60%), aldehydes (31.96%), esters (3.94%), and hydrocarbons (6.58%).

It has fresh, herbal, invigorating aroma. The physical characteristics are as given below (Prakash 1990).

| | U.S. oil | Indian oil | Russian oil |
|---|---|---|---|
| Optical rotation | +3°32′ | +2°1′ | +2°33′ |
| Refractive index | 1.4540 | 1.4548 | 1.4555 |
| Specific gravity | 0.849 | 0.849 | 0.8524 |
| Solubility in alcohol 20% at 25°C | 3.5% | 1.5% | Insoluble |

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## Oleoresin

Shade-dried leaves on extraction with hexane, ethyl acetate, or a mixture of acetone and hexane will yield an oleoresin that reflects the flavor contributed by the essential oil.

On testing, the leaf extract with ethyl ether and oil showed that the oil has powerful inhibitory effects on *Escherichia coli* and *Staphylococcus albus*, but not on *Aspergillus* species (Lu et al. 2007).

## Uses

Both oil and oleoresin can be used in processed foods corresponding to the cooked foods where the leaf is used for flavor.

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Coriander leaf oil | – | – | – | – |
| Coriander oleoresin | – | 8008-52-4 | – | – |

## References

Lu, Zhanguo; Guo, Hong-Zhuan; and Li, Wei. 2006. GC/MS analysis of chemical components of essential oil from coriander leaf. *Shipin Yu Fajiao Gongye* **32** (2), 96–98 (Chinese) (*Chem. Abstr.* 148:190622).

Lu, Zhanguo; Guo, Hong-Zhuan; and Sun, Shen-min. 2007. Chemical constituents and antimicrobial activity of the essential oil from coriander leaf by Soxhlet extraction. *Huaxue Yanjiu* **18** (1), 70–73 (Chinese) (*Chem. Abstr.* 148:401757).

Prakash, V. 1990. *Leafy Spices*. Boca Raton, FL: CRC Press, pp. 31–32.

# 44 Cumin

## *Cuminum cyminum* L (*Umbelliferae*)

### Introduction

Cumin is a seed spice which has been known to Egyptians since 5000 BC, as it has been found in ancient pyramids. Ancient Romans and Greeks believed it helped to produce a pale complexion. There are also many other stories. In Southern Europe, cumin represented greed, while in Germany it was used by newlyweds as a symbol to ensure loyalty to one another.

Cumin looks like caraway, but they differ greatly in taste. Fennel also looks similar to cumin but is more greenish in color and larger.

### Plant Material

Cumin is the dried fruit, popularly known as the seed, of an annual herb, which grows to a height of around 40 cm. The seeds come in pairs or separate carpels. The seeds are 3–6 mm long and are relatively straight with longitudinal ridges and tapering ends. Dry seeds have 2–5% of volatile oil. Of this, a fair portion is made up of cuminaldehyde. The odor of the seed due to oil is penetrative but highly pleasant, especially for savory purposes and occasionally for sweets.

Cumin originated in Iran and the Mediterranean region and was introduced to the Americas by Spanish and Portuguese colonists. It is now widely cultivated in many regions, including India, China, Europe, the Middle East, and Latin America. Seeds are used extensively in cooking in India, Morocco, Middle Eastern countries, Europe, and the Americas. It is an ingredient of many curry powders.

Some medicinal properties are attributed to the seeds, the most notable being its ability to relieve flatulence and colic. It is useful in controlling indigestion and nausea.

### Chemistry

The main constituent of cumin is cuminaldehyde (Fig. 44.1). It is an aromatic aldehyde and related to benzaldehyde. It is also closely related to perillaldehyde.

### Essential Oil

Good quality cumin seeds, on crushing and steam distillation, yield 4–5% essential oil. Seeds are passed through a roller mill to be crushed into coarse particles. These are fed into a suitable sized stainless steel still, and steam at normal pressure is passed

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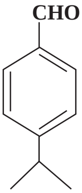

**Figure 44.1.** Cuminaldehyde.

through the bed. The distillation time is about 20 hours. The vapors of oil and water are condensed so that oil rises on top of the water. These are separated in a three-stage Florentine flask arrangement with separation designed for oil that is lighter than water.

Cumin oil is a colorless to pale yellow mobile liquid, with a tendency to darken on long storage. It has an intensely spicy and curry-like aroma. About 25–30% of the oil is made up of cuminaldehyde; 7–16% will be an allied compound, perillaldehyde. Commercially, cuminaldehyde is generally presented as a combination of cuminaldehyde proper and perillaldehyde. Thus, in a cumin oil with 30% cuminaldehyde, two-thirds of the cuminaldehyde is composed of cuminaldehyde and the rest perillaldehyde.

The monoterpenes of cumin oil consist of 13–18% $\beta$-pinene, 14–18% *p*-cymene, and as much as 25–30% $\delta$-terpinene. Cumin oil contains a small percentage of safrole. This is a natural mutagenic compound, but it will degrade at cooking temperatures.

Among the 62 compounds detected by GC-MS, 49 have been identified, accounting for cuminaldehyde 32.26% and safranal 24.46%. There were many monoterpenes, sesquiterpenes, aromatic aldehydes, and aromatic oxides (Yan et al. 2002). By hydrodistillation, a yield of 3.8% essential oil is obtained. This on GC-MS study shows 37 compounds, which represent 97.9% of the oil. Compounds identified include cuminaldehyde (36.31%), cuminic alcohol (16.92%), $\gamma$-terpinene (11.14%), safranal (10.87%), *p*-cymene (9.85%), and $\beta$-pinene (7.75%) (Li and Jiang 2004). In a study carried out in Iran, the compounds detected are $\alpha$-pinene, 1,8-cineole, and linalool (Gachkar et al. 2007) However, Singh et al. (2006) found the significant constituent to be cuminaldehyde (40.7%), along with terpinene (16.7%) and *p*-cymene (14.5%). Antifungal properties are also noticed. The essential oil of cumin is found to be a more effective antimicrobial agent than oil of rosemary (Gachkar et al. 2007).

According to the FCC, cumin oil occurs as a light yellow to brown liquid with a strong and somewhat disagreeable odor. It is relatively soluble in most fixed oils and in mineral oil. It is very soluble in glycerin and propylene glycol.

Physical characteristics as defined by the FCC are as follows.

| | |
|---|---|
| Optical rotation | +3° to +8° |
| Refractive index | 1.500–1.506 at 2°C |
| Specific gravity | 0.905–0.925 |
| Solubility | 1 mL dissolves in 8 mL 80% alcohol (solution can become hazy on addition of more alcohol) |

It is customary to specify the cuminaldehyde content in trade.

## Oleoresin

To obtain the oleoresin, coarsely ground powder is fed into a stainless steel percolator and extracted using hexane. Since most of the flavor is contributed by the essential oil, oleoresin obtained by extraction using other solvents may not drastically affect the flavor of the oleoresin. Compared with oil, oleoresin will give a more rounded flavor as the fixed oil and resinous matter will act as a fixative. It is customary to specify the volatile oil content required in the oleoresin, and pricing will generally be determined by the oil content, which is adjusted between 1% and 30%.

## Uses

Both essential oil and oleoresin are used in processed foods to replace the cumin seed. It gives excellent flavor to meat- and cereal-based food products. It is particularly popular for use in cheese in Northern Europe, baked goods in Germany, and snacks in India. Cumin oil enhances the flavor of chewing gum and other confectioneries.

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Cumin seed oil | 2343 | 8014-13-9<br>84775-51-9 | 182.20 | – |
| Cumin oil | 2340 | 8014-13-9 | 182.10 | – |
| Cumin seed oleoresin | – | 8014-13-9<br>84775-51-9 | – | – |
| Cuminaldehyde | 2341 | 122-03-2 | 172.515 | – |

## References

Gachkar, Latif; Yadegari, Davood; Rezaei, Mohammad; Bagher, Taghizadeh Masood; Astaneh, Shakiba; Astaneh, Shakiba Alipoor; and Rasooli, Iraj. 2007. Chemical and biological characteristics of *Cuminum cyminum* and *Rosmarinus officinalis* essential oils. *Food Chem.* **102** (3), 898–904.

Li, Rong; and Jiang, Zi-Tao. 2004. Chemical composition of the essential oil of *Cuminum cyminum* L from China. *Flavour Fragrance J.* **19** (4), 311–313.

Singh, Gurdip; Marimuthu, Palanisamy; de Lampasona, M.P.; and Catalan, Cesar A.N. 2006. *Cuminum cyminum* L. chemical constituents, antioxidant and antifungal properties of its volatile oil and acetone extract. *Indian Perfumer* **50** (3), 31–39.

Yan, Jian-hui; Tang, Ke-wen; Zhong, Ming; and Deng, Ning-hua. 2002. Determination of chemical components of volatile oil from *Cuminum cyminum* L by gas chromatography–mass spectrometry. *Se Pu* **20** (6), 569–572 (Chinese) (*Chem. Abstr.* 139:12420).

# 45 Curry Leaf

## *Murraya koenigii* L (*Rutaceae*)

### Introduction

Fresh curry leaves are widely used in the culinary practices of South India. The delicate, savory aroma is so well liked that it finds use in almost all curries and preparations of vegetables, meat, and fish in India. But the taste of the actual leaf is so unwelcome that the first thing a person does who is eating a meal that contains the leaves is to remove them. It is to be concluded that once the aroma is absorbed, the leaf has no value. In fact, it has some nonvolatile toxic constituents. How convenient it would be if there were an essential oil that had all the volatile characteristics but none of the nonvolatile ones. However, the whole leaf is believed to have some curative effect, as it is recommended in the treatment of ailments such as dysentery, as a febrifuge for fever, and as a general tonic in Ayurvedic therapy. After boiling in milk and grinding, it is applied to external eruptions and venomous bites. But its primary use is as a food flavor.

### Plant Material

The curry leaf tree is grown mainly in India and Sri Lanka. It is a small tree of 4–6 m in height and has a narrow trunk of 15- to 30-cm width. Leaves are pinnate with 10–20 leaflets, each 2–5 cm long and 1–2 cm broad (see Photo 12). The leaves emit the characteristic aroma of the plant. The leaves resemble the leaves of a neem tree. Because of this, the vernacular names of both are similar.

The flowers are relatively small and white in color. The tree has small dark berries whose seeds are toxic. However, the fresh leaves are in demand as a seasoning. The plant grows well in warm conditions with full or partial sun. The tree is found in almost all of India but thrives best in Southern India and Sri Lanka. On a dry basis, the leaf has about 6% protein, 1% fat, 16% carbohydrate, and 6–7% crude fiber. It has minerals, a fair amount of vitamin A, ascorbic acid, and some B vitamins. However, it is reported to have over 1% oxalates, and for this reason the leaves are rarely eaten as such (Pruthi 1976). The fresh leaves have 2.6% volatile oil, which is the significant constituent of the curry leaf.

### Essential Oils

Well before the advent of GC-MS, analyses of the curry leaf had been carried out. Water distillation yields 1% essential oil, which contains mainly *l*-pinene, dipentene,

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**Photo 12.** Curry leaf. See color insert.

*l*-terpineol, *l*-caryophyllene, and *l*-cadinene (Nigam and Purohit 1961). The oil is reported to be a bright yellow mobile liquid. In the 1950s, other workers found pinene, dipentene, caryophyllene, cadinene, and a few compounds (Prakash 1990).

In recent years, Rana et al. (2004) have used GC-MS to analyze the essential oil from fresh leaves growing wild in the Himalayan region. They identified 34 compounds representing 97.4% of the oil. The major components are $\alpha$-pinene (51.7%), sabinene (10.5%), $\beta$-pinene (9.8%), $\beta$-caryophyllene (5.5%), limonene (5.4%), bornyl acetate (1.8%), terpinen-4-ol (1.3%), $\gamma$-terpinene (1.2%), and $\alpha$-humulene (1.2%). Chowdury and Yusuf (2008) find that the curry leaf contains 39 compounds, of which 3-caryone 54.2% and caryophyllene 9.2% are the most notable components.

Oil obtained by steam distillation of curry leaves grown at 1750 m elevation in Uttarakand, India, showed $\alpha$-pinene (8.08%), sabinene (44.10%), $\beta$-caryophyllene (12.22%), $\beta$-phellandrene (3.19%), terpinen-4-ol (3.25%), $\beta$-cubebene (4.05%), $\alpha$-humalene (2.80%), germacrene D (3.09%), bicyclogermacrene (3.11%), and a few other components in small proportions (Pande et al. 2004).

The free and glycosidically bound aroma compounds from the curry leaf are isolated and separated on column and eluted. The aroma compounds are released by $\beta$-glucosidase hydrolysis and analyzed by GC-MS. Linalool has been found to be the main component out of 67 constituents. Out of 78 free aroma fractions, octyl acetate is the major component. In the hydrolyzed oil, $\beta$-caryophyllene is the major compound out of 56 compounds identified (Padmakumari 2008).

Studies of the levels of antioxidants in fresh curry leaves show that lutein is present to a level of 9744 ng, $\alpha$-tocopherol 212 ng, and $\beta$-carotene 183 ng/g fresh weight (Palaniswamy et al. 2003).

In this author's lab, it has been seen that $\beta$-phellandrene is the major component, accounting for 40–55%, followed by $\beta$-caryophyllene 12–20%, 3-carene 4–8%, $\alpha$-pinene 2–5%, and $\beta$-pinene 1–4%.

The oil obtained is light yellowish mobile liquid with a green note combined with a curry-like aroma. The average yield obtained on fresh weight basis is 0.12–0.20%.

Physical characteristics are as follows.

| | |
|---|---|
| Optical rotation | +3 to +12° at 25°C |
| Refractive index | 1.4800–1.4900 at 25°C |
| Specific gravity | 0.8520–0.8750 |

Oleoresin is not generally made, mainly because of unwanted nonvolatile components such as oxalic acid.

## Uses

The curry leaf is used in a wide range of curries, chutneys, soups, and snacks, all of which are hot to taste. When processed foods are made, it is more convenient to use the essential oil. The oil is used in diluted buttermilk, which is becoming popular as a soft drink. Use of the leaf may be a source of contamination. Curry leaf oil allows Asians who have settled in the West to add a highly prized native flavor to their savory preparations.

Srivastava et al. (2007) have found that essential oil and carbazole alkaloids from the leaves have antifungal properties. The activity is found to be enhanced by derivatization into *N*-methyl compounds, although hydrogenation reduces the activity. Such observations are encouraging factors in making curry leaf oleoresin a flavor material, provided that toxic components such as oxalic acid are removed.

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# 46 Date

## *Phoenix dactylifera* L (*Palmae*)

### Introduction

The date is the fruit of a palm tree and is valued as an unprocessed food. It is generally eaten after some drying. The date has been a staple food of the Middle East. It was believed to have originated in the Persian Gulf region. It was in use in ancient Mesopotamia (present Iraq) and Egypt from around 4000 BC. There is evidence that it was cultivated in Arabia even as early as 6000 BC, in lands adjacent to the desert where cultivation of other food crops is rather difficult. From Arab countries it was introduced to European Mediterranean countries. Spaniards introduced date palms to Mexico and California in the mid-eighteenth century.

### Plant Material

Like many palm trees, the date palm is an erect tree that grows to a height of 20–30 m. The date palm has spread all over the world, sometimes in a haphazard manner. Therefore, there is great variation in size and other characteristics. In some cultivars, several trunks spring from the same root system. Covered over the trunk will be an overlapping, upward-pointing woody leaf base. The leaves are pinnate, each 2–5 m in length, with spines on the petiole having a sturdy midrib and with 120–160 leaflets. Each leaflet comes as a sheath that divides into a network of fibers at the base.

The date palm is dioecious, having separate male and female plants. Small fragrant flowers are born on a branched spadix divided into a number of strands. The female flowers are whitish, male flowers, waxy and light yellow-colored. The fruits are oblong, with a length of 3–8 cm, with a thin or thick skin when ripe. Inside it has a hard, oval-shaped stone which is grooved on one side. The inside fleshy portion is yellow or reddish-brown in color, but develops into a darker color when dried.

The tree can be grown from the hard seed, but the disadvantage of this method is that only 50% of the trees will be date-bearing female plants. Therefore, commercial farms use cuttings of heavily cropping cultivars that produce a large number of sweet fruits. Plants thus grown from cuttings will bear fruits 2–3 years earlier than plants produced from seedlings.

Dates are naturally wind-pollinated plants, but today, it is common to use manual pollination. By such a method, one male tree can pollinate about 100 female trees. Manual pollination is carried out by skilled workers who climb on a ladder or use a climbing tool that wraps around the trunk of the tree.

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Date trees thrive best in sandy, clayey, or other heavy soils. They are tolerant of alkalinity and a moderate degree of salinity. The tree needs full sun and grows best in warm, dry weather. It can withstand periods of drought, but for greater yield it needs water.

Dates are harvested when they are fully ripe, when the pulp turns soft from a crunchy texture. It is eaten after the shell is removed and usually after some sun drying. Fully ripe fruits are also available after the hard stony seed is removed and are often chopped, usually longitudinally. They can also be dehydrated and ground and blended with grain or combined with almonds, walnuts, cashew nuts, or candied citrus peel.

According to the Food and Agricultural Organization of the U.N. report of 2007, the top producers are Egypt (1.3 million tonnes), Iran (1 million tonnes), and Saudi Arabia (0.98 million tonnes). Other major producers are United Arab Emirates, Pakistan, Algeria, Iraq, Sudan, Oman, and Libya.

The dried date has about 73% carbohydrates, much of which are sugars. One hundred grams of dried dates accounts for approximately 275 kcal of energy. They are rich in vitamins and minerals and are therefore a wholesome food. In some countries, palms are tapped for the sweet sap, which is converted into palm sugar and alcoholic beverages. Date seeds, after soaking in water and being partially disintegrated, are used as cattle feed. Date fruit has polyphenolic compounds such as flavanols and caffeoyl shikimic acid which, by the action of phenolase enzyme, bring about browning during drying and storage. Polyphenolic constituents also contribute a mild, desirable astringency to the fruit.

## Extractives

Dates have no essential oil. Since the main constituents are carbohydrates, date extract is made with hot water.

A typical process carried out in this author's lab is as follows. About 30 kg of ripened and dried dates with seeds are boiled in a kettle provided with a steam jacket in the bottom and sides. It is brought to boiling after adding 15 L of water. When boiling starts, it is maintained for about 10 minutes. During this time, the cooked and softened dates are broken by pressing with a flat ladle so as to crush the pulp. The pulp is then filtered through a filter cloth, while being stirred gently so that all the juice passes through. The residue is then transferred to the kettle, water added and boiling continued as before, using the ladle to further break the pulp. After filtration, the residue is given one more extraction with boiling water. Generally, the extraction will be complete after three boilings. This can be checked by tasting the residue for a sweet taste. If needed, a fourth boiling is done.

The combined filtrate, approximately 40 L after evaporation and absorption by the pulpy residue, is then placed in a flat kettle with more surface area and provided with a steam jacket in the bottom. The extract is concentrated until a total soluble solid strength of 75–80° Brix is obtained. The yield will be 50–55%. Seeds will account for 20%. The rest will be insoluble fibrous residue. About 750 ppm of citric acid is added so that the pH is 3.7–3.9. The final water extract will have a reddish-brown color and a viscous consistency. It will have the rich sweet taste of dates.

## Uses

Date extract is used as a flavor in tobacco. It gives a fine, mild, sweet taste during smoking. Date extract serves the same purpose as the extract of carob fruits, which is also used widely.

In the Ayurveda, sweet *rasayans* are made using dates. *Rasayans* are rich nutrient broths prescribed to improve general health. Currently, date extracts are used, because they are a more standardized product.

Date extract can be used as a sweet flavor in cakes, puddings, and sweet sauces.

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Date extract | – | 90027-90-0 | – | – |

# 47 Davana

## *Artemisia pallens* Wall (*Asteraceae, Compositae*)

### Introduction

The main part of the davana plant is the inflorescence, which has a fine aroma. The flowers are used to make garlands for religious purposes. South Indian women adorn their hair with the fragrant flowers. Davana is also distilled for its aromatic oil. Davana oil is an expensive oil used in food and beverage products and sometimes in perfumery. Ernest Guenther visited Mysore, India, and made observations of the crop and the oil (Guenther 1952). There are two cultivars, but the one whose oil gives a rich fruity note is the most highly valued. Today, there is a small but systematic cultivation and distillation of this plant to obtain the desired sensory characteristics.

### Plant Material

The main centers of cultivation of the davana plant are in South India, especially in the Karnataka State. The state of Tamil Nadu, which used to grow the inferior variety, is now switching over to the more desired variety with support given by the Central Institute of Medicinal and Aromatic Plants, Lucknow (Aktar et al. 1988).

Davana is an annual plant. It has an erect stem with near vertical branches. The height of the herb can be 45–60 cm. The leaves are alternate and lobed to pinnatisect gray. The inflorescence consists of glabrous florets, which have five lobes and are bisexual.

The davana plant prefers light showers, bright sunshine, mild winters without frost, and heavy morning dew. The crop cannot tolerate very heavy rainfall. For propagation, seeds are sown in nursery beds and seedlings are transplanted. From 1 ha, 12–15 tonnes of fresh herbage is obtained. On distillation, this can yield 10–12 kg of davana oil.

### Essential Oil

The herbage is partially dried in the shade, which requires 2–3 days. Generally, the weight decreases by half due to the escape of moisture. Bright sunlight may be damaging to the oil and will also cause evaporation of some of the oil. The yield is reported to be 0.2% (Aktar et al. 1988).

In this author's lab, commercial distillation is carried out first by a short period of drying in the shade. By exposing the plant to shade drying for 4–6 hours, moisture loss is only 5–10% of the original 80–88%. No advantage in loading capacity, yield

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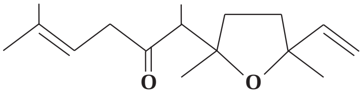

**Figure 47.1.** (+) Davanone.

of oil, or quality of oil was noticed by drying for longer duration. Steam is admitted at low pressure and distillation is allowed to proceed very slowly. After 8 hours, the yield obtained is 0.07–0.1 on the basis of original fresh weight. The oil obtained is a slightly oily liquid with a reddish-yellow color and a fragrant, herbal, and fruity aroma. Davanone content is generally 45%. With fractional steam distillation and by restricting the yield of oil to 0.05%, the davanone content can be raised to above 50%.

Physical characteristics are as follows.

| | |
|---|---|
| Optical rotation | +40° to +60° |
| Refractive index | 1.4780–1.4900 at 25°C |
| Specific gravity | 0.9200–0.9800 |

Aktar et al. (1988) have summarized the early work on this plant very well. The most important constituent is a ketone, davanone, which is usually present to the extent of 50–60% in good quality oil. In fact, pricing is dependent on the davanone content. Fenchyl alcohol, cinnamyl cinnamate, caryophyllene, cadenene, and some phenols and acids have been reported. Some of the alcohols noted are linalool and dehydro-$\alpha$-linalool. Davanafuran, isodavanone, dihydrorosifuran, *nor*-diterpenoid furan derivatives, *n*-alkanes, hydroxyl davanone, geraneol, and nerol are the other constituents found in the oil. The chemical structure of davanone (Catlan et al. 1990) is presented in Fig. 47.1.

Recently, davana has been introduced in Kashmir, in the north of India, where it has proved to yield a high davanone content. GC-MS studies show the components to be davanone (74.59%), ethyl cinnamate (8.40%), $\beta$-eudesmol (3.20%), methyl cinnamate, davanol isomers 1 and 2, and other compounds (Shawl et al. 2009).

## Uses

Davana oil is a highly prized flavor for expensive food and beverage products such as liquor and liqueurs. It is also used in perfumery. The crop is grown only in India, but the appeal of the oil is universal.

The flowers themselves are valued more for their fragrance and aroma rather than for their attractiveness when used for temple offerings and for adorning women's hair.

## Identification Numbers

| | FEMA No. | CAS | US/CFR | E-No. |
|---|---|---|---|---|
| Davana oil | 2359 | 8016-03-3 | 172.510 | – |
| | | 91844-86-9 | | – |

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# 48 Dill

## *Anethum graveolens* L, *A. sowa* DC (*Umbelliferae*)

### Introduction

Dill is used in Europe for its soothing effect on the digestive system. It is indigenous to the Mediterranean region and the south of Russia. There is a belief that dill originated in Eastern Europe, but wild dill is found widely in the Mediterranean region and West Asia.

Dill was regarded as a magic herb in Medieval Europe where brides used to wear a small branch in their hair and footwear for good fortune. Mexicans believed that dill could protect them from witchcraft and evil spirits. There is evidence that dill was used in Babylonia and Syria. Romans used it as a stimulant for their gladiators.

Later dill became a staple of Northern European cuisine. Both dill seed and dill weed have gained popularity in North America. The name is perhaps derived from Norse word *dilla*, which means “to lull” since it was used to lull babies to sleep as well as to get relief from stomach disorders.

### Plant Material

Dill seed is the dried fruit of an annual (or occasionally biennial) herb which belongs to the parsley group. European dill is *Anethum graveolens* L; Indian dill is *Anethum sowa* DC. The former is grown in Egypt, Mediterranean countries, Eastern Europe, North America, and some parts of Latin America. *A. sowa* is grown mainly in India.

Dill herb grows to a height of 90 cm. The leaves are dissected with a clasping base. The fully grown leaf is 50 cm long and a little less than 30 cm in maximum spread. Its flowers are light yellow in color. Dill seeds are brown in color and have an oval shape. One side is nearly flat with two longitudinal ribs. The other side is convex with three ribs. The length of the seed is about half a centimeter. The Indian variety’s seeds are slightly bigger, but have less of an aroma. Photo 13 shows the Indian dill plant and seeds.

The leaves and stalks of the dill plant are also aromatic. These, in fresh condition together with immature fruits, are known as dill weed or herb and are used in pickling and in soups.

### Chemistry

The main constituent is carvone (see Chapter 27 on caraway seed). Indian oil from *A. sowa* has a somewhat toxic constituent known as dillapiole (Fig. 48.1). This is a high-boiling heavy fraction (density 1.163 g/mL) with a structure close to that of apiole.

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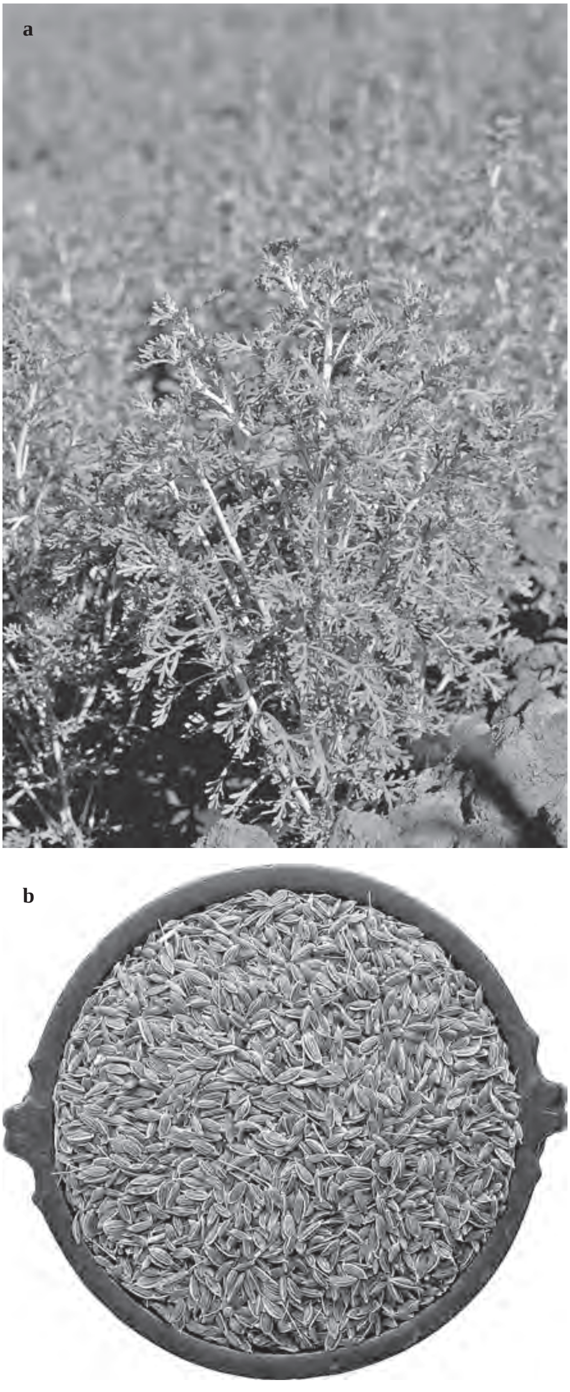

**Photo 13.** (A) Dill plant. (B) Dill seed. See color insert.

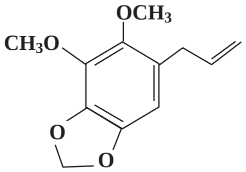

**Figure 48.1.** Dillapiole.

## Essential Oil

Although dill seed oil used to be made in different parts of the world including the United States, today India has emerged as the major producer.

Seeds are size-reduced by passing through a roller mill and then fed into a stainless steel distillation unit. Steam is introduced at normal pressure and distillation continues for 24 hours, to obtain a yield of 2.4% without cutting the dillapiole fraction.

The oil is a pale yellow to brownish liquid. The main constituent is carvone, which is present in 30–60%. Other major constituents are $\alpha$-phellandrene, 3,9-epoxy-*p*-menth-1-ene, myrcene, *p*-cymene, and limonene.

Especially for pharmaceutical use and use in food, it is necessary to remove dillapiole by fractional vacuum distillation. Since it is a heavy fraction, it distills out last and can be easily removed. Generally, it is better to use a two-stage vacuum distillation. The first stage separates the lower boiling fraction from the heavy fraction. The second stage is to recover the low boilers from the separated heavy dillapiole fraction, so as to get a satisfactory yield of good oil.

Dill oil from Reunion Island reveals 36 components with $\alpha$-phellandrene (56.5%), dill ether (20.8%), limonene (10.9%), and *p*-cymene (3.8%) accounting for 92% of the oil (Vera and Chane-Ming 1998). Indian dill oil, when analyzed using GC-MS, shows 21 compounds, with limonene (42.67%), carvone (22.50%), and dillapiole (15.92%) being the main ones (Shankaracharya et al. 2000). It is surprising, however, that dillapiole is seen in high proportion in *A. graveolens* by Vietnamese workers (Le et al. 2006). They found $\alpha$-phellandrene (44.21%), $\beta$-phellandrene (11.01%), and dillapiole (27.69%).

The FCC describes European dill seed oil as a pale yellow to light yellow liquid with a caraway odor and flavor. It is soluble in most fixed oils and in mineral oils. It is soluble with slight opalescence in propylene glycol but it is practically insoluble in glycerin.

Physical characteristics of oil from *A. graveolens* (European type) as defined by the FCC are as follows.

| | |
|---|---|
| Optical rotation | +70° to +82° |
| Refractive index | 1.483–1.490 at 20°C |
| Specific gravity | 0.890–0.915 |
| Solubility | 1 mL dissolves in 2 mL 80% alcohol |

According to the FCC, Indian dill seed oil occurs as a light yellow to light brown liquid with rather harsh caraway odor and flavor. It is soluble in most fixed oils and in mineral oil, occasionally with slight opalescence. It is sparingly soluble in propylene glycol and practically insoluble in glycerin.

Physical characteristics of oil from *A. sowa* (Indian type) as defined by the FCC are as follows.

| | |
|---|---|
| Optical rotation | +40° to +58° |
| Refractive index | 1.486–1.495 at 20°C |
| Specific gravity | 0.925–0.980 |
| Solubility | 1 mL dissolves in 0.5 mL of 90% alcohol |

American-type dill weed oil, according to the FCC, is a light yellow to yellow liquid. It is soluble in most fixed oils and in mineral oil. It is soluble, with opalescence or turbidity, in propylene glycol but it is practically insoluble in glycerin.

Physical characteristics of the above are as follows.

| | |
|---|---|
| Optical rotation | +84° to +95° |
| Refractive index | 1.480–1.485 at 20°C |
| Specific gravity | 0.884–0.900 |
| Solubility | 1 mL dissolves in 1 mL of 90% alcohol, frequently with opalescence, which may not disappear on dilution to as much as 10 mL |

There is very little production of dill oleoresin, oil being the well-used extractive. However, a CAS number is given for extract.

Dill weed oil, consisting of oil from the leaves and immature fruits, is different from dill seed oil. Dill seed oil is pungent and reminiscent of caraway, while dill weed or herb oil has a mellow and fresh flavor. Dill weed oil contains carvone, $\alpha$- and $\beta$-phellandrene, and monoterpenes.

## Uses

Since both dill seed and herb are used in pickling, salad dressings, and processed food, especially meat, cheese, and bread, oil can replace either in processed food.

Dill seed oil has therapeutic value due to its antispasmodic, carminative, diuretic, and stomachic properties. One of the largest outlets for dill oil, especially in India, is for use in "gripe" mixture, which is administered to babies to give relief from stomachache and related ailments.

## Identification Numbers

| | FEMA No. | CAS | US/CFR | E-No. |
|---|---|---|---|---|
| Dill (*A. graveolens*) | 2382 | 8006-75-5 | 184.1282 | – |
| Dill seed oil (*A. sowa*) | 2384 | 8016-06-6 | 172.510 | – |
| Dill weed oil | 2383 | 8006-75-5<br>90028-03-8 | 184.1282 | – |
| Dill seed extract | – | 8006-75-5<br>84775-84-8 | – | – |
| Dill weed oleoresin | 2382 | – | – | – |

## References

Le, Van-Hac; Do, Thi Ninh; and Nguyen, Xuan Dung. 2006. Study on chemical composition of the essential oil of *Anethum graveolens* L from Nghe An and Ha Tinh. *Tap Chi Duoc Hoc* **46** (5), 28–29, 31 (Vietnamese) (*Chem. Abstr.* 146:235416).

Shankaracharya, N.B.; Rao, L.; Jagan, Mohan; Puranaik, J.; and Nagalakshmi, S. 2000. Studies on chemical and technological aspects of Indian dill seed (*Anethum sowa* Rxb). *J. Food Sci. Technol.* **37** (4), 368–372.

Vera, R.R.; and Chane-Ming, J. 1998. Chemical composition of essential oil of dill (*Anethum graveolens* L) growing in Reunion Island. *J. Essent. Oil Res.* **10** (5) 539–542.

# 49 Fennel

## *Foeniculum vulgare* Miller (*Umbelliferae*)

## Introduction

Ancient scholars considered fennel seeds to be endowed with many characteristics which promote an active and healthy life. Aside from this, it has also been regarded as a spice valuable in cooking. In India, it is also used as a masticatory after a heavy meal, as it acts as a mouth freshener and an aid to good digestion.

In ancient times, fennel was believed to have some esoteric uses. In Greece, fennel is regarded as a symbol of success. In Rome, young fennel shoots were eaten as food. It is believed to improve vision and even to be an antidote for poison. Other uses attributed to the seed are rejuvenator, to stop hiccups, to cure wheezing, to ease stomach pain, to give additional milk to nursing mothers, to be good for the kidneys, and so on.

## Plant Material

Fennel is a perennial or biennial plant which grows to a height of 1.5–2 m. India is a major producer, but it is also grown in Eastern European, Mediterranean, and North African countries. Its seeds are bigger than those of cumin and are greenish in color, with a length of 5–7 mm (Photo 14). The seeds have longitudinal ridges, sometimes slightly curved. India is a major consumer of fennel seeds.

Fennel seed has 1–6% of essential oil. The oil content of the average Indian variety is about 1%. The seed has about 10–15% fixed oil. The fatty acid composition shows about 60% petroselinic acid, 22% oleic acid, 15% linoleic acid, and the rest mostly palmitic acid. It has many vitamins, such as vitamin A, ascorbic acid, thiamine, riboflavin, and niacin. But it must be remembered that the amount of fennel seeds eaten in a day is very limited and hence its nutritional advantages should not be taken seriously. Fennel spice has a mild, pleasant, spicy aroma and a slightly sweet taste.

## Essential Oil

Steam distillation of size-reduced fennel seeds yields an essential oil. Only coarse grinding is necessary and for this it is best to pass through a roller mill. Coarsely

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**Photo 14.** Fennel seeds. See color insert.

ground dry seeds are packed in a stainless steel distillation unit. Steam, at normal pressure, is passed through the bed where a mixture of oil vapor and water vapor will be formed. On cooling in a water-cooled condenser, this condenses as an immiscible mixture of fennel oil and water. This is separated in a Florentine flask separator for lighter-than-water oils. The oil floats on top. The escaping water is passed through twice more for separation to ensure that the entire quantity of oil is recovered. The usual distillation time is 18 hours.

The oil tends to be colorless or pale yellow. The major constituents of the oil are anethole (Fig. 7.1) and fenchone. Depending on the variety of fennel, there are sweet fennel oils (a special variety being “dulce”) and bitter fennel oils. The Indian variety is the latter and has an anethole content of 68–72% and fenchone content of 5–6%. Sweet oils from European sources are produced in very small quantities and are sometimes considered superior in aroma. Such oils have 85–90% anethole and very little fenchone. *d*-Phellandrene and *d*-limonene are also present in smaller amounts.

Anethole is 1-methoxy-4-prop-1-enyl benzene. It has a double bond and, therefore, has geometric isomers. The more commonly found and natural isomer is *trans*-

anethole. It is soluble in ethyl alcohol and only slightly soluble in water. The clear colorless *trans*-anethole has a boiling point of 234°C and a condensation point of 20°C. Fenchone is a 10-carbon cyclic monoterpene with a keto group. It is a colorless oily liquid with camphoraceous odor.

Spanish fennel seed essential oil shows methyl chavicol and fenchone. The leaves also contain methyl chavicol, $\alpha$-phellandrene, limonene, and fenchone, while the stem has anethole, $\alpha$-pinene, $\alpha$-phellandrene, *p*-cymene, limonene, and fenchone (Garcia-Jimenez et al. 2000). In a Chinese study, *trans*-anethole represents 65–78% of the volatile oil (Wu et al. 2001). In an investigation in Iran, hydrodistillation using a Clevenger trap yielded 2% oil, while open steam distillation yielded only 1.2%. Anethole is the major component (Ashnagar et al. 2007). Chemical examination of fennel cultivated in different climatic conditions in Israel by hexane extraction and GC-MS examination reveals as many as 18 compounds, with estragole, *trans*-anethole, fenchone, limonene, and $\alpha$-pinene as the main constituents (Barazani et al. 1999).

Extraction of fennel waste shows nonvolatile compounds having antioxidant activity, one of them being rosmarinic acid. The strong radical scavenging activity of these may explain the pharmacological effects of fennel (Perajo et al. 2004).

As per the FCC, fennel oil is a colorless or pale yellow liquid with the characteristic odor and taste of fennel. If solid material separates, the sample should be carefully warmed until it is completely liquefied and should be mixed before using.

Physical characteristics as defined by the FCC are as follows.

| | |
|---|---|
| Optical rotation | +12 to +24° |
| Refractive index | 1.532–1.543 at 20°C |
| Specific gravity | 0.953–0.973 |
| Solubility in alcohol | 1 vol dissolves in 1 vol 90% alcohol |

## Oleoresin

When coarsely ground seeds are extracted using hexane, oleoresin is obtained. Ethylene dichloride, ethyl acetate, and a mixture of acetone and hexane can also be used for extraction, with slightly varying quality. The main flavor characteristic will be contributed by the essential oil. The oleoresin will have all the fixed oil and resinous matter. These will act as a fixative and therefore the product will have a more toned flavor.

## Uses

Fennel extractives have a pleasant, spicy aroma and are useful in flavoring foods such as meat, soup, sauces, and bakery products. They also have some medicinal value, especially as a digestive. Fennel helps to increase digestive juices and has diuretic and mild antiseptic properties. Use of fennel oil in chewing gum is recommended to take advantage of its mouth-freshening properties.

## Identification Numbers

| | FEMA No. | CAS | US/CFR | E-No. |
|---|---|---|---|---|
| Fennel oil | 2483 | 8006-84-6<br>84455-29-8 | 182.20 | – |
| Fennel extract/oleoresin | – | 92623-75-1 | – | – |
| Fenchone | 2479 | 4695-62-9 | 172.515 | – |

## References

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Wu, Meihan; Nie, Lingyun; Liu, Yun; Zhang, Lei; and Wei, Liping. 2001. Study on chemical components of essential oil in *Foeniculum vulgare* from different areas by GC-MS. *Yaowu Fenxi Zazhi* **21** (6), 415–418 (Chinese) (*Chem. Abstr.* 137:145162).

# 50 Fenugreek

## *Trigonella foenum-graecum* L (*Leguminosae*)

## Introduction

Fenugreek has been used in food and for medicinal purposes for a long time. It is bitter, but its aroma develops on roasting.

Fenugreek, from *feonum-graecum*, is probably derived from the Latin word for Greek hay. It has a long history, having been recovered from the tomb of Tutankhamen. It was most likely used for embalming. In Iraq, charred seeds have been radiocarbon dated back to 4000 BC. There are records of fenugreek in some ancient recipes. In olden times, it was believed to be a hair tonic and a cure for baldness. It is believed to give sexy bosoms for harem women.

## Plant Material

The fenugreek plant grows to a height of 30–60 cm. It has light green leaves, which are eaten as leafy salad greens in some regions and are cooked as a vegetable in some parts of India.

The fenugreek seed, however, is valued as a spice. The seed is contained in slender, beaked pods generally 10–15 cm long. The smooth, hard seeds, shaped like a tiny, irregular brick, are about 3 mm in length. A pod contains, on an average, about 15 brownish-yellow seeds. On roasting, the color turns darker due to caramelization. The interaction of proteins and carbohydrates initiates a Maillard reaction. The thermal reaction between sugar and amino acids in many plant products produces volatile compounds such as pyrazines and lactones. An appropriate level of roasting gives the correct intensity of aroma and flavor.

Fenugreek seeds are rich in protein (9–10%), carbohydrates (40–45%), and fixed oil (7–10%). They contain calcium, iron, phosphorus, and vitamins. The ground seed is made into a bread in Ethiopia and other North African countries and into *chappati* in India. In a recent study of Chinese fenugreek, crude protein is found in levels of 54.06% and polysaccharide of 8.72% (Yang et al. 2003).

Fenugreek seeds contain saponins such as diosgenin, yamogenin, and other related compounds. Recently, two new compounds have been identified: methyl protodiocin and methyl protodeltonin (Yang et al. 2005). It also has alkaloids such as choline and trigonelline. Being rich in galactomannan, seeds are galactagogue and are therefore used by lactating women to increase milk production. Extracts are also marketed as testosterone- or muscle-boosting supplements. In the past, Eastern women have been

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known to use fenugreek seeds to give a boost to their busts. Efforts to debitter in order to add to wheat flour at low levels of 1.5–9% shows that the protein level can be increased only at the cost of levels of gluten and carbohydrate (Sharma and Chauhan 2000).

The seeds are used in the Islamic world as a cream, in tea, and in candies. It is a Jewish custom to eat seeds just after the New Year. In the United States, fenugreek extract is used to flavor artificial maple syrup.

Experiments done with fenugreek seeds in both insulin-dependent and nondependent diabetic patients show their usefulness in lowering blood glucose levels. Similarly, fenugreek seed has been known to lower serum triglyceride and low-density lipoprotein. However, more reliable experimental data are required.

Fenugreek seeds have a negligible amount of essential oil. The flavor develops due to thermally affected compounds, and hence the major extractive is extract of roasted seeds.

## Oleoresin

Roasting of fenugreek seeds is carried out at different intensities. When roasted at around 120°C for 10–20 minutes, they give an intense roasted aroma and flavor. Seeds can then be powdered by a roller mill and extracted with methanol or ethanol. The product may be very thick, so that it must be diluted with propylene glycol while still warm. This aims to give sufficient flow characteristics so that the product can be withdrawn from the bottom opening and handled during blending with other ingredients. In Indian curry formulations, an intense flavor is desired.

A milder roasting can be done at 80°C for 10–15 minutes, and extraction can be carried out with 80% aqueous ethanol. During desolventization, all the ethanol is removed, which leaves small traces of moisture. This will make the product water-dispersible even without use of propylene glycol. In Western formulations, a less intense roasted flavor is preferred.

Although use of methanol will give a satisfactory result, use of a potable solvent such as ethanol is needed, especially since the flavor is added at a very high level in products such as artificial maple syrup, which may be used in great quantities, especially by children. For the same reason, avoidance of propylene glycol and emulsifiers is preferable.

A more satisfactory method of making extract is by performing extraction first and then roasting. Fenugreek seed is ground by passing through roller mill. The seed is then extracted using aqueous ethyl alcohol 50–60%. A second and, if needed, third extraction can be carried out. The combined extract is then freed of all alcohol, leaving a small amount of water. For this, the miscella is distilled by gentle boiling with slow stirring so that no mechanical carryover of extract takes place. The product will be soluble in water. The extract is then roasted at 110–120°C for 8–10 hours to develop the desired roasted note. Moderate pressure of above 1 bar is needed in closed systems to get the above temperature. Great skill and knowledge of the flavor are required to obtain the product used as a flavor for artificial maple syrup. Excess temperature or roasting time will result in a burned note instead of the required roasted note. There are minor differences in the flavor developed by different manufacturers. Generally, the roasted extract is used at a level of about 10% in corn syrup with 10–15% commercial liquid caramel product added to adjust to the optimum shade and flavor.

Another extract that is expensive and used in very low levels is fenugreek absolute. Originally, this was extracted with alcohol, but could also be an alcohol-soluble fraction separated from a regular oleoresin. The level of roasting depends on the aroma requirements for the specific use. Chilling and removal of waxes is carried out to develop a perfect absolute, almost like a floral absolute. Different absolutes prepared to the exact aroma characteristics required for each manufacturer are very expensive and unique. Absolute finds use in high-priced cigarettes, special perfumes, and rare beverages.

## Uses

The greatest use for fenugreek extract and oleoresin is for flavoring artificial maple syrup, which is very popular in the United States and Canada. Roasted fenugreek extract has a strong, curry-like flavor and therefore can be used in a wide range of savory cooked products. The extract of unroasted seeds mainly contains fixed oil with a celery-like odor and is extremely tenacious, and therefore has attracted the attention of fragrance experts. Fenugreek extract is also used in tobacco flavoring.

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Fenugreek extract | 2485 | 84625-40-1 | 182.20 | – |
| Fenugreek oleoresin | 2486 | 84625-40-1 | 182.20 | – |
| Fenugreek absolute | 2486 | 84625-40-1 | 182.20 | – |

## References

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Yang, Yong-Li; Sun, Shuang-yan; Cui, De-feng; Zhang, Yu-Lan; Yao, Jian; and Zhang, Ji. 2003. Study on physical and chemical contents in seeds of *Trigonella foenum-gracum* L. *Xibei Shifan Daxue Xuebao, Ziran Kexueban* **39** (1), 64–65, 73 (*Chem. Abstr.* 138:317522).

Yang, Weixing; Huang, Hongyu; Wang, Yongjiang; Jia, Zhiyan; and Li, Linlin. 2005. Study on chemical constituents in total saponins from *Trigonella foenum-graecum*. *Zhongguo Zhongyao Zazhi* **30** (18), 1428–1430 (Chinese) (*Chem. Abstr.* 147:296080).

# 51 Galangal: Greater

## *Alpinia galanga* (L) Willd (*Zingiberaceae*)

### Introduction

Greater galangal (also called galanga) is native to Java and Malaysia and is therefore referred to as "Java galangal." It is also called "blue ginger" or Thai galangal as it is a spice used in Indonesian and Thai cooking. There are some galangal roots belonging to the ginger family, and collectively they are sometimes referred to as false ginger.

In early records, some references may apply equally to greater galangal and lesser galangal. The earliest reference is by the Arabian geographer Ibn Khurdabah in the ninth century AD. He included galangal in the list of products from a country, Sila, believed to be China (Pruthi 1976). A few years later, Plutarch described galangal as a fumigating spice used by Egyptians. It was also mentioned by Edrisi as a spice imported from Aden, probably for use in Egypt. Marco Polo also referred to the production of galangal in China.

### Plant Material

The greater galangal plant, which grows from a rhizome, consists of stiff stalks with a large number of long leaves. The plant grows to a height of 3–3.5 m. The leaves are green in color and are lanceolate, elongated elliptically with pointed ends. The plant bears red fruits and small, greenish-white flowers. The fruits have an aroma reminiscent of cardamom and are used in traditional Chinese medicines.

The rhizome has the flavor and is the source of oil. The rhizome is much harder than normal ginger and its separation requires cutting with a heavy knife. It is easier to slice when fresh; after drying, even greater effort is needed for slicing. The creamy white inside has a flavor that slightly resembles pepper and pine with an underlying camphoraceous note. It is generally deskinned by scraping. The slices are preserved in brine or dried. Galangal is heavily used in the cooking of Thailand, Indonesia, Malaysia, and, to a limited extent, in Caribbean culinary practices. See Photo 15.

Early studies show that greater galangal has methyl cinnamate, cineole, camphor, and dipentene. It has flavonoids such as quercetin and condensed products from polyphenols. In the rhizome from Malaysia, 40 components have been identified, representing 83–93% of the oil. These include chavicol and chavicol acetate, in addition to eugenol, eugenol acetate, monoterpenes, alcohols, esters, and sesquiterpenes (De Pooter et al. 1985). In recent years, l′-acetoxy chavicol acetate has been reported; this has cosmetic qualities for use in skin care. This is also believed to be the reason for the traditional use of greater galangal as a treatment of pityriasis versicolor and other

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**Photo 15.** Cut pieces of greater galanga. See color insert.

diseases (Nguyen and Huynh 2005). Greater galangal has vitamins A and C and minerals such as sodium and iron. The nonvolatile constituents give it anti-inflammatory and antioxidant properties. l′-Acetoxy chavicol acetate has recently been studied with reference to its clinical significance (Zhuo and Li 2007).

A recent review (Wang and Wang 2008) has shown that the major components of *Alpinia* plants include diarylheptanoids, terpene, flavone, volatile oil, phenyl propanoid, and steroids.

## Essential Oil

After drying, size reduction, and steam distillation, greater galangal yields a volatile oil. In commercial manufacture, full yield of 2.5% is obtained after steam distillation for about 16 hours.

The oil is a light yellow mobile liquid with the mildly pungent, earthy, and camphoraceous aroma typical of the rhizome. The physical characteristics obtained in the author’s lab based on commercial production are as follows.

| | |
|---|---|
| Optical rotation | +4 to −12° at 25°C |
| Refractive index | 1.4620–1.4690 |
| Specific gravity | 0.8500–0.8750 |

**Table 51.1.** Analysis of java galangal oil

| Constituent | Content (%) |
|---|---|
| $\alpha$-Pinene | 1–2 |
| 1,8-Cineole | 22–28 |
| Eugenol | 2–3 |
| Caratol | 30–40 |

An extensive study of the volatile oils obtained from different parts of the plant has been carried out by Menon in 2006. The oil from the rhizome contains carotol (26.7%), 1,8-cineole (30.3%), $\beta$-pinene (6.5%), camphor (5%), and fenchyl acetate (7.2%). The root oil is shown to have fenchyl acetate (30.5%), along with 1,8-cineole and limonene. The major constituents of the leaf oil are fenchyl acetate (20.7%) and $\beta$-caryophyllene (40.5%), while that of stem oil is cubenol (28.4%).

Based on commercial production, results of the analysis of the oil are presented in Table 51.1. Caratol is the major component followed by cineole.

The oleoresin can be obtained from dry material which has been size-reduced by roller mill and extracted using hexane. The yield obtained is 1.8–2%. The oleoresin shows a volatile oil content of around 12%.

## Uses

Greater galangal rhizome is a frequently used seasoning in Southeast Asian cooking. In processed foods, the oil and oleoresin are quite useful because of standardization of the flavor strength. When particles of rhizome are used, they can be a source of contamination. Such problems can be avoided if extractives are used.

The extract, which contains acetoxy chavicol acetate, can be used in medicinal and cosmetic preparations.

## Identification Numbers

| | FEMA No. | CAS | US/CFR | E-No. |
|---|---|---|---|---|
| *Alpinia* species root oil | 2500 | 8024-40-6 | 182.20 | – |
| *Alpinia* species root extract | 2499 | 8024-40-6 | 182.20 | – |

## References

De Pooter, Herman L.; Muhammad, Nor; Omar, Coolsaet; Brigitte, A.; and Schamp, Niceas M. 1985. The essential oils of greater galangal (*Alpinia galanga*) from Malaysia. *Phytochemistry* **24** (1), 93–96.

Menon, N.A. 2006. Chemical composition of the volatile oils of *Alpinia galanga* plant parts from Kerala. *J. Essent. Oil-Bearing Plants* **9** (3), 277–282.

Nguyen, Dinh Nga; and Huynh, To Quyen. 2005. Determination of chemical structure of *Pityrosporum orbiculare* antifungal agent from *Alpinia galanga* Swartz from Vietnam. *Tap Chi Duoc Hoc* **45** (4), 17–21 (Vietnamese) (*Chem. Abstr.* 144:428869).

Pruthi, J.S. 1976. *Spices and Condiments*. New Delhi: National Book Trust, pp. 123–125.

Wang, Xiuqin; and Wang, Peixian. 2008. Chemical constituents of *Alpinia* plants. *Xibei Yaoxue Zazhi* **23** (2), C3–C4 (Chinese) (*Chem. Abstr.* 149:528591).

Zhuo, Xin-ming; and Li, Bo-an. 2007. Current research progress in the biological activity of ACA, a kind of natural chemical compound. *Guowai Yixue, Yaoxue Fence* **34** (3), 181–186 (Chinese) (*Chem. Abstr.* 148:345693).

# 52 Galangal: Kaempferia

## *Kaempferia galanga* L (*Zingiberaceae*)

## Introduction

Because of its widespread availability, *Kaempferia galanga* is often referred to somewhat erroneously as “lesser galanga.” It is sometimes known as *kencur* or sand ginger. In any case, it is one of the three or four “false” gingers, resembling galangal rhizome in flavor and appearance. It is known to some botanists as “resurrection lily.” Generally, however, it is referred to by its vernacular name.

The rhizome is ground and used in dishes in Bali. The leaves are finely sliced and eaten as a salad in Malaysia. Both the rhizome and leaves are used to flavor fish curries. Tender leaves are also eaten as a raw vegetable with shrimp paste.

## Plant Material

*K. galanga* is glabrous, perennial, aromatic herb, which is generally pleasing to the eye. It has two or more leaves which spread flat on the ground (Warrier 1993). The petiole is very short, round-ovate, thin, and deep green. The flowers are white with purple spots, in axillary fascicle with a corolla tube 2.5 cm in length and connected to one another, producing a quadrate, two-lobed appendage. Its fruits are oblong, three-celled and three-valved capsules with arillate seeds.

The aromatic undergrowth is the important part of the plant. This has one or more prominent, vertically oriented, tuberous rootstocks. There can be many secondary tubers and roots whose tips become tuberous. The rhizome, roots, and leaves have medicinal properties. The rhizome is bitter, thermogenic, and acrid, and is a carminative, diuretic, expectorant, digestive, and stimulant. It is recommended for use in Ayurvedic therapy. It has a peppery, camphoraceous flavor.

## Essential Oil

On grinding using a roller mill, followed by steam distillation, the *K. galanga* rhizome yields an essential oil of around 1%. The distillation time with steam at low pressure is around 24 hours.

The oil is a light or greenish-brown mobile liquid with odor characteristic of the rhizome, namely, peppery and camphoraceous. Physical characteristics obtained in the author’s lab are as follows.

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**Table 52.1.** Constituents of galangal oil

| **Constituents** | **Content (%)** |
|---|---|
| $\alpha$-Pinene | 1–2 |
| Camphene | 2–3 |
| 3-Carene | 8–14 |
| Limonene | 3–6 |
| Ethyl-*p*-methoxy cinnamate | 30–44 |

| | |
|---|---|
| Optical rotation | –3 to –6° at 25°C |
| Refractive index | 1.4700–1.4855 at 25°C |
| Specific gravity | 0.8620–0.8850 |

The chemical analyses from a number of commercial producers of galangal oil are presented in Table 52.1. The most prominent constituent is ethyl-*p*-methoxy cinnamate.

The volatile oil obtained by water distillation of *K. galanga* can be examined by GC-MS (Tewtrakul et al. 2005). The major components identified are ethyl-*p*-methoxy cinnamate (31.77%), methyl cinnamate (23.23%), carvone (11.13%), eucalyptol (9.59%), and pentadecane (6.41%). While some antimicrobial activity is noticed, antioxidant activity is negligible. Hot drying of the leaves of *K. galanga* generally affects the antioxidant activity (Chan et al. 2009).

## Uses

The rhizome of the *K. galanga* is widely used in the culinary practices of Southeast Asia. In processed foods, the oil is the natural choice, because of freedom from contamination and ease of standardization. The oil is also useful in medical preparations.

## References

Chan, E.W.C.; Lim, Y.Y.; Wong, S.K.; Lim, K.K.; Tan, S.P.; Lianto, F.S.; and Yong, M.Y. 2009. Effects of different drying methods on the antioxidant properties of leaves and tea of ginger spices. *Food Chem.* **113** (1), 166–172.

Tewtrakul, S.; Yuenyongsawad, S.; Kummee, S.; and Atsawajaruwan, L. 2005. Chemical components and biological activities of volatile oil of *Kaempferia galanga* Linn. *Songklanakarin. J. Sci. Technol.* **27** (2), 503–507.

Warrier, P.K. 1993. *Indian Medicinal Plants*. Madras: Orient Longman, vol. 3, pp. 274–278.

# 53 Galangal: Lesser

## *Alpinia officinarum* Hance (*Zingiberaceae*)

## Introduction

This is another type of galangal (also written galanga) plant which is used in South and Southeast Asia, both in cookery and in medicine. There is considerable confusion about the different members of the galangal. This rhizome is popularly known as "China root." Lesser galangal differs from greater galangal (*Alpinia galanga*) and *Kaempferia galanga*.

Long before the plant was botanically classified, the rhizome was in use in Europe for over half a millennium. The root originated on Hainan Island in Southern China. It was cultivated in the coastal regions of South China and was exported from Shanghai. Like greater galangal, this root also has an Arabian connection; the name "galanga" is derived from the Arabic. However, in many historical descriptions, the three varieties of galangal roots are confused.

Even in use for cooking, the availability of the galangal plant may be the deciding factor, as all three varieties have similar flavor characteristics of pungent and spicy notes. They are all related to ginger, thereby justifying the name of "false ginger" given to galangal roots.

## Plant Material

The lesser galangal herb is about 2 m in height, with the elongated narrow leaves characteristic of ginger. The leaf is parallel, smooth-veined, and sharply acuminate with a length of about 30 cm and breadth of 5–10 cm. Flowers are simple terminal spikes and have short, superior, and tubular calyx and white corolla consisting of three lobes. There is a large ovate labellum with red veins. Each flower has a single stamen that bears the anther and a pistil with an inferior ovary and a thin style.

The lesser galangal rhizome itself has branches. The total length of the rhizome is 4–7 cm and its thickness less than 2 cm. Generally, they are cut transversely into imperfect cylindrical shapes with whitish scars left by stems, which are removed. The outside color is reddish brown, with pale colored inner matter. The aroma of the rhizome is similar to other galangals, that is, peppery and pungent combined with a camphoraceous note. The dried material is tough and difficult to break.

Earlier literature shows starch as a major component. It has a volatile oil and resinous component containing nonvolatile fractions such as galangal, galangin, and

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kaempferid. Galangin is a dioxyflavanol. Kaempferid actually consists of three parts, fusing at 220°C, insoluble in water but soluble in ether.

China root galangal is a stimulant, carminative, and flatulent. It is useful in treating stomach disorders, vomiting, and fever. It is a good medicine for cattle.

## Essential Oil

Very limited information is available about commercial production of lesser galangal's volatile oil. However, there is a report from Indrayan et al. (2007) about the analysis of oil obtained by hydrodistillation of the rhizome collected from West Bengal, India. 1,8-Cineole (53.39%) is the major constituent. Also reported are $\delta$-3-carene (8.96%), $\beta$-pinene (4.29%), camphene (2.81%), limonene (2.80%), isocaryophyllene (2.52%), camphor (2.35%), $\alpha$-pinene (2.27%), $\gamma$-terpinene (2.23%), and $\gamma$-cardinene (2.17%). The oil also shows antibacterial activity against both gram-positive and gram-negative bacteria and antifungal activity against *Candida albicans*.

## Uses

The rhizome is used in many culinary practices in Asia. The oil has a convenient flavor for use in processed foods. In addition, extracts with medicinal properties can be developed.

## Reference

Indrayan, A.K.; Garg, S.N.; Rathi, A.K.; and Sharma, V. 2007. Chemical composition and antimicrobial activity of *Alpinia officinarum* rhizome. *Indian J. Chem. B Org. Chem.* **468** (12), 2060–2063.

# 54 Garcinia Fruit

## *Garcinia cambogia* Desr (*Guttiferae*)

## Introduction

In recent years, the garcinia fruit has attracted much attention because of the ability of the acid from the fruit to control the weight of its consumer. However, the fruit, popularly known as "Malabar tamarind," has for years been a favorite in South Asia as a much liked acidulant in food. People of Southwest India and Sri Lanka use the dried rind in fish curries and other food preparations. To some extent, it is an acquired taste as its sourness is combined with astringency. It is believed that its high level of acid can preserve food very effectively. In the days before the refrigerator became a household item this was an important consideration.

Garcinia also makes food satisfying and filling. Generally, in the ancient Ayurvedic system of medicine, acidic foods activate the metabolism. In ancient times, the natural gum oleoresin that oozes out from the bark was used for various ointments.

However, it is the fruit that is used as a seasoning and can yield an extract that becomes a flavor. The fact that the fruit has special properties to guide metabolism to effectively control fat accumulation and weight gain is a further bonus.

## Plant Material

The garcinia plant is a small evergreen tree. It has a rounded crown and relatively drooping horizontal branches (Majeed et al. 1994). The tree, whose trunk has smooth bark, attains a height of 5–8 m. The leaves are shining dark green and elliptical to oval-shaped. The flowers are unisexual, sessile, and axillary. It has four yellowish and rounded sepals and an equal number of large, rose-colored petals. It has four- or eight-celled and globular ovaries.

Though smaller in size, the fruit resembles a small yellowish- or reddish-colored pumpkin in shape. The sweet and sour tasting fruit is globular and has juicy white pulp inside. The rind is thick and tough. Embedded in the pulp are six to eight seeds. On drying, the fruit assumes a near black color. It is tougher and less pulpier than tamarind. Photo 16 shows the garcinia fruit and dried pulp.

## Chemistry

About 30% of the fruit is made up of an acid, which has been identified as (–)hydroxycitric acid (Lewis and Neelakantan 1965). The structure of this acid is presented in

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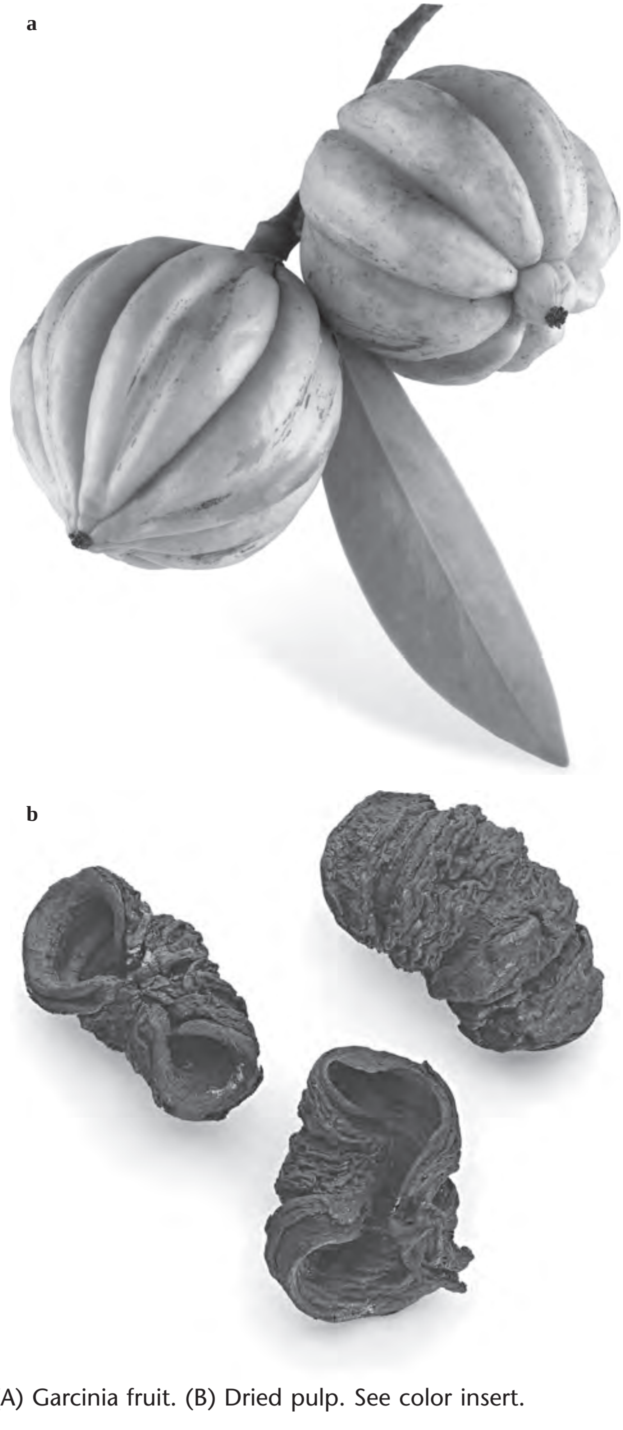

**Photo 16.** (A) Garcinia fruit. (B) Dried pulp. See color insert.

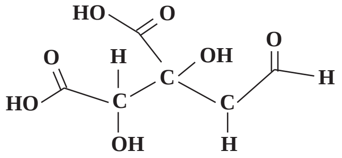

**Figure 54.1.** Hydroxycitric acid.

Fig. 54.1. Hydroxycitric acid is a derivative of citric acid and is found in some tropical fruits. On storage it can convert into a lactone. The characteristic compound cambogin has been identified (Rama Rao et al. 1980).

## Extract

The garcinia fruit has no essential oil. The dried fruit can be extracted with boiling water. After extraction is repeated three or four times, the extracts are combined, strained through a suitable filter, and concentrated through the evaporation of water. The thick extract with total soluble solids of 60–70° Brix comes out as a dark syrupy liquid. This is used as the flavor concentrate.

In recent years, emphasis has shifted to the hydroxycitric acid that can be obtained from the fruit. The acid readily undergoes lactone formation. Lactone is not an effective chemical for intervention in fat formation. To avoid this, the acid is converted to a calcium salt, which is more popular, although a potassium derivative can also be made.

The extraction is done in a stainless steel boiling kettle with a batch size of 300–600 kg. Generally, three times the plant's weight in water is used for extraction. About half the quantity of water is added in the first extraction and the remaining in two parts in the subsequent extractions. The mixture is heated with a steam jacket and stirring. The soluble constituents, mainly hydroxycitric acid, go into the water miscella. This is decanted and kept aside. A further two extractions are carried out. The extraction is done at a temperature of 60–70°C. The combined extract is concentrated and then treated with sodium hydroxide to bring the pH to between 8 and 9, while temperature is maintained at 70°C. A calculated quantity of calcium chloride is added to convert the acid to the calcium derivative. The calcium salt is carefully washed to remove any excess chemicals. However, excessive or careless washing will remove some valuable calcium derivative of hydroxycitric acid, which is slightly soluble. A convenient form of filtration and washing is by using a basket centrifuge fitted with filter cloth. When freed of water, the wet cake is removed and dried in a cabinet dryer at 90–100°C. The dry cake is ground to a powder as per customer specification. Since the calcium hydroxycitrate is used in capsule form, the bulk density has to be adjusted to fill the appropriate capsule.

The calcium derivative of (–)hydroxycitric acid is a pale brownish-gray powder with mildly salty taste but with no odor. The particle size is adjusted as per customer specification. A bulk density of 0.5–0.7 g/mL is typical.

The moisture content is kept below 6% for optimal storage. The calcium content is generally between 18% and 21%. Hydroxycitric acid determined by HPLC using a pure standard is required to be, as per market need, between 55% and 65%. On dissolving at 10% level, the pH must be between 8 and 10.

## Mechanism of Action

During metabolism, in the Krebs cycle, citrates are converted into acetyl coenzyme A with the help of an enzyme system, citrate lyase (Majeed et al. 1994). When (–) hydroxycitrate is fed during this phase, part of the enzyme will be utilized by this acid, and thereby formation of acetyl coenzyme A is slowed. The acetyl unit is the building block of fat synthesis. Therefore, consumption of (–)hydroxycitric acid brings about a slowing of fat synthesis and hence fat accumulation. But for effective intervention, hydroxycitric acid has to be in straight chain form and not as a lactone. This is achieved by conversion to a metal derivative. Calcium hydroxycitrate is liberated to free acid which remains in straight chain form for some time so that it can function effectively. The best time to take the calcium salt is about 1 hour before the main meal. In the marketing process, some micronutrients are added to increase its value. Calcium itself is a good nutrient, and for this reason potassium salt has disadvantages.

Recently, the role of hydroxycitric acid as an inhibitor of ATP-citrate lyase, as well as its structure and characteristics, has been reviewed (Yamada et al. 2007).

## Uses

The water extract of the Malabar tamarind can be used in place of the fruit itself. The extract can be used even in places where fruits are not available. The extract is particularly appreciated by South Indians who have settled abroad, as they can procure their favorite seasoning for use in their well-liked fish curries. The extract, being acidic, will help in preservation of food preparations.

The garcinia fruit's greatest value is its use as a supplement to regulate weight. The calcium derivative when taken before the main meals helps in regulating metabolism to reduce formation of triglycerides.

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# 55 Garlic

## *Allium sativum* L (*Alliaceae*)

## Introduction

Garlic belongs to the onion family. It was known to ancient Romans and Egyptians, was referred to in writings from the time of Moses, and is believed to have originated in West Asia. In the pre-Christian era, citizens of Greece and Rome thought that garlic had supernatural qualities; thus, sailors carried it hoping that it would save them from the dangers of the sea. There is mention that Israelites developed a taste for garlic during their journey from Egypt.

Though many diverse qualities were attributed to garlic by ancient people, its primary value is for food flavoring. There are, however, groups of people who detest its flavor and avoid its consumption. Some elite groups in China used to consider garlic flavor in food as objectionable as it causes an offensive smell in the breath of people who eat it.

## Plant Material

Garlic is the underground bulb of a perennial plant with flat leaves and small white flowers. Since the valued part of the plant is under the earth, the plant has to be pulled out of the ground to be used, so in effect it needs replanting each season. The bulb consists of 6–35 smaller bulblets called "cloves" which are surrounded by a thin white, yellow, or pink paper-like sheath. Photo 16 shows the garlic bulb and cloves.

Garlic needs a slightly richer soil than does the onion. A well-drained, moderately clayey soil is suitable. Ideally, it needs a cool, humid period for growth and a relatively dry season while maturing. The crop will be ready in 4–5 months, when the top turns slightly yellow or brown. After plucking from the earth, the bulbs are cured for 3–4 days in the shade before being stored in ambient conditions after removing the top vegetative parts.

Garlic is grown in many different regions of the world which are free of extremes of climate. The largest producer of garlic is China, which, according to statistics, grows 75% of the estimated world production of 15,000–16,000 tonnes. Other producers are India (4%), South Korea (2%), Russia (1.6%), and the United States (1.4%). In the United States, most production is centered around Gilroy in California, which calls itself the "Garlic Capital of the World." However, with the development of Silicon Valley and consequent growth of building construction, that position is fast changing.

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**Photo 17.** Garlic. See color insert.

## Chemistry

The aroma and flavor of garlic is released on bruising or processing. When the cells are broken, the alliin present is broken down on contact with the enzyme allinase to produce the sulfur-containing compound allicin. This being unstable, it further disintegrates into simpler sulfur-containing volatile compounds such as diallyl disulfide and other sulfides.

Alliin, the precursor of allicin, is quite sensitive to heat, and extraction with ethanol should be carried out at temperatures below 0°C. Allicin itself is also sensitive to the high temperature employed in GC studies and can be converted into cyclized compounds through dehydration reaction (Singh 2009). This factor has to be taken into account while interpreting data on GC analysis.

The chemistry of aroma formation is quite complicated but well studied. For more detail, the reader is referred to various reviews (Abraham et al. 1976; Choi et al. 2007).

## Essential Oil

Special care is needed for distillation of garlic oil, which is a heavy oil. Modification of the still is made to allow refluxing and water-steam distillation. Otherwise, it is very difficult to release the oil from the cells. A practical arrangement would be recycling of condensed water and simultaneous admission of steam to allow water-steam distillation. The oil will be distilled and collected in 7–10 hours depending on the garlic variety and the pressure of steam. The yield with Indian garlic will be 0.2–0.3%. Some varieties of Chinese garlic have even higher yields.

Use of enzymes to break down structural tissues has led to an increase in the yield of volatile oil. Cellulose, pectinase, and protease increased the yield during both steam and water distillation (Sowbhagya et al. 2009). Crushed garlic is treated with aqueous solutions of enzymes, pH-adjusted to 4.5–5.0 with aqueous citric acid, and incubated at 50 ± 2°C for 90 minutes before distillation. The best result is obtained by pectinase when the yield increased from 0.28% to 0.51%.

Garlic oil is yellowish-brown in color. It has a strong and pungent aroma which may be disagreeable due to its high concentration; it must be suitably diluted when used in food preparations. The constituents of the oil are about 60% diallyl disulfide and 20% diallyl trisulfide, with traces of alliin and allicin. The characteristic aroma of garlic may be derived from diallyl disulfide.

Different varieties of garlic yield oils of different strength. Indian garlic is usually much stronger than Chinese garlic. The oil can be 500–1000 times stronger in aroma than fresh garlic.

According to the FCC, garlic oil occurs as a clear yellow to red-orange liquid with a strong pungent odor and a flavor characteristic of garlic. It is soluble in most fixed oils and in mineral oil. It is insoluble in glycerin, propylene glycol, and ethyl alcohol.

Physical characteristics as defined by the FCC are as follows.

| | |
|---|---|
| Refractive index | 1.550–1.580 at 20°C |
| Specific gravity | 1.050–1.095 |

The author’s lab has found no optical rotation for garlic oil but it can be given as 0 to +1°.

## Oleoresin

Both unroasted and roasted oleoresins are used in food flavoring. For the “green” or unroasted oleoresin, the garlic is disintegrated and mixed with small quantity of water. The aqueous juice is squeezed or drained out along with added water. This step can be repeated once more with a small quantity of water. After this, the residue is extracted with hexane. For this process, solvent is admitted from the bottom of the vessel that contains the residue, and miscella is collected from the top at ambient temperature. After two or three such extractions, the combined hexane miscella is freed of the solvent to obtain an oily flavor concentrate with a yield of 0.2–0.3% on raw material basis. This is then added to the water extract to obtain a green oleoresin with satisfactory flavor characteristics. The yield of total water-soluble oleoresin will depend on the quantity of water used, but for effective strength, it is best to limit the total yield to 10–15%.

For roasted oleoresin, the garlic after disintegration is roasted at a temperature of 100–120°C for a short duration determined by the intensity of roasted aroma desired. After cooling, the material is extracted with hexane. The solvent is removed from the combined miscella to obtain a flavor concentrate with a yield as low as 0.1–0.2%.

This is then suitably diluted with a fixed oil or mono- and diglyceride to obtain roasted oleoresin.

Considerable variation in the manufacture of oleoresin is possible by combining water extraction of the press-juice and hexane extraction of the nonpolar aroma constituents and roasting to the desired level. Roasted hexane extract can also be blended with water extract so that it becomes water-soluble. Addition of emulsifiers and diluents will not only reduce the cost per unit weight, but will also increase the convenience of handling. Addition of some steam-distilled oil will improve the aroma but the cost will also increase.

In recent years, a considerable amount of research on the chemical constituents of garlic has been carried out, particularly in China. Organosulfur compounds in fresh garlic are studied by using cold on-column injection and cold extraction under cryogenic conditions. The major compounds that exist before thermal degradation are 3-vinyl-4H-1,2-dithiin and 2-vinyl-4H-1,3-dithiin (Zheng et al. 2006). Various allyl sulfides, some previously known, have been studied in different conditions (Jirovetz et al. 2001; Guo et al. 2005; Tian et al. 2005).

Extraction with supercritical carbon dioxide followed by analysis by GC-MS reveals 16 compounds in garlic. They include diallyl disulfide, 3-ethenyl-1,2-dithiacyclohex-5-ene, 2-ethenyl-1,3-dithio-cyclohex-5-ene, and diallyl trisulfide (Zhang et al. 2002). The oil volatiles obtained through supercritical extraction and steam distillation have been compared: in supercritical extraction, 23 compounds were identified, and by steam distillation, 21 are seen. The excesses in the former are 3-methyl butylallyl sulfide and *n*-hexanal. The differences in the contents of constituents have been discussed (Luo et al. 2008).

## Uses

Garlic is a widely used flavor in savory foods. Extractives can be used in processed foods such as soups, dressings, curries, and dry preparations.

Extracts of garlic are reported to inhibit platelet aggregation and to help lower cholesterol level. They also show hypoglycemic effect and have antimicrobial effect on fungi belonging to *Aspergillus* and *Candida*. These qualities can be exploited in processed food. Consumption of garlic reduces the risk of cardiovascular disease and cancer (Lin et al. 2000).

Garlic has a high sulfur content which makes it suitable for making skin, hair, and nails supple and smooth. Garlic also has selenium, which, with an antioxidant such as tocopherol, can arrest the aging process of tissues. Besides their antimicrobial action, garlic extractives can also be an effective insect repellent (Singh 2009).

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Garlic oil | 2503 | 8000-78-0 | 184.1317 | – |
| Garlic oleoresin | – | 8000-78-0<br>8008-99-9 | 184.1317 | – |

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# 56 Ginger

## *Zingiber officinale* R (*Zingiberaceae*)

## Introduction

Ginger was used in ancient India for its both culinary and medicinal properties. Its benefits in digestion and as a carminative have been recognized in Ayurvedic therapy.

The family to which ginger belongs, *Zingiberaceae*, has several shrubs including turmeric and galangal. It is believed that many members of this group originated in the tropical forests of Asia. Historical records show that ginger was popular in ancient Greece and Rome, where it was supplied by Arab traders. It is believed that the first gingerbread was made by a Greek baker in about 2500 BC. Romans distributed the crop to different parts of their empire. Description of ginger is noted in the writings of Confucius, the Chinese philosopher, and Dioscorides, the Greek medical expert. Marco Polo also noted the beneficial effects of ginger during his travels in China. In the fifteenth century, Vasco da Gama mentioned ginger in his account of his exploration of the Kerala coast of India.

Ginger is cultivated throughout the world for culinary purposes, though some countries process it as dry ginger. In earlier times, a large quantity of ginger was made into dry ginger by being dipped in slaked lime solution. This was to control contamination and especially infestation. With better drying conditions, storage systems, and transportation, less and less "lime ginger" is made. Sun-dried ginger is the raw material for extractions.

## Plant Material

Ginger is produced by a perennial plant. It has a thin stem and reaches a height of 0.5–1 m. The leaves are narrow with a length of 15–20 cm and breadth of 1.5–2 cm and with a green color. The midrib is somewhat prominent. Its flowers are greenish-yellow in color, generally streaked with purple. Fruits are rarely formed, but when formed, they are a triangular oval capsule bearing a large number of irregular and dark-colored seeds. See Photo 18.

The plant part of commercial interest is the rhizome, which grows under the soil surface. It is thick-lobed, pale yellow, and of irregular shape and size. Several branches of rhizome are referred to as fingers. There are some secondary and occasionally tertiary branches. The root proper grows from the side and underside of the rhizome. Rhizomes have a typical spicy, aromatic flavor. Since the plant has to be pulled out for harvesting of the rhizome, it must be planted each year like an annual.

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**Photo 18.** (A) Ginger field. (B) Uprooted rhizome. (C) From bottom left clockwise: peeled dry ginger, oleoresin ginger, two samples of ginger oil, and fresh ginger. See color insert.

Ginger is grown in different regions of varying geography and climate. This is reflected in the characteristics of the ginger such as size, shape, amount of fiber, juiciness, and flavor. Countries that have excess process it in dry form. The major producers of dry ginger include India, China, Nigeria, Sierra Leone, and Jamaica. Until a few years ago, Jamaican ginger was highly rated. Most of it was lime-treated. However, the total quantity that is produced is so low that it is no longer considered an important commercial variety of dry ginger. India's Cochin ginger is now regarded as a top variety. To facilitate sun drying, the flat sides of the rhizome are scraped with an iron knife. It is a laborious process and the dry ginger obtained is called "peeled ginger." Nigerian ginger is also gaining in popularity. Here, the rhizome is cut longitudinally to make two flat halves, which is known as "split ginger."

Cochin ginger and Nigerian ginger are the most popular raw materials for oil and oleoresin. China has ginger that is thicker and larger, but its flavor is generally considered inferior. However, because of its lower price and the possibility of production in large quantities, it is gaining in importance. Australian ginger has an excellent lemony flavor and so most of it is utilized in fresh condition to produce candied and salted products useful in bakery, confectionery, and other products. Harvesting of this type is also done a little early to obtain a good lemony note.

## Chemistry

Dry ginger has about 8.6% protein, 6.4% fat, 5.9% fiber, minerals, water-soluble vitamins, and vitamin A. While the aroma of ginger is very characteristic, it cannot be attributed to any single compound as in some spices.

The main pungent components are a group of allied compounds known as gingerols (Fig. 56.1). They are three homologues: 6-gingerol, 8-gingerol, and 10-gingerol. Other pungent compounds noted are shogaols, paradols, and zingerone. Connell and coworkers have done pioneering work and have shown that shogaols, paradols, and zingerone can be produced from true gingerols during storage and processing (Connell 1969; Connell and Sutherland 1969). In a series of elegant work, they demonstrated the possibility of converting gingerols into shogaols, paradols, and zingerone. Fresh ginger will have more gingerol, while poorly processed and stored dry ginger will have more shogaols and zingerone. A new component that has been identified in Chinese ginger is zingiberolide (Peng et al. 2007).

## Essential Oil

Considerable work has been carried out regarding the essential oil content of different cultivars from different regions. On an average, dry ginger yields about 2% essential

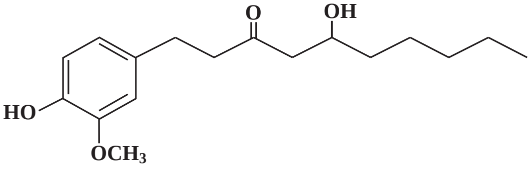

**Figure 56.1.** 6-Gingerol.

oil. It has already been mentioned that the two commercial types that are used for distillation are Cochin ginger from India and Nigerian ginger from Africa.

For commercial production of oil, ginger is coarsely ground using a hammer mill, then flattened by passing through a roller mill. Steam is admitted at low pressure to the ginger packed in a stainless steel still. Depending on the size of the batch, distillation time can vary from 20 to 40 hours. In a tall still, steam distillation of volatiles through a thick bed is time-consuming. Smaller batches require less time. However, the great demand for this spice requires large batches and overnight distillation. On an average, both peeled Cochin and split Nigerian gingers yield around 2% ginger oil.

Ginger oil is light yellow mobile liquid with a warm, spicy aroma. Several monoterpenes, sesquiterpenes, and oxygenated compounds have been reported (Govindarajan 1982). Zingiberene, $\beta$-bisabolene, and *ar*-curcumene can be considered to be major constituents. Others that are present at significant levels are citrals, geraniol, 1,8-cineole, camphene, farnasene, sesquiphellandrene, and $\beta$-phellandrene. Detailed studies have shown a large number of compounds, of which 83% are hydrocarbons, 10% oxygenated derivatives, and the rest unidentified (Lawrence 1984). A typical examination of Cochin ginger oil by GC is presented in Table 56.1. After many attempts to determine the possible contribution of various constituents of ginger aroma, it has been concluded that ginger aroma with a touch of pungency cannot be explained by one or a few compounds. The characteristic aroma of ginger has to be taken as a combined effect of most of its constituents.

Dry ginger and fresh ginger juice obtained on screw pressing have been analyzed (Nirmala et al. 2007). Some minor constituents not previously reported have been found by these authors. Lawrence (2008) has summarized a number of recent analytical studies. He emphasized rightly that pungent constituents such as gingerols and shogaols, being nonvolatile, will not be present in the oil as reported by an investiga-

**Table 56.1.** GC analysis of cochin ginger oil (Rajakumari region)

| Constituent | Area Percentage |
|---|---|
| $\alpha$-Pinene | 0.5–2.0 |
| Camphene | 3.0–6.0 |
| $\beta$-Pinene | <1.0 |
| Myrcene | <1.0 |
| Limonene | 2.0–4.0 |
| Cineole | <0.5 |
| Linalool | 0.5–1.50 |
| Camphor | <0.5 |
| Geraniol | <1.0 |
| Citral | 0.5–1.50 |
| Zingeberene | 35.0–42.0 |
| $\beta$-Bisaboline | 3.0–8.0 |
| Curcumene | 2.0–6.0 |
| $\beta$-Sesquiphellandrene | 14.0–17.0 |

Column Innowax; carrier gas $N_2$; flame ionization detector (FID); temperature 80–220°C.

tor. Those who would like to learn the details of the composition of ginger oil are advised to refer to the review.

According to the FCC, ginger oil is a light yellow to yellow liquid with the aroma characteristic of ginger. It is soluble in most fixed oils and in mineral oil. It is soluble, usually with turbidity, in alcohol but is insoluble in glycerin and in propylene glycol.

Physical characteristics as defined by the FCC are as follows.

| | |
|---|---|
| Optical rotation | –28 to –47° |
| Refractive index | 1.488–1.494 at 20°C |
| Specific gravity | 0.870–0.882 |

## Oleoresin

Oleoresin can be made either through direct extraction or by extracting deoiled material and blending the resin obtained with the required amount of ginger oil obtained earlier by steam distillation. Both acetone and ethylene dichloride are good solvents.

By direct extraction with acetone, Cochin ginger yields about 5–6% oleoresin. When Nigerian ginger is used, the yield is 6–7%. In the export market, there is specific requirement for both. The popular grade of oleoresin has 25–28% v/w of volatile oil content. Under normal circumstances, Nigerian ginger will have a slightly lower price than Cochin ginger, mainly because of slight increase in yield of oleoresin.

Ginger oleoresin is a dark brown viscous product with the characteristic odor of ginger and the typical hot taste. By two-stage extraction, the volatile content can be adjusted to the wide range of 5–40%. The price will be dependent on the oil content.

For special pharmaceutical uses, there is demand for high gingerol content and low shogaol content. Heating during processing increases conversion of gingerol to shogaols. In such cases, processing is carried out at temperatures below 70°C. A typical analysis of ginger for such purposes will give the value for true gingerols above 20% and shogaols below 6%.

As in some other spices, in ginger there is scope for making an absolute. This is carried out by dissolving oleoresin in 95% ethanol and filtering out insolubles. Alcohol-soluble ginger oleoresin is necessary in soft drinks and alcoholic beverages to prevent the formation of turbidity.

## Analytical Methods

Total gingerols can be determined using HPLC separation and adding up the values of all the pungent constituents such as gingerol, shogoals, and zingerone. Paradols will usually be very low. Capsaicin is used as the standard.

Generally, gingerol content is not specified. But for special use in medical preparation, gingerols and shogaols may have to be estimated separately. HPLC separation is carried out using $C_{18}$ column with mobile phase of mixture of acetonitrile (55%), dilute aqueous 0.1% phosphoric acid (44%), and methanol (1%). UV detection is at 282 nm.

## Uses

Ginger as a spice is used all over the world for its special pungency and typical aroma. Most savory foods use it. Ginger is used in bakery products such as gingerbread and biscuits. Similarly, ginger is a favorite ingredient in soft drinks. When conventional foods are made into processed products, ginger oil and oleoresin replace ground ginger. Many meat, seafood, and vegetable preparations, as well as snacks, dressings, and soups, can be flavored by ginger oleoresins. Oleoresins give mild pungency in addition to aroma.

Candied ginger finds use in bakery and confectionery items. Ginger is regarded as a digestive and therefore ginger oleoresin can be used in preparations for this benefit. Gingerol may reduce nausea caused by motion sickness or pregnancy (Ernst and Pittler 2000).

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Ginger oil | 2522 | 8007-08-7<br>84696-15-1 | 182.20 | – |
| Ginger oleoresin | 2523 | 84696-15-1<br>8002-60-6 | 182.20 | – |
| Ginger extract | 2521 | 86696-15-1<br>8007-08-7 | 182.20 | – |

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# 57 Grape

## *Vitus vinifera* L (*Vitaceae*)

### Introduction

Grapes are a popular food item, used as a table fruit; as fruit products such as nonalcoholic beverages, juice concentrates, and jam; and as a fermented alcoholic beverage, wine. Brandy is a distilled alcoholic drink made from wine. When grapes are eaten alone and in preparations like fruit salad, the hard seed is undesirable and so seedless grapes have been developed. When excess fruit is available due to short shelf life, it may be dried and converted into raisins for use in baked products, puddings, and other sweet preparations.

Statistics have shown that French people, despite eating fatty foods, have a lower incidence of heart-related disorders. Researchers have concluded that some antioxidants, mainly resveratrol, present in the grape skin could be the key. This polyphenolic compound is an effective antioxidant and can be positively linked to inhibiting cancer, heart disease, degenerative nerve disorders including Alzheimer's disease, and some viral infections.

The natural food color present in the grape is anthocyanin and is found mostly in the skin of crimson, black, or dark blue grapes. Generally, during wine making, a high percentage of anthocyanin pigment remains in the spent skin after the liquid wine is decanted out. In normal processing for fruit products, skin and seeds are removed so that a homogeneous clear liquid will be obtained. Such skin that comes out as by-products is a good raw material for preparation of anthocyanin-based natural food color.

### Plant Material

Grapes grow on perennial and deciduous woody vines belonging to the genus *Vitis*. This genus has about 60 species that are all vining plants with flowers. *Vitis* plants have petals that are joined at the tip and detach from the base when falling as a cap. The calyx is very small. There are both sterile and fertile flowers. Sterile flowers have five long filaments, erect stamens, and poorly developed pistils. Fertile flowers, on the other hand, have well-formed pistils with five stamen. Four or fewer fruits will be formed from a flower through aborted embryos. The fruits are round and juicy and can be botanically considered to be a true berry. It is a nonclimacteric fruit.

Although in the wild, the grape is generally dioecious, under developmental agriculture, the right variants with bisexual characteristics have been selected. Grapes are cultivated in different regions all around the world. This has resulted in plants of

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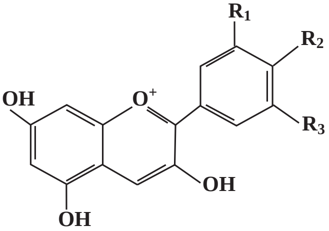

**Figure 57.1.** Anthocyanidins. Pelargonidin: $R_1$ = H, $R_2$ = OH, $R_3$ = H; cyanidin: $R_1$ = OH, $R_2$ = OH, $R_3$ = H; delphinidin: $R_1$ = OH, $R_2$ = OH, $R_3$ = OH; peonidin: $R_1$ = $OCH_3$, $R_2$ = OH, $R_3$ = H; malvidin: $R_1$ = $OCH_3$, $R_2$ = OH, $R_3$ = $OCH_3$; petunidin: $R_1$ = OH, $R_2$ = OH, $R_3$ = $OCH_3$.

different characteristics adapting to the agro-climatic conditions and requirements of the desired fruit quality. The top four grape producers are Italy with 8.52 million tonnes, China with 6.79 million tonnes, the United States with 6.38 million tonnes, and France with 6.04 million tonnes of grapes annually as per the data of the FAO for 2009. Other major producers are Spain, Turkey, Iran, Argentina, Chile, and India.

On a wet basis, the fruit has 18.1% carbohydrate, of which 15.5% is sugar; 0.16% of fat; and 0.72% of proteins. It is rich in B vitamins, ascorbic acid, and minerals. While primary use of the grape is as a fruit and as a raw material for wine making, only the skin of highly colored ones are the raw material for extraction of color.

## Chemistry

Grape colors are anthocyanins, which are glycosides of anthocyanidins. The structure of anthocyanidins is presented in Fig. 57.1. Anthocyanins occur in a dissolved state in the cell sap of flowers, fruits, and other parts and are generally present as glycosides. On boiling with 20% hydrochloric acid for about 3 minutes, anthocyanins become hydrolyzed to yield anthocyanidins and one or more sugar moieties. The most commonly found sugars are glucose, galactose, rhamnose, and, in a few cases, gentibiose and xylose. These are, in the majority of cases, attached to 3 position and, less frequently, the 5 position.

Based on hydroxyl groups, anthocyanidins are pelargonidin, cyanidin, and delphinidin. In addition, methylated derivatives are present. Delphinidin with three hydroxyl groups will have very slight reddish tint, while pelargonidin with only one hydroxyl group will have very slight bluish tint.

The most common anthocyanidins in grape skin are peonidin, malvidin, delphinidin, and petunidin (Leung and Foster 1996). Of these, all except delphinidin are acylated compounds, which are more stable to conditions such as heat, light, and chemical reduction. They are also less affected by changes in pH.

## Extractives

Grape skin anthocyanins are extracted with water or aqueous ethanol; pure alcohol is a very poor solvent. It is stable at the acidic pH of 3. As the pH is increased to neutral and further to 8, the color changes from red to purple and blue.

The blue-black grape variety is the best source for anthocyanins. Generally, while extracting with water, a small percentage of sulfur dioxide helps to prevent fermentation activity caused by natural spoilage of the yeast present in the skin. The aqueous extract separated from solids and concentrated gives a pigment strength of 1% in liquid form (Emerton 2008). Anthocyanins are more stable in acidic pH, generally as a salt of chloride or other ions.

As in most plant products, grapes have minor amounts of leucoanthocyanidins, which on treatment with hot acid become converted to anthocyanidin salt of the acid used. But in the extract, these proanthocyanidins are colorless.

In a recent study, Syrah grapes harvested at different stages showed nine anthocyanins. The total amount of anthocyanins during ripening was significantly higher in conventionally grown grapes than the amount found in organic production (Vian et al. 2006).

In red wine, the pigment concerned is anthocyanin. But on long aging, anthocyanins coming from grapes turn into secondary pigments, which are responsible for the color of old wines (Kennedy 2008). Resveratrol, an antioxidant in grapes, has acquired prominence in recent years. This component is regarded as responsible for the beneficial effect of red wine for many diseases and conditions (Creasy and Creasy 1998).

## Uses

With the rising trend of using natural colors instead of synthetic colors, anthocyanins are useful for giving red-related colors. The pigment is soluble in water and not in fat, and so it is suitable for water-based products. It is stable at acid pH and therefore fruit juice and wine are most suitable for its use. Chilling helps its stability during storage.

Grape extract is used for coloring red-tinted fruit products like black currant drinks, jams, preserves, and yogurt. Sourish products that have an acidic pH, such as boiled sweets, gums, jellies, dry mix desserts, and drink powders, are ideal for using grape anthocyanin colors. Because of their freezing temperatures, ice creams can be colored with grape extract. One of the main uses is in supplementing the color of red wines.

## Analytical Method

The AOAC has a method of determining anthocyanin levels in fruits using paper chromatographic separation, elution, and reading at the maxima for the concerned compound. The maxima of anthocyanins are in the region of 540–560 nm.

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Anthocyanins | – | – | – | 163(i) |
| Grape skin extract | – | – | – | 163(ii) |
| Black currant extract | – | – | – | 163(iii) |

## References

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# 58 Grapefruit

## *Citrus paradisi* Mae fayden (*Rutaceae*)

## Introduction

Grapefruit is a bitter fruit that grows on a subtropical citrus tree. It originated in the Caribbean islands. Although there is a theory that it was a gift from the New World to the Old World, research has shown that it originated in the Old World. It is probably a hybrid of the Jamaican sweet orange (*Citrus sinensis*) and the Indonesian pomelo (*Citrus maxima*). It is believed that Captain Shaddock brought pomelo seeds to Jamaica and bred grapefruit during the eighteenth century. In Barbados, it was first named "forbidden fruit," probably because of bitterness. It is also called Shaddock after its creator. However, the popular and current name "grapefruit" came from the fact that fruit on the tree grows in clusters and often appears similar to grape bunches.

In the present times, grapefruit has become a valuable agricultural product of Barbados. In the early nineteenth century, it was introduced in Florida. Development of the Ruby Red variety in the twentieth century made the fruit an important agricultural product in Texas. The latest is Rio Red, which is promoted as Reddest and Texas' choice.

The major uses of most citrus fruits are as fruit or as a source of fruit juice. Grapefruit have a strong flavor, but it is not widely used in flavoring other food products. The flavor that is obtained is the oil that is extracted from the peel. Thus, the major food product is the fruit itself; the peel oil is a by-product. However, peel oil, being a valuable flavor, contributes substantially to the economy of the citrus industry.

## Plant Material

The tree on which grapefruit grows is large, with a height of up to 10 m. There are numerous cultivars developed by hybridization, so it is difficult to give a brief standard description. The fruits are generally large.

The source of grapefruit essential oil is the rind or peel of the fruit. The diameter of an American grapefruit is between 9.5 and 14.5 cm. In the early days of its cultivation, fruits with seeds such as the Duncan variety were the main type grown in Florida. However, toward the end of the nineteenth century, the marsh Seedless variety was introduced. Both these types are now grown (NIIR Board 2009). Presently, the United States is more than self-sufficient in grapefruit production, compared with earlier years when the fruit was imported from South Africa.

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Oil glands are located deep in the grapefruit peel, which also contains a thick layer of sponge-like albedo.

According to an FAO estimate of 2007, the United States is the main producer of grapefruit with a production figure of 1,580,000 tonnes per year. Other major producers are China (547,000 tonnes), South Africa (430,000 tonnes), Mexico (390,000 tonnes), and Syria (290,000 tonnes). Others, in descending order, are Israel, Turkey, India, Argentina, and Cuba, with production figures ranging from 290,000 to 175,000 tonnes.

## Essential Oil

Grapefruit oil is produced by cold expression. Because of the location of oil cells, that is, deep inside the peel, there is a chance for the spongy albedo to absorb the oil as soon as it is released from the flavedo (NIIR Board 2009). Even with moderate pressure, the yield of oil is low compared with that of an orange or lemon. With screw presses, the yield is only around 0.06%. This is far less than the theoretical yield of 1.25% obtained by steam distillation of the minced peel. But by using special peel press oil, a yield of 0.09% is achievable.

The chemical investigations on the constituents of grapefruit essential oil are rather old, and very few reports have been published in recent years. Leung and Foster (1996) have reviewed the subject excellently and a summary of it is given here. The main constituent is the most characteristic constituent of citrus fruits, limonene. Changes during irradiation have been studied and investigators have found that *d*-limonene and myrcene contents become reduced due to irradiation (Vanamala et al. 2005). In the fruit itself, they found that irradiation helps to preserve flavonoids such as naringin and narirutin. Lycopene content is found to be affected, while $\beta$-carotene is preserved in irradiated lots as compared with the control. Other volatile compounds reported in the grapefruit are sesquiterpenes (cadinene and paradisiol), aldehydes (neral, geranial, perellaldehyde, citronellal, $\alpha$-sinensal, and $\beta$-sinensal), esters (geranyl acetate, neryl acetate, perillyl acetate, octyl acetate, decyl acetate, citronellyl acetate, *trans*-carvyl acetate, 1,8-*p*-menthadien-2-yl acetate, and 1,8-menthadiene-9-yl acetate), and a dicyclic sesquiterpene ketone, nootkatone (Guenther 1949; Leung and Foster 1996). Other components reported are coumarins and furocoumarins (bergaptens). The typical bitterness of the fruit is due to naringin, the bulk of which is present in the peel. The aroma of the grapefruit is caused by nootkatone and esters such as geranyl acetate, neryl acetate, octyl acetate, and 1,8-*p*-menthadien-2-yl acetate (Leung and Foster 1996).

Various alcohols, carbonyls including aldehydes, monoterpenes, and sesquiterpenes have been reported in cold-pressed grapefruit oil (Nagy et al. 1977). One sesquiterpene ketone, nootkatone, is shown to be responsible for grapefruit oil's flavor (MacLeod and Buigues 1964).

Recently, a cyclic acetal of marmin and two cyclic acetals of 6′,7′-dihydroxy bergamotin have been isolated from grapefruit peel oil by Cesar et al. (2009). They also found previously reported compounds of marmin, bergamotin, and dihydroxy bergamotin.

Generally, citrus oil, especially limonene, is affected by oxidation, particularly in the presence of moisture. Moisture alone without air may be endured during storage. Avoidance of air is beneficial in extending storage life, so providing an inert carbon dioxide atmosphere and, to a lesser extent, keeping container full and tightly closed aid in this purpose. Cool storage temperatures are helpful.

As in other citrus oils, removal of terpene hydrocarbons will improve the flavor. Similarly, a naringin-rich fraction will give bitter taste to products, which is welcome in some cases.

Cold-pressed grapefruit oil, according to the FCC, is a yellow and sometimes red liquid, which often shows a flocculent separation of waxy material. It is soluble in most fixed oils and in mineral oil, often with opalescence or cloudiness. It is slightly soluble in propylene glycol and insoluble in glycerin. It may contain suitable antioxidants.

Physical characteristics as defined by the FCC are as follows.

| | |
|---|---|
| Optical rotation | +91° to +96° |
| Refractive index | 1.475–1.478 at 20°C |
| Specific gravity | 0.848–0.856 |

## Uses

Grapefruit essential oil is a valuable citrus oil used in various foods such as baked goods, puddings, candy, and dairy-based desserts. Both alcoholic and nonalcoholic beverages are flavored with the oil. A naringin-rich fraction gives a welcome bitterness, if used in the right proportion, for alcoholic beverages, soft drinks, some special baked products, and even candies.

Grapefruit oil is not injurious to skin and is used in some cosmetics and toiletries.

## Identification Numbers

| | FEMA No. | CAS | US/CFR | E-No. |
|---|---|---|---|---|
| Grapefruit oil, expressed | 2530 | 8016-20-4 | 182.20 | – |
| | | 90045-43-5 | | – |
| Grapefruit oil, terpeneless | | 90045-43-5 | 182.20 | – |

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# 59 Green Leaves

## i) Spinach: *Spinacia oleracea* L (*Amaranthacea*)
## ii) Alfalfa: *Medicago sativa* L (*Fabacea*)
## iii) Mulberry: *Morus alba* L (*Moraceae*)

## Introduction

Chlorophyll, which is present in green leaves, became very important during the early twentieth century when it was used in toothpaste. Chlorophyll toothpaste became quite popular, as chlorophyll was thought of as a way to produce an active oxygen atmosphere in the mouth. Many dental experts felt that bad breath in the mouth is caused by anaerobic bacteria that proliferate in certain conditions. The mouth has plenty of carbon dioxide, from exhaled breath, and water. The argument was if plants can utilize the above two chemicals and produce carbohydrate and active oxygen, the same can be achieved in the mouth if chlorophyll is introduced. However, it was soon found that chlorophyll from toothpaste isolated in the mouth and as a part of a dynamic plant system are two different things. Chlorophyll in toothpaste, however, did achieve success as a pigment, though its stability was poor. This was solved by making copper derivatives, such as copper chlorophyllin, which have a good stability.

The main raw materials for chlorophyll are the green leaves that plants produce in quantity and are generally valued as food or feed.

## Spinach

Spinach was probably first cultivated in Nepal, but the early history of the plant is in the Indian subcontinent. India and Nepal are predominantly vegetarian regions, and spinach, known locally as *palak*, is a valued food item. For this reason, spinach generally commands a good price. Spinach spread to China in the seventh century and to the Arab world in the eleventh century. In the sixteenth century, the plant was introduced to Italy, France, and other regions.

Spinach is rich in iron. This fact made the leaves very popular in the United States, especially after the cartoon character “Popeye” popularized spinach as a food which gives strength.

### *Plant Material*

Spinach is an annual plant, though in very rare cases it can be biennial. It grows to a height of 30 cm. The leaves are alternate, simple, and ovate or triangular. The size of

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leaves can vary from 2 to 30 cm in length and 1–15 cm in breadth. Leaves at the bottom are larger than those at the top. The flowers are yellow-green in color and are small, with a diameter of 3–4 mm, and mature into a small, hard, dry, lumpy cluster, which contains many seeds.

Spinach is rich in various vitamins and some minerals especially iron. There are many varieties of spinach, as it is a favorite food all over the world, mainly for its nutritive value. It is the leaf that is the valuable product.

Recently, a method to produce chlorophyll a from spinach leaves has been developed using solvent extraction and column chromatography. From 100 g of freeze-dried leaves, 23–24 mg of chlorophyll a can be obtained (Dikio and Isabirye 2008).

## Alfalfa

Alfalfa is a flowering plant belonging to the pea family and used as an important forage crop. Its primary use is for the feeding of dairy cattle because of its nutritive value. It is an important legume and is even harvested as hay. It is considered to be a crop that encourages lactation. The tender shoots are sometimes consumed as a leafy vegetable. Like other legumes, its root systems have nodules that house bacteria capable of nitrogen fixing.

### *Plant Material*

Alfalfa is a cool season perennial plant with a life of 3–12 years depending on variety and climate. The plant grows to a height of 1 m. Its deep root system makes it very adaptable in drought conditions. The crop exhibits autotoxicity and is therefore rotated with other plants like corn or wheat.

## Mulberry

Fresh mulberry leaves are eaten by silkworms. In the early twentieth century, silk production ceased in Europe, though it has spread to Asia, in China, India, and Thailand. The Chinese used mulberry leaves a source of chlorophyll, since they are available because of silkworm culture. India also has a thriving silk industry, but production of chlorophyll is somewhat limited. Use of mulberry leaves has brought down the cost of chlorophyll. When silkworms consume the leaves, they metabolize only protein, carbohydrates, and fat. The chlorophyll is excreted out. The excreta yield chlorophyllin with a higher concentration and greater purity. Some Chinese producers have incorporated this into their technology, but the idea of using excreta as raw material is not well accepted. Fresh leaves are the best raw material. Mulberry seems to be replacing other sources, such as spinach and alfalfa, as a cost-effective raw material.

### *Plant Material*

Mulberry is a genus of several species of deciduous tree grown in tropical and subtropical regions of the world, particularly in Asia. The mulberry tree grows very fast at first but growth slows; a height of 10–15 m is attained. The leaves are alternate and simple. They are serrated on the edge and are lobed, more so while young.

The fruit of the mulberry tree is really a multiple fruit which when immature is white, pale yellow, or green, but turns red when ripening and dark purple when fully ripened. The fruits, which are 2–3 cm in length, are edible, sweet, and have a good flavor. The fruit contains anthocyanins, which give its color. There are also white mulberry fruits. Although *Morus alba* is the most common plant, there are several plants in the same genus. Naturally, there are some variations in the description of plant material. It is the leaf that is used as a source of chlorophyll.

## Chlorophyll: Chemistry

Chlorophyll is responsible for the green color of plants, especially the leaves. It helps the plant synthesize carbohydrates by absorbing energy from sunlight. The building units of these carbohydrates are carbon dioxide and water. For this purpose, in the leaf chlorophyll is positioned between layers of lipids and proteins, all of which form the chloroplast. The chloroplast is held close to the cell wall along with some carotenes and xanthophylls.

The German scientist Richard Martin Willstatter won the 1915 Nobel Prize for his pioneering work on chlorophyll's structure and properties. The total synthesis of chlorophyll by Nobel laureate Robert Burns Woodward about 50 years ago was a significant milestone in the history of synthetic organic chemistry. Chlorophyll is a large molecule consisting of tetrapyrrole unit chelated by a magnesium iron placed in the center of the molecule. It has a long side chain phytol esterified to the tetrapyrrole unit. In addition, the central unit has small side groups including a methyl ester and some carbon side chains. There are two types of chlorophyll. In chlorophyll a, R is methyl, while in b, it is an aldehyde group.

This chapter is primarily limited to chlorophyll's use as a food color. For further details of this chemistry and function in photosynthesis, readers are advised to refer to the large number of books and reviews available on the subject.

## Extractives

Chlorophyll extraction reached its zenith during the days when chlorophyll toothpaste was very popular. The earlier raw material of spinach, which is a human food, was replaced by alfalfa, mainly a cattle feed and a cheaper raw material. But with the decline in chlorophyll toothpaste, the pigment lost its purpose. Chinese and, to a limited extent, Indian manufacturers have started making the pigment at a much cheaper price by using mulberry leaves as the starting material.

Chlorophyll extract, being a natural pigment, is approved in the food laws of many countries. A satisfactory extraction solvent is a mixture of acetone and hexane in the ratio of 70:30. Acetone enables the solvent to enter the cells and the mixture can be extracted from dried ground leaves fairly well. Unfortunately, chlorophyll has poor stability. It was in the days of chlorophyll toothpaste that copperization was developed as a way of obtaining stability and intensity of green color. In fact, the present method of making chlorophyll extract is mainly based on the steps developed in the United States in the first half of the twentieth century (Judah 1954). These steps include extraction, saponification, and reaction with copper sulfate to produce copper chlorophyllin.

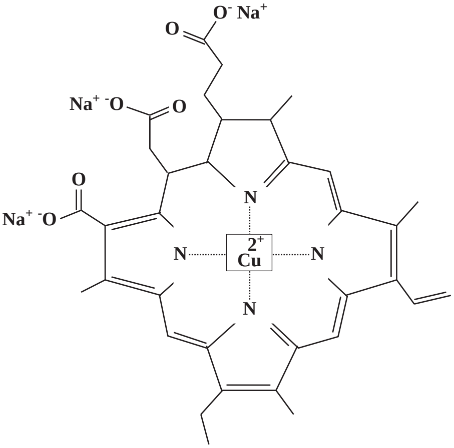

**Figure 59.1.** Chlorophyllin.

A simple, general method of making copper chlorophyllin is given as follows. Dried, cut mulberry leaves are extracted by gravity percolation at ambient temperature using a mixture of acetone and hexane in the ratio 70:30. The combined miscella is desolventized at a temperature not exceeding 60°C to obtain chlorophyll extract.

The extract is saponified using 1 N methanolic potassium hydroxide at 70°C by refluxing for 1 hour. The amount of 1 N alkali used is 75% by weight of the chlorophyll extract. The resultant mass is neutralized with 1 N hydrochloric acid. The neutralized material is made into a copper derivative by stirring well with 5% aqueous copper sulfate. The mixture is kept for 24 hours to complete the reaction. The watery layer is removed to obtain copper chlorophyllin as a deep green, thick mass (Fig. 59.1). This may be washed with water to remove excess free copper.

The result is a dark green, oily liquid with a mild herbaceous odor. The product is soluble in oil. It can be made water-soluble by using additives such as propylene glycol and polysorbate. Chlorophyll, after extraction and saponification, can be made into iron or magnesium chlorophyllin by using ferric chloride or magnesium chloride, respectively. Magnesium treatment is done for the latter because of possible disturbance during saponification.

There are minor variations in the procedure, adopted by different people. In the early U.S. process, there was a provision to recover the xanthophylls that invariably associate with chlorophyll. The Chinese currently recover phytol, which is a raw material for the synthesis of vitamins such as tocopherol and vitamin K.

## Uses

Chlorophyll has a unique natural green color which can be used in foods, especially those which do not need heat treatment, such as ice cream and other chilled food products. Chlorophyll's limitation is its poor stability and low intensity of color.

Copper chlorophyllin has excellent intensity of color and stability. Wherever food laws allow, it can be used as a green color. Copper chlorophyllin is only a seminatural color because of copperization. It has an E-number and is approved for use in the United States. Copper chlorophyllin can be used in food, cosmetics, and toiletries, including toothpaste.

## Analytical Method

Chlorophyll content including that of raw material can be determined by the AOAC method of spectrophotometric measurement after extraction.

For copper chlorophyllin, one method that is used for chlorophyll toothpaste involves mixing the samples with polysorbate 80 so it is in water-soluble form, then measuring the absorbance at 405 wavelength.

$$\text{Chlorophyllin content} = \frac{\text{Absorbance} \times 1000 \times 5}{565 \times \text{weight (g)} \times 2}$$

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Spinach extract | – | 68917-48-6 | – | – |
| Alfalfa extract | 2013 | 84082-36-0 | 182.20 | – |
| Chlorophyll | – | – | – | E140 |
| Copper chlorophyll | – | – | – | E141 |
| Chlorophyll copper complex | – | – | – | E141 (i) |
| Chlorophyll copper complex<br>Sodium and potassium salt | – | – | – | E141 (ii) |

## References

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# 60 Hops

## *Humulus lupulus* L (*Urticaceae*)

## Introduction

Hops are the female flower cluster referred to as cones or strobiles of a plant generally grown in the northern hemisphere. The extract of hops is used as a flavor and stabilizer of beer.

It is believed that over 2000 years ago, Germans began using hops as a beer flavor, an art which they learned from the tribal people of Finland. About 1000 years ago, an Arabian physician claimed that use of hops helps to induce sleep and improve the nervous system. This is a belief still prevalent among some people. Benedictine monks used to cultivate the hops plant to be used as a spice and in salads. Many early Europeans found hops to be a useful vegetable for salads. There are historical records of its cultivation and use in beer in sixteenth-century England. Later, it was introduced to the United States (Farrell 1990).

## Plant Material

The hop plant is a vigorous, climbing, herbaceous perennial usually grown on strings or wires. A commercially cultivated field is called a hop field, hop garden, or hop yard. Although it is sometimes referred to as a vine, the hop plant does not use tendrils or sucker roots to attach itself to the support. It has stout stems with stiff hairs that help it climb on the support. The length of the climber can be as high as 10–15 m, always twisting clockwise on the support, though the height is also dependent on the support that is available.

The peculiarity of the plant is that female and male flowers are borne on separate plants. The female flowers are important for flavoring purposes. Leaves are opposite with a petiole that is 6–12 cm in length. The leaves are palmately lobed blades of 12–25 cm in length. The leaves are broad, with edges which are vaguely toothed. When there is no more support for climbing, horizontal shoots sprout between leaves of the main stem to form a complicated network of stems, which wind around each other.

Because female flowers are important and the plant is vegetatively propagated, the male plants are often cut off if plants are grown using seeds. This way the pollination and seed formation can be avoided. Seed formation is regarded as undesirable for flavoring in beer. Harvesting of female flower cobs is labor-intensive, so today harvesting is done mechanically.

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The major producers of hops in the world are Germany (about 38%), the United States (about 26%), and China (about 12%), of the total annual production of 90,000 tonnes. East European countries, especially the Czech Republic (about 9%), and the United Kingdom and Spain are other producers.

## Varieties

Each variety of hops gives the beer of the region specific organoleptic characteristics. Pale beers of Continental Europe (Germany, Austria, Czech) use “Noble” hop varieties such as Saaz Hallertan, Spalt, and Tettnanger. They give the low bitterness reflected in European beers and are primarily used for their aroma. On the other hand, English varieties such as Fuggle and East Kent have resemblance to Noble hops, but they have better bittering capacity as they age. Recently, seven varieties of hops cultivated in China have been analyzed for $\alpha$-acids, $\beta$-acids, cohumulone, and essential oil composition. Qingdaodahua and Qilinfenglu are bitter varieties, and Yulebite and Fubei-1 are aroma varieties and have better brew qualities (Zhao et al. 1999). Similarly, a wide range of varieties of hops have been analyzed in America. Their specific characteristics are studied with reference to trace compounds and characteristics (Hampton et al. 2002).

## Bitterness and Aroma

Hops have two types of acids which influence the bitterness and aroma they impart to the beer. $\alpha$-Acids contribute to bitterness. They are composed of humulone and the related compounds of cohumulone, adhumulone, prehumulone, and posthumulone. $\beta$-Acids, on the other hand, have lupulone and other allied compounds such as colupulone and adlupulone (Leung and Foster 1996). $\alpha$-Acids isomerize during boiling with wort, making them soluble and capable of making the product bitter. On the other hand, $\beta$-acids do not isomerize during boiling and therefore have a low effect on bitterness. High $\beta$-acid hops are used for their aroma.

There are two types of hops: bitterness-contributing and aroma-contributing. Naturally, bittering hops have a higher $\alpha$-acid content. Noble hops have an $\alpha$-acid content of 5–9%. The newly developed American hops have 8–19% $\alpha$-acids. Aroma hops with very mild bitterness have below 5% $\alpha$-acid and contribute less to bitterness and more toward aroma.

## Essential Oil

Hops generally contain 0.3–1% of volatile oil. Compounds such as humulene, $\alpha$-caryophyllene, myrcene, $\beta$-caryophyllene, and farnesene account for 90% of the essential oil. There are more than 100 compounds that ultimately contribute to the aroma-giving oil (Leung and Foster 1996).

Harvested hops are dried in kilns at a temperature not more than 66°C. When dried, hops will have a moisture content of about 10%. On steam distillation, a green, slightly acrid oil of hops is obtained with a yield of about 0.5% (Farrell 1990). The main constituents are myrcene and humulene, with low amounts of lupelone, xanthohumol, ceryl alcohol, lactaric acid, dipentene, caryophyllene, linalool, and methyl nonyl ketone.

According to the FCC, hops oil is a light yellow to green-yellow liquid with hops' characteristic aromatic odor. On aging, the oil darkens and becomes viscous. It is soluble in most fixed oils and with opalescence in mineral oil. It is practically insoluble in glycerin and in propylene glycol. It is a flavoring oil.

Physical constants as per FCC are as follows.

| | |
|---|---|
| Optical rotation | –2° to –2°5′ |
| Refractive index | 1.470–1.494 at 20°C |
| Specific gravity | 0.825–0.926 |
| Solubility | 1 mL usually is not soluble in 95% alcohol; older oils are less soluble than fresh oil |

## Extract

For convenience of handling, hops are available in extract form. One extraction procedure involves use of pure ethyl alcohol by percolation (Bisnel 1995–2009). The extract, which is rich in lupulin, is then boiled in water for an hour followed by straining and washing. The alcoholic and water extract is freed of the solvent by evaporation at low temperature into thick material.

Supercritical carbon dioxide extract of hops creates characteristics useful for the production of beer. All useful ingredients, such as $\alpha$-acid, $\beta$-acid, and aroma oil are obtained very satisfactorily. One of the advantages of supercritical carbon dioxide extraction is that specificity of extraction can be obtained by manipulating the pressure. Since there are different valuable constituents and some undesirable constituents such as resin, tannins, fats, and waxes, supercritical fluid extraction is especially suited for hops.

## Uses

The main use of hops is to flavor beer. They contribute to bitterness and, in some cases, to aroma. Generally, there are specialized varieties for this. However, dual-use hops are now available.

Hops are also used in some soft drinks, as well as to flavor confectionery, tobacco, baked products, chewing gum, and some pharmaceutical preparations. Hops are also used in herbal medicines as a treatment for anxiety and restlessness. A pillow filled with hops is a popular folk medicine remedy for sleeplessness. Hop shoots are also sometimes used in salads and soups where the bitterness is welcome.

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Hops oil | 2580 | 8007-04-3 | 182.20 | – |
| Hops extract | 2578 | 8060-28-4 | 182.20 | – |
| Hops extract solid | 2579 | 8060-28-4 | 182.20 | – |
| Hops absolute | – | 8060-46-5 | – | – |

## References

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# 61 Hyssop

## *Hyssopus officinalis* L (*Labiatae*)

### Introduction

Hyssop is referred to in many ancient books and therefore must have been a highly regarded herb and medicine. There is mention of it in quotes connected with Moses, Solomon, and Christ. It has been in use in European Mediterranean countries long before Christ. Hyssop is mentioned in the Torah and is believed to have been used in early rituals of the Catholic Church. The name “hyssop” is probably derived from Greek, although it may have Hebrew origins. Hyssop belongs to the mint family and is grown in gardens as a decorative plant.

### Plant Material

Hyssop grows wild in some Mediterranean countries. It is cultivated in Europe, especially in the south of France, as an herb. It is also cultivated in some Middle Eastern countries and Himalayan slopes as a commercial crop.

The plant thrives in light, rich soils of temperate regions. It is propagated by seeds, cuttings, and divisions. It is a hardy evergreen shrub which grows to a height of 60 cm. The leaves are opposite and very narrow and oblong, 2–6 cm long. In the summer, the plant produces purple-blue flowers which are borne on the upper parts of the branches clustered around leaf axils. The herb has a camphor-like spicy aroma and has a bitter but pleasant mint-like taste.

Harvesting is done best on a dry day when the herb has reached full maturity so that it will have the highest oil content and aroma characteristics. The best time for harvesting is just before the flowers open. They should be dried in the shade without delay, so that their flavor is retained. With good air circulation at a temperature below 32°C, the herb should be dried within a week; longer duration may result in a loss of color and aroma.

The herb contains fat, carbohydrates, and polyphenols. It has small amounts of carotene, xanthophylls, and the antioxidant ursolic acid. The fresh herb is reported to contain iodine.

### Essential Oil

The aerial part of the plant, on steam distillation, yields an essential oil. The yield of oil from the dried herb is only 0.3–0.8%.

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Hyssop essential oils of Bulgarian and Italian origins have been recently investigated using GC-MS. Bulgarian oil shows a higher quantity of terpenoids with isopinocamphone and its biogenetic precursor, $\beta$-pinene; camphor; 1,8-cineole; cubenene; and germacrene B. In Italian oil, $\beta$-pinene is a minor component, while safrole derivative and benzyl benzoate are noticeable. Anethole, estragole, caffeic acid methyl ester, eugenol, methyl eugenol, thymol, and carvacrol have been recently detected in hyssop oil (Manitto et al. 2004). In the herb from Iran, both antibacterial properties and mild antioxidant power have been reported (Rastkari et al. 2007). Forty-four compounds have been identified.

There is very little report of production of solvent-extracted oleoresin on a commercial scale.

## Uses

The herb is used in vegetable and meat preparations, as well as cheese spreads. Oil is a convenient replacement in processed foods. Oil is also used in liqueurs and eau de cologne. It has potential for use in soups and salad dressings made commercially.

## Identification Numbers

| | FEMA No. | CAS | US/CFR | E-No. |
|---|---|---|---|---|
| Hyssop oil | 2591 | 8006-83-5<br>84603-66-7 | 182.20 | – |
| Hyssop extract | 2590 | 84603-66-7 | 182.20 | – |

## References

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# 62 Japanese Mint

## *Mentha arvensis* L (*Labiatae*)

### Introduction

The flavor of mint has acquired great popularity in recent times. Its exciting cool feel, refreshing aroma, and fine taste all contribute to make mint a great flavor. But of all varieties of mint, Japanese mint, also known as corn mint, has gained in popularity mainly because of its adaptation and cultivation in Asian countries. In recent years, research laboratories in India have done such extensive work that India has gained the title of world's leading producer. It is useful in making menthol crystals.

The name "mint" or a close variation is prevalent in most European countries. The botanical name *mentha* was probably derived from the Greek name *minthe*. There is mention of mint in the Bible, Arabic literature, and Hebrew writings.

### Plant Materials

The main cultivation of Japanese mint is in Brazil, Argentina, and Paraguay in South America; Japan, China, Thailand, and India in Asia; Angola in Africa; and the United States. The major producers of mint oil now are India, China, Brazil, and the United States.

Mint is a perennial herb with roots running just over and just under the ground (Aktar et al. 1988). There are three subvarieties: one with a purple stem and broad, obtuse leaves; another with a green stem and broad or narrow leaves; and a third with a purple-green stem and narrow leaves. The plants are 60–90 cm in height with branches which are rigid and pubescent. The leaves are lanceolate to oblong with a length of 4–10 cm. The leaves are hairy, with edges sharply toothed and sessile or shortly petiolated. The flowers are minute with a purplish color and arranged in cyme. The calyx is 2.5–3 mm long.

India has recently acquired a near top position in production, mainly by introducing improved hybrid varieties. At the Central Institute for Medicinal and Aromatic Plants, Lucknow developed two varieties, Himalaya and Kosi, which are early-maturing, high-yielding, disease- and pest-resistant, and have a higher content of menthol. Medium to deep soil containing humus is suitable for Japanese mint. While the soil should have a water-retaining quality, waterlogging is discouraged.

In Indian practice, Japanese mint is ready for harvesting after 100–120 days of planting (Aktar et al. 1988). This is when the lowest layer of leaves starts turning yellow. If there is delay in harvesting, there will be loss as the leaves start falling. For

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good yield of oil, the harvesting is best carried out on a bright sunny day. Second and third crops can be taken 80 days after the first harvest. The harvest depends on the health of the plants. But a very good crop can be around 48 tonnes of fresh leaves from each hectare. In good conditions, an average crop can give 20–25 tonnes of fresh herb in three harvests. Fresh herb has an oil content of 0.4–0.7%. A farmer can obtain 75–100 kg of essential oil per hectare under normal conditions.

Mint leaves have their maximum oil content when the plant has just reached the flowering stage. However, in some regions there can be a delay in flowering and in such cases the yellowing of lower leaves can be a good guide for harvesting. The freshly cut aerial part is generally left in the open field for 3–4 hours, if there is good sunshine. Thus, the herb gets partially dried. Dried herb is then made into bundles and shade-dried so that the weight is reduced to 25–33% by escape of moisture. Care should be taken to see that the herb is not overdried by becoming crisp. This latter part of drying should not be done in the sun as the oil will escape in substantial quantities.

The main use of Japanese mint is for steam distillation to produce oil. In India, mint leaves, locally called *pudina*, are often used for culinary purposes as a leafy spice. Chutney made out of mint is very popular as a condiment. *Pudina* is also a popular home remedy for cold and cough.

As has been already mentioned, scientific input from research institutes has made India a main producer of Japanese mint and its oil. About 5 years ago, the quantity of *Mentha arvensis* oil produced in India was estimated to be 14,000 tonnes. Its cultivation was spread over 70,000 ha, giving employment to about 1 million people.

The increase in mint production has been achieved by helping farmers to use cropping patterns of rice-wheat-mint, rice-potato-mint, rice-garlic-mint, and rice-potato-onion-mint. Together with advice on plant protection measures, the system has become quite successful, helping India become a leader in Japanese mint production. Today, Japanese mint oil may perhaps occupy the second position, quantity-wise, among all essential oils, after orange oil.

## Chemistry

Japanese mint, apart from its use in culinary and medical practices, is mainly grown for its essential oil. The main ingredient of the oil is menthol, which is generally isolated as crystals.

Menthol is a soft crystalline material, clear or white in color. It melts at any temperature above room temperature. The structure is presented in Figure 62.1. It

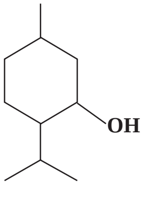

**Figure 62.1.** Menthol.

generally occurs as (–)menthol, which is referred as the α-form. The melting point of α-form is 42–45°C and that of the racemic mixture is 36–38°C. It has a density of 0.890 g/mL. The boiling point is 212°C.

## Essential Oil

Both fresh and dried leaves of *M. arvensis* can be steam-distilled to obtain mint oil. Because they have less bulk, it is cheaper to distill the dry herb. Drying also makes the oil cells weak and more easily allows the entry of steam. The leaves and flowering top give the best yield, at about 2%.

With good steam pressure, the distillation time required is about 2 hours. The amount of time and the subsequent yield depend to some extent on the design of the still. In a large-scale operation, a yield of 75 kg oil is satisfactory from 1 ha. In optimum conditions, following good agricultural practices and avoiding the falling of leaves, a yield of 100 kg oil per hectare is easily achieved. However, it is reported that in China, the productivity is 239 kg from 1 ha, there seems to be scope for improvement.

Improved strains have also resulted in higher yield of oil. From an original yield of 2.5% from dry herb (equivalent to 0.4–0.7% for fresh herb), the yield has risen to nearly double that amount.

The production of Japanese mint oil was only around 1200 tonnes in early 1990s. But more than 10 years later, in 2004–2005, the area of cultivation increased to 70,000 ha and the production of essential oil to 14,000 tonnes.

Japanese mint oil is a clear yellow mobile oil with the typical flavor of menthol associated with peppermint. On inhaling or tasting it gives a welcome cooling sensation. Its physical characteristics are as follows (Prakash 1990).

| | |
|---|---|
| Optical rotation | –33°.0′ to –38°.7′ |
| Refractive index | 1.4578–1.4585 at 20°C |
| Specific gravity | 0.9052–0.9329 at 20°C |
| Solubility | 1 mL dissolves in 2 mL of 70% alcohol |

The main use of *M. arvensis* oil is for manufacture of menthol crystals. Natural oil has over 50% menthol. Most of this can be separated by cooling when menthol in crystalline form separates. The remaining has value as dementholized oil. Research and development has helped many companies to get a high yield of menthol with most of it as large crystals which fetch a higher price. By using precise and optimal conditions, it is possible to get 40–50% as crystals and 50–60% as dementholized mint oil, which can be used in place of peppermint oil for flavoring. The dementholized oil will have a substantial quantity of menthol as well as menthyl acetate, menthone, ketone, and hydrocarbons such as α-pinene, α-*l*-limonene, caryophyllene, and cademene.

In recent years, the oil has been studied using GC and GC-MS. Using GC-MS, the major components found in oil from Central India are menthol (71.40%), *p*-menthone (8.04%), isomenthone (5.4%), and neo-menthol (3.18%) (Pandey et al. 2003). Singh et al. (2005) of the Central Institute of Medicinal and Aromatic Plants, Lucknow, analyzed six cultivars in North India and found a high level of 77.5–89.3% menthol.

They also found 0.3–7.9% of menthone and 3.7–6.1% of isomenthone. A high level of menthol in a cultivar increases its value, since the yield of menthol crystal will be higher.

In a study of cultivars introduced to Bangladesh, Chowdhury et al. (2005) found that the Sivalika variety yields 77% menthol and 11% isomenthone among over 20 compounds found. Another cultivar, CIMAP-77, contains, among 20 compounds, menthol (72.7%), menthone (12.1%), and isomenthone (5.5%) as the major compounds.

## Uses

Japanese mint is used in chutney and as a flavor in a number of Indian vegetable preparations. Its flavor is particularly welcome in tandoori chicken, chicken tikka, and related dishes. For processed foods of this nature, the oil is useful.

Mint flavor is used in a wide range of meats, salads, sauces, and fish dishes. For these, oil is a convenient form to use.

But the greatest use of Japanese mint oil is in candies and confectionery, cookies, chewing gum, ice cream, and jellies. It is also popular as a cigarette flavor because of its cooling effect. For this, menthol crystals are the most useful. After menthol is crystallized, dementholized oil can be used in place of peppermint oil as flavor.

The extractives find use in a number of medicinal preparations such as cough drops, inhalation preparations, vapor rubs, and preparations for stomach disorders.

In China, the herb is made into an infusion and used for its carminative and antispasmodic action. In Ayurvedic medicine, it also has importance. The oil can replace the herb when more complex preparations are made.

## Identification Numbers

| | FEMA No. | CAS | US/CFR | E-No. |
|---|---|---|---|---|
| *M. arvensis* oil | – | 68917-18-0<br>90063-97-1 | – | – |
| Menthol (natural) | 2665 | 2216-51-5 | 172.515 | – |

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# 63 Juniper Berry

## *Juniperus communis* L (*Pinaceae*)

## Introduction

As much as it is now valued as a flavoring material, juniper berry has been historically valued for its medicinal properties. Dioscorides, the Greek physician who wrote an influential book on medicine immediately after Christ, attributed several curative properties to it.

Juniper berries have been discovered in many Egyptian tombs including that of Tutankhamen. The ancient Greeks believed that it improved their performance in Olympic events. Ancient Romans used it in place of black pepper, which had to be obtained from the East at a very high price.

There are several varieties of juniper spices throughout the world. However, only *Juniperus communis* is used as a seasoning in European cookery. It is also probably the only spice produced from a coniferous plant. Besides its use as spice in food, it is also used to give gin its unique flavor.

## Plant Material

The juniper berry is not a true berry in the botanical sense. It is the female seed cone, which has a berry-like appearance. The plant is a low, coniferous evergreen shrub, which usually grows to 1 m. It sometimes attains the height of a small tree. It has a straight trunk with spreading branches, which are covered with shredded-looking bark. The leaves are dirty green colored, straight and rigid, with elongated oval needles with rather sharp points.

The male and female flowers are produced on separate plants, the male in short catkins and the female in short cones. The berry-like fruits have a fleshy outer, usually with a purple-blue color but sometimes with a dark purple or dark blue color. The fruit is 6–10 mm in diameter. There are usually three elongated, oval, bony seeds embedded in the pulp. The fruits ripen in the second year of growth. The dried fruits are the juniper berry of commercial interest (see Photo 19). The plant itself has a woody, resinous odor, while its crushed berries have a gin-like flavor with a bitter aftertaste.

The juniper berry contains about 33% sugars, along with some resinous matter, proteins, wax, pectins, organic acid, and polyphenol glycosides. It has a bitter component, juniperin. It also contains potassium and ascorbic acid. However, its most valuable constituent is its essential oil.

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**Photo 19.** Juniper berry. See color insert.

## Essential Oil

Dried juniper berries contain 2–3% of volatile oil. It is believed that berries from warmer regions have more aroma than those from colder regions.

In commercial steam distillation, the round berries are passed through a roller mill to reduce size efficiently and then are loaded into a stainless steel steam distillation unit. Steam is passed at low pressure and a yield of 3.5% v/w is obtained after 30 hours. The oil is a pale yellow, mobile liquid with a soothing and pleasant odor. Results of analyses of hydrocarbons from several batches of commercially produced oil from Himalayan berries reveal that the hydrocarbons myrcene, limonene, and $\alpha$-pinene are present in reasonable amounts.

The conditions for extraction of the terpene constituents using supercritical carbon dioxide have been determined (Barjaktarovic et al. 2005). Oxygenated compounds require more pressure, as determined after GC-MS examination. GC-MS analysis of the chemical composition of ripe and unripe berries showed interesting results (Butkiene et al. 2004). The major component was found to be $\alpha$-pinene, followed by myrcene and $\alpha$-cadinol. Amounts of $\alpha$-pinene, sabinene, $\beta$-pinene, and bornyl acetate decrease during ripening, while amounts of myrcene, terpinen-4-ol, and $\alpha$-terpineol increase. Column chromatography of steam distillate of Egyptian berries (*Juniperus* *drupacea* L) shows α-pinene, thymol, methyl ether, and camphor as major components (El-Ghorab et al. 2008). Detailed analysis of oils and of supercritical carbon dioxide extract from India, Greece, and Montenegro have been well reviewed (Lawrence 2008). Further work by Butkiene et al. (2005, 2006) on juniper berry oils from Lithuania has revealed more than 100 components.

The FCC describes the oil as a faintly green or yellow liquid with the characteristic odor and aromatic, bitter taste of juniper. It is soluble in most fixed oils and in mineral oil. It is insoluble in glycerin and propylene glycol. The oil tends to polymerize on long storage.

Physical characteristics are as follows.

| | |
|---|---|
| Optical rotation | –15 to 0° |
| Refractive index | 1.474–1.484 at 20°C |
| Specific gravity | 0.854–0.879 |

## Oleoresin

The deoiled material can be extracted with ethylene dichloride or a mixture of hexane and acetone. After distilling off the solvent from miscella, the yield obtained is between 5% and 7%. To this, volatile oil previously collected can be added as per specification. When, after size reduction in a roller mill, the berry is directly extracted, the yield obtained is 9–11% with volatile oil content of 25–35% in the oleoresin. Juniper berry oleoresin is a dark green, viscous liquid with a pleasant odor and mildly bitter and medicinal taste.

Aqueous alcoholic extract of the berry is also in demand as a flavoring material.

## Uses

Juniper berry oil is used for flavoring gin, liqueurs, cordials, and certain liquors. It has value as a fragrance material and for pharmaceutical purposes because of its carminative, diuretic, and antirheumatic properties.

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Juniper berry oil | 2604 | 8002-68-4<br>84603-69-0 | 182.20 | – |
| Juniper extract including $CO_2$ ext. | 2603 | 84603-69-0 | 182.20 | – |
| Juniper absolute | – | 8012-91-7 | – | – |

## References

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# 64 Kokam

## *Garcinia indica* Choisy (*Guttiferae*)

### Introduction

Kokam (also spelled kokum) is a tree that grows in Southwest India, where its sour taste is appreciated. It is used in the preparations of Maharastra, Karnataka, and other nearby regions. In recent years, kokam has attained some importance due to its hydroxycitric acid content. Its flavor is more smooth and its sourness more moderate than that of tamarind. It has an agreeable flavor with a sweetish, acidic taste. It therefore finds use in soft drinks and sweet preparations. However, it has gained international recognition due to the presence of hydroxycitric acid.

### Plant Material

Kokam is a slender evergreen tree with drooping branches (Pruthi 1976). The leaves are ovate to oblong and lanceolate. The normal length of its leaf is 6–9 cm with a breadth 2–4 cm. The color of the upper surface is dark green, while that of the lower surface is slightly paler green. It has spherical or globose fruits generally with a diameter of 2.5–4 cm. The fruits have a dark purple color when fully ripe. It usually has five to eight large seeds. The rind after drying is the source of kokam, which has value in both food and medicine. On drying, the rind assumes a near black color. It is a forest crop rather than a cultivated one.

Dried kokam rind has a sour-sweet flavor and is used in many foods of South India. It has about 10% malic acid and a small amount of tartaric acid. It also has (–)hydroxycitric acid, which has made it a useful raw material in the preparation of weight-reducing products, similar to *Garcinia cambogia*, or Malabar tamarind. For the chemistry of hydroxycitric acid, see Chapter 54 on the garcinia fruit.

The fruit is anthelmintic and cardiotonic. It is believed to be effective in curing piles, dysentery, tumors, and even heart complaints (Pruthi 1976). The seeds of the fruit yield a valuable fat known as kokam butter, which is extracted by boiling the fruit with water and then scooping out the melted fat. The fat has a saponification value of 187–192 and an iodine value of 25–36. The main fatty acids are stearic and oleic. It is used in ointments and other pharmaceutics.

Krishnamurthy et al. (1982b) have found garcinol and isogarcinol in kokam. Garcinol, $C_{38}H_{50}O_6$, has a melting point of 122°C. It has been identified based on UV and IR spectra. Isogarcinol is a colorless isomer of garcinol, which is identified based

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on UV, IR, and NMR spectra. Two anthocyanins based on cyanidin have also been found in kokam (Krishnamurthy et al. 1982a).

## Extract

Kokam has no essential oil; the aqueous extract of the rind is used as the natural flavoring material. The dried fruit can be extracted with boiling water two to four times. The combined extract is strained through a filter cloth. This can be concentrated by boiling in an open stainless steel steam kettle. A thick extract of 60–70° Brix is used for flavoring.

In recent times, the importance of kokam has been as a source of (–)hydroxycitric acid. The garcinia fruit (Malabar tamarind) is a better source, but when the demand is high, kokam extract is also used.

The process involves extraction by hot water (60–70°C), followed by adjustment of the pH to 8–9 using sodium hydroxide and then reaction with calcium chloride solution to gain the calcium derivative of hydroxycitric acid. The precipitated calcium salt is filtered through a basket centrifuge, washed carefully to remove excess chemicals, and dried in a cabinet dryer at 90–100°C. The dried cake is powdered as per the customer's specification.

The hydroxycitric acid content of kokam is lower than that of the Malabar tamarind and therefore adjustments must be made to increase the strength of the active component. The product from kokam is generally a little darker than that from *G. cambogia*. In a way, it is advantageous to use a mixture of both.

As explained in the case of *G. cambogia*, the mechanism of action is similar. (–) Hydroxycitric acid tends to turn into lactone, and to prevent this, calcium or potassium derivative is made. Hydroxycitric acid competes with citrates in the Krebs cycle for the enzyme system so that less acetyl coenzyme A is formed (Majeed et al. 1994). Due to this, fat formation and accumulation of triglycerides are reduced. Thus, the extract of kokam is helpful in controlling weight when consumed in the right form. Specific details about this process are described in Chapter 54 on the garcinia fruit.

## Uses

Aqueous extract of kokam is used for various preparations, including fish curry. It also has a taste that can be pleasant in candies and confectionery. Kokam extract is used as a soft drink in the summer months. The calcium derivative of (–)hydroxycitric acid has value as a weight-reducing supplement.

High antioxidant activity has been noticed (Mishra et al. 2006) and this adds one more positive attribute to its known medical properties when used in cooking, in soft drinks, and in home remedies. The garcinol present in kokam has been confirmed to have antioxidant properties (Sang et al. 2001). Further studies (Sang et al. 2002) have revealed that garcinol, which is a polyisoprenylated benzophenone, has the ability to contribute to chromopreventive activity, although the actual mechanism of its action is unclear. Further study on this aspect of garcinol may be very valuable.

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# 65 Kola Nut

## *Cola acuminata* (Beauv), *C. nitida* (Vent) Schott *et* Endl (*Sterculiaceae*)

## Introduction

Kola, also called "cola," belongs to a family of several trees of the African rainforest. It is related to the cocoa tree. It is a plant product made well known through popular cola-based soft drinks.

In West Africa, the kola nut is used as a masticatory. Since Muslims are forbidden to consume alcohol, kola nuts are an effective substitute for alcohol's mild stimulant properties. In traditional African culture, kola nuts are ceremonially presented to tribal chiefs and important guests. It is believed that chewing the nut prevents hunger pangs, and therefore underfed native workers use it during working hours to overcome fatigue. However, modern-day urban youths consider the chewing of kola to be unsophisticated and the habit has become less and less popular. Continued use of kola for chewing can result in stained teeth. Statistically, there is a high incidence of oral and gastrointestinal cancer among users.

## Plant Material

Kola nuts grow on a tropical tree native to Central and West Africa. The tree was introduced to South America by African laborers. The tree attains a height of around 12 m. The leaves are 15–20 cm in length and appear leathery. It has yellow or sometimes white flowers with red or purple patches. Fruits are of somewhat irregular shape and contain 10–12 seeds with light-colored shells. The dried seed, after removal of the seed coat, is called a nut because of its hard texture.

The dried seed contains alkaloids: caffeine, 1–2%; and theobromine, less than 0.1%. It has catechin type flavan-3-ols, carbohydrates (with a large amount of starch), proteins, and some fat. The nut tastes bitter because of its alkaloids and polyphenols (Leung and Foster 1996).

## Extractives

Kola nuts have no worthwhile essential oil as they are not known for their aroma. Their significant components are nonvolatile and therefore an extract is the sensible option. Procedures used by major soft drink companies are confidential. However, extraction is believed to be carried out by aqueous ethanol so that both polar

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constituents such as polyphenol and nonpolar constituents such as alkaloids can be extracted. A 20% aqueous ethyl alcohol solution gives a satisfactory result for soaking and decanting.

## Uses

Kola nut extracts are widely used in soft drinks. They can also be used in alcoholic drinks, confectionery, and bakery items. Because of its stimulant action, kola extract is also used in energy foods.

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Kola nut extract (*Cola acuminata*) | 2607 | 89997-82-0 | 182.20 | – |
| Kola nut extract (*Cola nitida*) | – | 84696-01-5 | – | – |

## Reference

Leung, Albert Y.; and Foster, Steven. 1996. *Encyclopedia of Common Natural Ingredients*, 2nd edition. New York: John Wiley and Sons, pp. 332–333.

# 66 Large Cardamom

## *Amomum subulatum* Rozhergh (*Zingiberaceae*)

### Introduction

Large cardamom is also known as Sikkim or Nepal cardamom, or “greater cardamom.” It is mostly used in India in Northern and Eastern Indian cookery. Many spices belonging to the same family are grown in different parts of Southeast Asia but are not much used.

### Plant Material

Large cardamom is the fruit of a perennial herbaceous plant. The leafy stem has oblong, lanceolate green leaves that are glabrous on both surfaces. The plants grow along small springs, in marshy places, on shady sides of mountain streams, and along hilly slopes. It thrives at an altitude of 750–1700 m above sea level. The main growing area is in the Himalayan slopes and foothills. Flowers and fruits are produced when plant matures in its third year. Harvesting is done between August and October.

The fruits are dark, 2–3 cm in length, each with 30–50 seeds, which are held together by a thick sugary pulp. The seeds have a taste similar to that of true cardamom (see Chapter 28). The fruit consists of 70% seeds and 30% skin by weight. The seeds contain protein at 6%, starch 43.2%, ash 4%, and volatile oil 2.5–3%.

The capsules used to be dried on a raised bamboo platform with heat generated from firewood burning underneath. This results in a slightly smoky flavor. Today, drying is done without contact with smoke. A room is heated by a series of tin pipes. Flue gas from a burner is pumped through the pipes. In some places, cross-flow electrical dryers are also used.

### Essential Oil

Seeds separated from husk on distillation yield 2.5% v/w of oil. This colorless oil shows optical rotation $[\alpha]^{20}_{D}$ –8.48, refractive index $n^{25}_{D}$ 1.4605, and specific gravity 0.9113. A study carried out with GC-MS showed 16.3% monoterpenes, 75.2% oxygenated monoterpenes, and 6.3% sesquiterpenes. Major constituents are 1,8-cineole 61.31%, $\alpha$-terpineol 7.92%, $\beta$-pinene 8.85%, $\alpha$-pinene 3.79%, and allo-aromadendrene 3.17% (Gurudutt et al. 1996).

A high level of cineole is noted by many workers. This gives the oil a camphoraceous note similar to that of eucalyptus oil. The pericarp (husk) of large cardamom

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yields 0.18% volatile oil in Clevenger hydrodistillation. The oil shows optical rotation of –7°7′, refractive index of 1.4733, and specific gravity 0.9148. GC-MS analysis reveals 37 components representing 98% of the oil. The major compounds are 1,8-cineole (38.7%), $\beta$-pinene (13.6%), $\alpha$-terpineol (12.6%), spathulenol (8.3%), 4-terpineol, germacrene, $\alpha$-pinene, and $\beta$-selinene (Pura Naik et al. 2004).

In commercial production, a full capsule containing seed and husk on steam distillation yields 1.5% oil. GC analysis shows 68–75% cineole, 7–9% $\beta$-pinene, 3–4% $\alpha$-pinene, 0.5–2% myrcene, and less than 0.5% linalool. The structure of 1,8-cineole is given in Chapter 28 on cardamom.

## Oleoresin

There is very limited production of large cardamom oleoresin. The deoiled whole capsule after steam distillation, drying, and extraction with a mixture of hexane and acetone gives a resin with a yield of 1.5%. This is generally blended with a vegetable oil such as sunflower seed oil, mono- and diglyceride, and a requisite quantity of volatile oil to obtain a satisfactory oleoresin. The product is a dark brown oily liquid with an aroma dominated by cineole and a taste typical of large cardamom.

## Uses

Large cardamom is used in a variety of traditional sweet preparations and in some vegetable curries. Some of the candies in which it is used are now made into processed items. In these, both oil and oleoresin blend very well.

## References

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# 67 Lemon

## *Citrus limon* L (*Rutaceae*)

### Introduction

The lemon is a small yellow citrus fruit that is primarily used for its pulp and juice. Lemon juice is rich in citric acid and is therefore quite sour. Although the pulp and juice have good flavor, they are generally not used to flavor other products. The major flavor ingredient is lemon peel oil.

The origin of the lemon is not very clear, although it is presumed that it was first grown in India, northern regions of Myanmar, and some regions of China. It was then brought to Iran and Iraq and, later, to Egypt around AD 700. There is an Arabic treatise about its farming and use as an ornamental tree in gardens. It was commonly used in Arab and Mediterranean countries by the eleventh century AD. It entered Europe around this time through Southern Italy during the time of ancient Rome. The word "lemon" may have originated from *nimbu* in Sanskrit. Arabs and Persians modified it into *limun* and Italians and French to *limone*. Major lemon cultivation in Europe began in the fifteenth century and from there Columbus took it to the Americas.

Lemon juice is made into popular beverages, such as lemonade. Its acid taste is made use of in many confectionary products. Lemon juice is used for the marination of fish and meat. In India, it is a popular base for hot pickles. A slice of lemon (or lime) gives a freshness to alcoholic cocktails.

### Plant Material

Lemons grow on trees that reach a height of 3–6 m. Its twigs usually have sharp thorns. The leaves are alternate with a reddish tint when young, becoming dark green above and light green below when fully mature. They are oblong, elliptical, or long ovate with a length of 6–11 cm. They are finely toothed with thin wings on the petiole. The flowers, which are mildly fragrant, are either singly or clustered in two or three on the leaf axil. Opened flowers have four or five petals, with a white inside and a purplish outside, with 20–40 combined stamens and yellow anthers. The fruits are ovoloid with longer axis, from stem end to tip measuring 7–12 cm. At the tip, there is a nipple-like projection.

The peel is light or bright yellow, sometimes with stripes of green, dotted with oil glands on the surface. The oil in lemon peel contains the most natural flavor. The thickness of the peel is 6–10 mm. Inside the fruit is divided into 8–10 segments full of juicy pulp. Lemons may contain seeds or be seedless.

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## Essential Oil

Lemon oil is produced by expression of the rind in a general process known as cold-pressed oil extraction (NIIR Board 2009). Many years ago, in Sicily, the oil was expressed with handheld devices. The lemon industry consisted of family units spread over the growing regions. Women and children participated by cutting lemons in half and scooping out the inside pulp. Men, sitting on low stools, pressed the oil from the rind into sponges held over mud pots. This sponge process was later replaced by primitive pressing gadgets, though the quality of the oil obtained by manual pressing was regarded as quite good. Subsequently, the simple gadgets were replaced by rotary rasping machines.

In the United States, lemon oil is mainly produced in California. Because of the high cost of labor, the Italian hand-operated method is unsuitable; therefore, more efficient presses were developed. Essentially, the whole fruit is pressed in stainless steel screw presses. As the fruits pass through the tapered screw and expeller, a dispersion of juice, oil, and cell debris comes out. From this, the lighter essential oil is separated by centrifugation from the heavier aqueous juice rich in acid and sugar.

The separation of the two phases should be done without much delay so that the flavor of the oil is unaffected. On long keeping, enzymes become active, resulting in unwanted oxidation and changes in the chemical nature of constituents like citral, a compound important in giving a lemony note to the essential oils.

A better yield of oil is obtained if the rind is minced and steam-distilled to obtain oil. While cold pressing gives a yield of 0.035%, on steam distillation the yield is 0.07%. This low yield for cold pressing is due to the fact that some oil will be trapped in the soft albedo portion of the peel.

The Spanish lemon oil industry also used the manual sponge-pressing method. It was replaced by a method that employed needle puncturing of the oil cells by mechanical means. The oil that oozes out is similar to cold-pressed oil.

Brazil has emerged as a major producer of citrus fruits meant for processing, including lemons. Here the oil is expressed using a mechanical screw press to remove emulsion of oil and juice and then separated by centrifugation.

Recent chemical studies on the constituents of lemon oil are scarce. The subject is briefly reviewed by Leung and Foster (1996). Almost 90% of the oil is made up of monoterpene hydrocarbons, and of this, as much as 70% is made up of limonene, which is a characteristic component of citrus oils. There are lesser amounts of other hydrocarbons, such as $\gamma$-terpinene, $\beta$-pinene, sabinene, $\alpha$-pinene, and myrcene; 2–6% are composed of aldehydes mainly citral. In addition, alcohols such as terpinen-4-ols, $\alpha$-terpineol, and geraniol are noted. Small amounts of sesquiterpenes, in the form of bisabolene, $\alpha$-bergamotene, and caryophyllene, have also been found.

The fine, appealing aroma of lemon oil can be increased by removing the terpene hydrocarbons to create terpeneless oil. Italian lemon oil, on fractional distillation at reduced pressure of 25 mm, yields an enriched fraction representing only 8%, with citral content boosted to over 40%. Similarly, sesquiterpenes are removed at 20 mm pressure, with citral enrichment of 60.5% with a yield of 5.36% (NIIR Board 2009).

Besides better aroma, the advantage of removal of hydrocarbons is better dispersibility in dilute alcohol. This quality is useful when used in soft drinks, where whole oil cannot be dispersed and instead creates a ring of oil floating on top. The removal of hydrocarbons such as limonene is also beneficial in reducing oxidative degeneration of flavor.

The oil obtained from the leaves, petioles, and small twigs of citrus trees is called petitgrain oil. Oil of petitgrain lemon is also produced by steam distillation. The oil has a lemony note caused by citral, which can be present to the extent of 50%. Generally, this oil is used in the fragrance industry rather than in the flavor industry.

According to the FCC, cold-pressed lemon oil (desert type) is a pale to deep yellow or green-yellow liquid with the characteristic odor and taste of fresh lemon peel. Oil is miscible with dehydrated alcohol and with glacial acetic acid. It may contain suitable antioxidants.

Physical characteristics of cold-pressed lemon oil as defined by the FCC are as follows.

| | |
|---|---|
| Optical rotation | +67° to +78° |
| Refractive index | 1.473–1.476 |
| Specific gravity | 0.846–0.851 |
| Solubility | 1 mL dissolves in 3 mL of alcohol, sometimes with haze |

According to the FCC, distilled lemon oil is a colorless to pale yellow liquid with the characteristic odor of fresh lemon peel. It is soluble in most fixed oils, in mineral oil, and in alcohol, though with haze. It is insoluble in glycerin and propylene glycol. It may contain suitable antioxidants.

The physical characteristics of distilled lemon oil given by FCC are as follows.

| | |
|---|---|
| Optical rotation | +55° to +75° |
| Refractive index | 1.470–1.475 at 20°C |
| Specific gravity | 0.842–0.856 |

## Uses

The biggest use of lemon oil is to boost the flavor of lemon-flavored soft drinks and juice-based products such as lemonade. It is a fine flavor for baked products, desserts and puddings, candies, and wide range of sweetened food products. Lemon oil is used in alcoholic beverages such as sweet liqueurs, vermouths, and bitters. For all lemon's uses in food, especially beverages in aqueous media, terpeneless oil is the most valuable.

A lemon note denotes freshness, and based on this, a lemon aroma is desirable in toiletries such as soaps, cleaning products, and polishes. For this purpose, petitgrain oil from leaves and twigs is best suited. Lemon oil is also used in some medicinal preparations to impart a fresh and hygienic aroma.

## Identification Numbers

| | FEMA No. | CAS | US/CFR | E-No. |
|---|---|---|---|---|
| Lemon oil (distilled) | – | 8008-56-8 | 182.20 | – |
| Lemon oil (expressed) | 2625 | 84929-31-7 | 182.20 | – |

## References

Leung, Albert Y.; and Foster, Steven. 1996. *Encyclopedia of Common Natural Ingredients*. New York: John Wiley and Sons, pp. 342–344.

NIIR Board. 2009. *The Complete Technology Book of Essential Oils*. Delhi: Asia Pacific Business Press, pp. 48–69.

# 68 Lemongrass

## *Cymbopogon citratus* (DC) Stapf; *C. flexuosus* (Stend Wats) (*Poaceae; Gramineae*)

## Introduction

There are two types of lemongrass oil, one West Indian (*Cymbopogon citratus*) and the other East Indian (*Cymbopogon flexuosus*). Both are valued as a source of lemongrass oil, which has great value as a low-cost fragrance oil in a number of toiletries.

One of the major uses of lemongrass oil was as a source of citral, from which vitamin A used to be made. Citral is the starting material for making $\beta$-ionone, which is a valuable intermediary for the synthesis of a number of compounds. Now alternate routes for synthesis of products such as vitamin A have been developed, and this has reduced the importance of lemongrass oil. Of the two, the East Indian variety typically yields a much higher level of citral.

Lemongrass as such is used as a spice in Southeast Asian cuisine, especially in that of Thailand, Vietnam, Malaysia, Indonesia, China, and in some parts of India. For this use, the West Indian grass gives a more balanced flavor. Food manufacturers are beginning to realize the utility of lemongrass oil and oleoresin as a flavoring material for processed foods.

## Plant Material

West Indian lemongrass (*C. citratus*) is a tall perennial grass. The plant emits the characteristic aroma of citral. The dense fascicle of leaves starts from the underground rhizome. The blade of the leaf is long and tapering to the top with a length of 90 cm and width of 1.7–2.0 cm. They are glabrous but may be smooth or rough on the upper side and along the edges. The inflorescence spatheate panicle is 30–60 cm long.

The plant thrives in an annual rainfall of 200–250 cm with an average temperature range between 23 and 27°C. The plant is mainly cultivated in the Caribbean islands, Guatemala, and certain parts of Brazil. In Southeast Asia where lemongrass is cultivated for use as a spice, the West Indian type of lemongrass is common.

The East Indian type of lemongrass (*C. flexuosus*) is indigenous to southwest coastal areas of India. Two types of grass are common, red grass and white grass. When the oil was valued for citral content, cultivation was at its height. A considerable amount of lemongrass oil with more than 75% citral content used to be exported from the port of Cochin.

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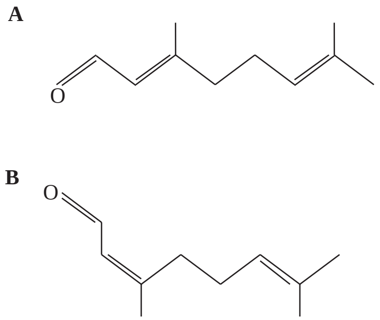

**Figure 68.1.** Citrals. (A) Geranial. (B) Neral.

The plant is an aromatic grass with a height of 2–3 m. The leaves are linear from the rhizome and lanceolate. The length of the leaves is 1–1.5 m with a width of 1.5–2 cm. Panicles are large and drooping, with a gray or grayish-green color, with raceme pairs spreading 1–1.5 m tall, and slightly hairy.

The lemongrass plant thrives in a warm and humid climate with a rainfall of over 250 cm. The plant is hardy and can resist drought up to a point. It grows well in altitudes of 100–1200 m and can tolerate relatively poor soil as is found on hillsides. It primarily grows in the rainy regions of South India. By extension work, the grass has been successfully cultivated in other parts of India.

Systematic research has produced other varieties that can be grown in other less favorable regions of India. *Cymbopogon pendulus* is one such variety.

## Chemistry

The main constituent of the grass is citral. It is a monoterpene aldehyde (Fig. 68.1). The oil from the East Indian variety contains 75–85% citral. The citral content of West Indian oil is 65–80%.

Citral, which is 2,3-dimethyl 2,6-octadienal, occurs in two geometric isomeric forms, geranial (citral A) and neral (citral B).

## Essential Oil

The main constituent of the grass is the essential oil. Because of its low value, it is common for local people to distill oil in crude stills using water distillation. The oil vapor mixed with water vapor passes through a tube to a receiver vessel kept cool by immersion in water, sometimes in the shallow running water of a small stream. Oil is decanted from the top of the still.

In larger production centers, large mild steel vessels are loaded with cut and slightly dried grass, and steam from an external boiler is introduced. These stills are capable of distilling 5–10 tonnes of grass. The vapors are cooled by water condenser and oil is collected in a Florentine flask arrangement. By this method, the yield of oil in the case of East Indian grass will be 0.2–0.4% and, for West Indian grass, 0.1–0.24% on a fresh weight basis.

The main ingredient of lemongrass oil is citral, which accounts for three-fourths of the oil. There are other terpene hydrocarbons. Among the alcohols, linalool, methyl heptanol, $\alpha$-terpineol, geraniol, nerol, farnesol, and citronellol have been reported in West Indian oil. Many volatile acids such as isovaleric, geranic, caprylic, and citronelic have also been noticed (Leung and Foster 1996). East Indian oil has similar constituents. Geraniol-dominated varieties are now being developed, but this oil is primarily used in the fragrance industry.

According to the FCC, East Indian oil is a dark yellow to light brown-red liquid and West Indian light yellow to light brown liquid. Lemongrass oil has a lemon odor and is soluble in mineral oil, freely soluble in propylene glycol, but practically insoluble in water and in glycerin. The East Indian type readily dissolves in alcohol but the West Indian type yields a cloudy solution.

The physical characteristics of lemongrass oil as defined by the FCC are as follows.

| | |
|---|---|
| Optical rotation | −10° to 0° |
| Refractive index | 1.483–1.489 |
| Specific gravity | |
| East Indian | 0.890–0.904 |
| West Indian | 0.869–0.894 |
| Solubility | |
| East Indian | 1 mL dissolves in 3 mL 70% alcohol |
| West Indian | Yields cloudy solution with 70–95% alcohol |

## Oleoresin

Since cut leaves are used as a leafy spice, oleoresin has some demand in the making of processed foods popular in some Asian countries and in the Western world where Asian populations live.

In this author’s lab, commercial extraction is carried out as described. The leaf is cut and sun-dried, giving a yield of 42% dry material with 10–12% moisture. This is pulverized in a hammer mill into a coarse powder, then passed through a roller mill and extracted by gravity percolation in a large stainless steel vessel using a mixture of hexane and acetone (75:25). After the removal of solvent from the miscella, oleoresin is obtained with a yield of 4.3% on dry basis and approximately 1.8% on wet basis. It can be diluted with vegetable oil.

Lemongrass oleoresin is a dark green viscous liquid with the characteristic aroma of lemongrass with a noticeably green flavor. By dilution with sunflower seed oil, the volatile oil content is adjusted between 5% and 10% of the oleoresin.

## Uses

While cut lemongrass is used as a flavoring spice in Asian cuisine, the oil has not been developed into an exact replacement. Oleoresin can serve this purpose. The oil, however, is used in various beverages, some baked goods, and confectionery. It may also find use in herbal tea.

Lemongrass oil has great value as a low-cost fragrance material in some toiletries and cosmetics. The use of the oil as a source of citral to make vitamin A and $\beta$-ionone is decreasing. Citral still has some value as the starting material for the synthesis of some compounds.

## Identification Numbers

| | FEMA No. | CAS | US/CFR | E-No. |
|---|---|---|---|---|
| Lemongrass oil (West Indian) | 2624 | 8007-02-1<br>89998-14-1 | 182.20 | – |
| Lemongrass extract (East Indian) | 2624 | – | – | – |

## Reference

Leung, Albert Y.; and Foster, Steven. 1996. *Encyclopedia of Common Natural Ingredients*. New York: John Wiley and Sons, pp. 344–346.

# 69 Licorice

## *Glycyrrhiza glabra* L (*Papillionaceae*)

## Introduction

Licorice (spelled liquorice in England) is the root of a perennial plant. Its alternate botanical name is *Liquiritia officinalis* L (*Leguminosae*). The root has a sweet constituent. The name licorice is derived from a Greek name meaning "sweet root."

Licorice was used in ancient Egypt, Rome, and Greece as a curative against cough and cold. The great Greek physician Theophrastus remarked that the root has the special property of quenching the thirst if held in the mouth and that it has sweet components that are safe for diabetic patients. Licorice probably originated in China, though among the plants grown in different regions, Chinese plants are the smallest. It is now grown in Central Europe, Turkey, Spain, Russia, and China. Licorice has value in Ayurvedic therapy and is grown in India. It is also used in traditional Chinese medicines. Many attributes such as prevention of stomach ulcers, reduction of low-density cholesterol, reduction of body fat, and control of HIV have been attributed to it, but glycyrrhizic acid, the sweet component, has the harmful effect of increasing blood pressure. In fact, in 2008, the European Commission suggested that intake of glycyrrhizic acid should be restricted to below 100 mg/day to avoid a rise in blood pressure, muscle weakness, chronic fatigue, and lowering of testosterone levels in men. The main use of licorice is as a flavor.

## Plant Material

The licorice plant is a legume, like peas and beans, native to Europe and some parts of Asia. Although anise, star anise, and fennel contain similar flavoring compounds, there is no botanical connection between these and the licorice plant.

It is an herbaceous perennial plant that grows to a height of 1–1.5 m. It has green, spreading, attractive foliage. It has pinnate leaves that droop during the night. Each pinnate leaf has 10–18 leaflets. The flowers, which are about 1 cm long, with pale blue to purple color, are produced in a loose inflorescence. The pod that comes out of the flower is 2–3 cm long containing five to eight seeds. The rhizome has a gray-brown color, and its inside is fibrous. It is the rhizome that gives the sweetness.

## Chemistry

The active component of the licorice rhizome is glycyrrhizin, which is the main sweet compound, being 30–50 times as sweet as sucrose. Chemically, it is a triterpenoid

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saponin glycoside of glycyrrhizic acid. On hydrolysis, it is converted to aglycone, glycyrrhetinic acid, and two molecules of glucoronic acid. Aglycone obtained on hydrolysis is free of sweetness. Although sweet, it is different from sugar. The sweetness of glycyrrhizin is slow to feel but lingers in the mouth for a longer time. It retains sweetness even on heating. It is generally recognized as safe (GRAS) in the United States as a flavor but not as a sweetener. It is used as a flavoring in candies, pharmaceutical, and tobacco products. The European Union advises people not to use more than 100 mg/day. In Japan where there has been a shift to plant-based sweeteners from synthetic sweeteners, it is used especially in combination with another plant-based sweetener, *Stevia*. The Japanese government, however, advises people to limit the usage of glycyrrhizin to 200 mg/day.

The aroma of the licorice plant is caused by a terpene anethole, which is the characteristic flavor of anise oil and star anise (see Chapter 16 on anise).

## Extraction

Licorice products are made from peeled or unpeeled dried rhizome. These are finely cut or powdered for use in teas, capsules, and medicinal tablets, as well as for extracts. To make extracts, roots are boiled in water to obtain a solution of water solubles. The insoluble solids are filtered off. The combined extract is then concentrated by evaporating off the moisture. The heavy, pasty product that results will contain 80–85% soluble solids. This represents 30–40% starch and gums, 16% sugar, and 12–20% glycyrrhizin (Farrell 1990). The concentrated pasty product is further dried under a vacuum or spray dried to a moisture level of below 5%.

The United States imports a large quantity in concentrated extract form usually in stick or solid block forms. Another common form is as concentrated extract, in which the active component is an ammonium salt (Leung and Foster 1996). Some extracts are freed of glycyrrhizin and are known as deglycyrrhizinated licorice (DGL). DGL does not harm adrenal glands or have other unwanted side effects. This is used mainly for medicinal purposes and not for flavoring.

## Analytical Method

The AOAC has a GC method for ammonium glycyrrhizinate and an HPLC method for both free acid and salts.

A reliable and efficient method of analysis is by first converting to aglycone followed by reverse-phase HPLC using C8 column and UV detector (Lauren et al. 2001). This method has a satisfactory recovery in a large number of analyses.

## Uses

Licorice extracts are used in the tobacco industry as a flavor. Licorice contributes a mellow, sweet, woody flavor, which enhances the taste of tobacco. The active component expands airways, enabling smokers to inhale more smoke, though at the same time it generates some of the toxins found in the smoke. It is also used widely in confectioneries. The extract and glycyrrhizin, both as such and in ammoniated form, are used in licorice candy where anise oil is also often used for better effect. The above are also used in alcoholic beverages such as beer, nonalcoholic beverages such as root beer, frozen dairy desserts, and meat products. Its sweet aftertaste is desisted in some soft drinks and herbal teas, and to disguise the unpleasant flavors of medical preparations. In Chinese cuisine, the rhizome flavor is used in savory products.

Ayurvedic therapy and Chinese medicine both recognize the medicinal qualities of licorice. It is an expectorant and is sometimes used in cough syrups. While it has many beneficial medicinal qualities, its negative effect on blood pressure should be kept in mind.

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Licorice extract | 2628 | 97676-23-8<br>84775-66-6 | 184.1408 | – |
| Licorice extract powder | 2629 | 68916-91-6<br>84775-66-6 | 184.1408 | – |

## References

Farrell, T. Kenneth. 1990. *Spices, Condiments and Seasonings*, 2nd edition. New York: Chapman and Hall, pp. 121–123.

Lauren, Denis R.; Jensen, Dwayne J.; Douglas, James A.; and Follett, John M. 2001. Efficient method for determining the glycyrrhizin content of fresh and dried root and root extracts of *Glycyrrhiza* species. *Phytochem. Anal.* **12** (5), 332–335.

Leung, Albert Y.; and Foster, Steven. 1996. *Encyclopedia of Common Natural Ingredients*, 2nd edition. New York: John Wiley and Sons, pp. 346–350.

# 70 Lime

## *Citrus aurantifolia* (Christm) Swingle (*Rutaceae*)

## Introduction

Limes are small citrus fruits with green or greenish yellow skin and flesh. Well-known varieties of limes are sour, being rich in citric acid, although sweet limes are also available. Sour limes have more sugar and citric acid than lemons and therefore have a tart taste. Sweet limes have less citric acid and taste sweeter. Limes originated in the Himalayan region of India.

The lime became important during the early days of exploration, when British sailors were prone to scurvy, which was identified as caused by a deficiency of vitamin C, or ascorbic acid. This was prevented by a daily ration of lime. While it was a satisfactory solution to the problem, it also led to the nickname of “limey” for all British people.

While lime juice is an important food flavoring material, for other food items it is the peel’s essential oil that is the important flavoring material.

## Plant Material

The lime tree is an evergreen tree that grows to a height of 4–6 m. It has sharp spines. Lime leaves have some characteristic flavor and are therefore used in Southeast Asia as an herb in cooking. West Indian trees are small and bushy, with fine twigs and small leaves. Tahitian and Persian trees are larger and more spreading. The twigs are coarser and almost free of thorns. The fruits are larger, with transverse diameter of 5–6 cm and longitudinal diameter of 6–7.5 cm. The rind is thin and smooth. The average diameter of an American lime is 3.8–5 cm; the transverse diameter is 3–6 cm.

Most production figures available are for limes and lemons combined, as in many places the two are considered together since their uses are similar. In India, both lemon and lime are used for making hot pickles. Excepting major branded items, even in soft drinks there is no strict differentiation. In household cooking and in use as fresh flavoring for alcoholic beverages, not much attention is paid to whether a lime or lemon is used. India accounts for 16% of the world’s overall production of lime and lemon, followed by Mexico (14.5%), Argentina (10%), Brazil (8%), and Spain (7%).

## Essential Oil

When the skin of a fresh fruit is punctured, oil oozes out on the application of some pressure. This is cold-pressed lime oil. When juice is expressed, some peel oil gets

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mixed with the juice due to the pressure. Since the density of essential oil is lower than that of aqueous juice rich in citric acid and sugar, these can be separated by centrifuging. Usually, both of these are obtained during processing. Cold-pressed oil is removed first. The remnant is then pressed to express the juice and remaining essential oil. However, since it is mixed with the juice and is then separated, the oil may not be as clear as the initial cold-pressed fraction. In some processing plants, there may be no separation of cold-pressed oil or facility to centrifuge. In such places, after the juice is extracted, the rind along with the spent inner pulp is kept aside. This is then taken for steam distillation to obtain steam-distilled lime oil. In fact, a large portion of lime oil is obtained by this method. Mexico, the West Indies, and India are producers of distilled oil. In fact, terpeneless distilled oil is produced from this type of oil.

In the West Indies, much oil is produced by hand processing by what is known as ecuelling method. The simple equipment for this consists of a shallow bowl usually made of copper with a central tube leading downward from the center of the bowl. The bowl is provided with projecting blunt short nails. When the fresh fruits are rolled over this by hand applying some pressure, the oil cells break, making it possible for oil to ooze out and be collected through the central tube to a collection vessel kept below. The oil floats on the aqueous phase and can be decanted. This is labor-intensive work and not particularly hygienic. Moreover, the process yields only about 20% of the theoretical yield. This accounts for about 0.1% of the fruit of average quality.

Generally, machines using expression meant for lemons are not very suitable for limes, which have a thin rind. Eventually, suitable machines for the cold pressing of limes were developed by modifying machines originally meant for lemons and oranges. These are used in Mexico. The entire fruit is crushed, pulp is separated on a strainer, and oil separated from clear juice in a high-speed centrifuge (NIIR Board 2009).

However, only a small amount of oil is separated by this method. A large amount of limes are processed for juice and the spent peel is subjected to steam distillation to obtain distilled oil. In India, only large processors use the cold-pressing method of obtaining oil. In other cases, the fruit is minced by hand-operated or mechanical machines. From the pulpy mixture, oil is recovered by steam distillation.

The cold-pressed oil has a superior flavor quality compared with distilled oil. It is therefore a practice in some places to dilute the cold-pressed oil with some distilled oil to reduce its cost. The major producers of distilled oil are the West Indies and Mexico.

Distilled lime oil, like other citrus oils, is rich in monoterpene hydrocarbons, which account for about 75%. This is mainly represented by limonene, along with small quantities of other monoterpene hydrocarbons. Oxygenated constituents include citral, $\alpha$-terpineol, 1,8-cineole, 1,4-cineole, linalool, and fenchol (Leung and Foster 1996). There are also sesquiterpenes such as bergamotene, $\beta$-caryophyllene, and $\beta$-bisabolene. Lime oil contains 0.35% of germacrene B, whose sweet, woody-spicy, geranium-like aroma distinguishes lime oil from lemon oil. Lime peel oil from Bangladesh obtained by hydrodistillation on GC-MS analysis revealed 44 compounds, with citral (18.3%), limonene (39.6%), $\beta$-pinene (18.7%), and sabinene (5.1%) as the major constituents (Chowdhury et al. 2006).

The composition of cold-pressed oil is similar to that of distilled lime oil, but is generally free of the degradation product *p*-cymene. It also contains anthranilates and some substituted coumarins (Leung and Foster 1996).

According to the FCC, cold-pressed lime oil is a yellow, brown-green, or green liquid, often showing a waxy separation, and has fresh lime odor. It is soluble in most fixed oils and in mineral oil but is insoluble in glycerin and in propylene glycol. It may contain suitable antioxidants.

Physical characteristics as defined by the FCC are as follows.

| | Mexican type | Tahitian type |
|---|---|---|
| Optical rotation | +35° to +41° | +38° to +53° |
| Refractive index | 1.482–1.486 | 1.476–1.486 |
| Specific gravity | 0.872–0.881 | 0.858–0.876 |

The FCC describes distilled lime oil as a colorless to green-yellow liquid with a mild citrusy and floral odor. It is soluble in most fixed oils and in mineral oil but is insoluble in glycerin and in propylene glycol. It may contain suitable antioxidants.

Physical characteristics as defined by the FCC are as follows.

| | |
|---|---|
| Optical rotation | +34° to +47° |
| Refractive index | 1.474–1.477 at 20°C |
| Specific gravity | 0.855–0.863 |
| Solubility | 1 mL dissolves in 5 mL of 90% alcohol |

## Uses

In the cuisine of Mexico, the Southwest United States, and Thailand, in particular, lime is valued for both its acidity and flavor. It is used for making hot pickles in Asian countries.

Lime oil is highly valued in soft drinks. Distilled oil, cold-pressed oil, and deterpenated oils are all used for this purpose. Additionally, lemon-lime flavor is highly valued in alcoholic beverages, candies, baked items, and meat products.

The citrus flavor represents freshness and, as such, lime oil is used in toiletries, cleaning lotions, and pharmaceutical preparations to give a good aroma.

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Lime oil, expressed | 2631 | 8008-26-2 | 182.20 | – |
| | | 90063-52-8 | – | |
| Lime oil, expressed, terpeneless | 2632 | 68916-84-7 | 182.20 | – |
| Lime oil, distilled | – | 8008-26-2 | 182.20 | – |

## References

Chowdhury, Jasim Uddin; Nandi, Nemai Chandra; and Uddin, Minhaj. 2006. Aromatic plants of Bangladesh: chemical constituents of the leaf and peel oil of *Citrus aurantifolia* (Christ) Swingle. *Indian Perfumer* **50** (2), 54–55.

Leung, Albert Y.; and Foster, Steven. 1996. *Encyclopedia of Common Natural Ingredients*. New York: John Wiley and Sons, pp. 352–354.

NIIR Board. 2009. *The Complete Technology Book of Essential Oils*. Delhi: Asia Pacific Business Press, pp. 189–215.

# 71 Long Pepper

## *Piper longum* L (*Piperaceae*)

## Introduction

Long pepper was recognized in Greece well before Christ; Hippocrates described it more as a medical plant than a spice. Historians might have confused black pepper and long pepper. It was recognized as a spice in ancient Europe before the discovery of the New World, although Pliny erroneously classified both black pepper and long pepper as originating from the same plant. However, in the first book of botany, Theophrastus clearly distinguished them. With the advent of red pepper (chili), the importance of long pepper declined. With improved processing and marketing of black pepper, long pepper was slowly sidelined. While it still plays a part in Asian cuisine, in the Western world it is almost a forgotten spice. Surprisingly, long pepper still has a place in Islamic North African cuisine, where it was introduced by Arab traders operating in the East.

## Plant Material

The long pepper plant is a slender, aromatic climber seen in evergreen forests. It is also cultivated, since it has more uses than simply as a spice. Like black pepper, there is rooting at nodes and attachment to the support tree. Although long pepper is similar to black pepper, the plant is not as high. The branches are erect and slightly swollen at nodes. The leaves are alternate, the lower ones broadly ovate and the upper ones more oblong. The leaves are thinner than those of black pepper and show mild heat when chewed. The flowers appear in solitary spikes (Warrier 1995). Its fruits are berries, small but completely buried in the fleshy spike, unlike those of black pepper where bigger berries are attached to the spike only at the stalk end. The berries are green but turn red when ripe and black when dried, as in the case of black pepper.

The dried spikes (see Photo 20) are acrid, as well as being mildly thermogenic, carminative, expectorative, laxative, and digestive. Thus, it finds use in the treatment of a wide range of diseases in Ayurvedic therapy. The plant is cultivated in different parts of India.

## Essential Oil

Dried long pepper, on size reduction and steam distillation, gives an essential oil with 0.7% yield (Pruthi 1976). It has a spicy aroma resembling that of pepper oil and ginger

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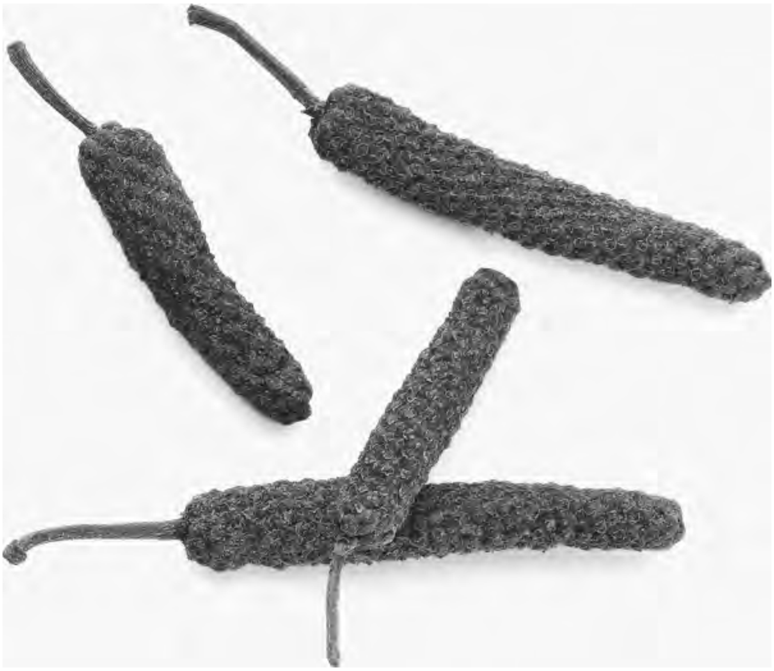

**Photo 20.** Dried spike of long pepper. See color insert.

oil. It shows optical rotation of 40°1′, refractive index of 1.4769, and specific gravity of 0.8484.

## Oleoresin

This author's lab has obtained a volatile oil yield of 0.8–1.4%. Extraction of deoiled spice with a mixture of hexane and acetone gives a resin fraction with a yield of 6–7%. When volatile oil is added, the oleoresin gives an overall yield of 6.8–8.4%. The oleoresin has a volatile oil content of 6–16% and a piperine content of 1.8–2.5%.

The oleoresin is a greenish-brown, oily liquid with a mild herbal aroma and a weak and delayed hot taste. When it is kept for some time on the tongue, there is a feeling of slight numbness. The oleoresin can be diluted with vegetable oil or glyceryl monooleate.

## Uses

Long pepper and its extractives can be used in food when only mild hotness is required. Today, very little is used in food as flavor. However, long pepper retains its use in medicine. The berries are effective for treatment of diseases of the respiratory tract, as a counterirritant and analgesic for applying locally for muscular pain and inflammation, and, taken internally, as a carminative and general tonic. In Ayurvedic therapy, a mixture of black pepper, ginger, and long pepper forms *trikatu* (Sankrit for "three acids"), which is used as a rejuvenating medicine.

## Reference

Pruthi, J.S. 1976. *Spices and Condiments*. New Delhi: National Book Trust, pp. 189–191.

Warrier, P.K. 1995. *Indian Medicinal Plants*, vol. 4. Madras: Orient Longman, pp. 290–296.

# 72 Lovage

## *Levisticum officinale* L. Koch; *Angelica levinticum* Baillon (*Umbelliferae*)

### Introduction

Lovage may have originated in China. Phoenicians and, later, Greeks and Romans, used it before Christ not only as a flavor but also as a medicine and in cosmetics. It probably thrived first in Mediterranean Europe and later in England where, as garden lovage, it is still cultivated occasionally for its medicinally useful root and, to a lesser extent, for its leaves and seeds. It has a coloring component that adds a crimson color to water or alcohol but turns blue if made alkaline. Lovage was a household medicinal remedy a few centuries ago but was also valued for its fine aroma. An infusion of lovage has antiseptic properties when applied to wounds and is also a weak antidote to indigestion.

### Plant Material

Lovage is a tall perennial plant, which resembles the angelica plant. Its cylindrical hollow stem grows to a height of 2–3 m. It has bright green leaves, which grow alternately. It has thick fleshy roots, resembling somewhat those of the carrot, but with a gray-brown outside color and white inside. The plant has terminal light yellow flowers growing in clusters. It has small, oval, yellow to brown seeds.

Growing of lovage is trouble-free. Propagation is either by division of roots or by seeds. Rich and moist but well-drained soil and sunny weather are ideal. Almost the entire plant has use. Roots, leaves, and seeds have value in medicine. The young stem, almost like angelica, has an aroma and some use as a flavoring material. Its fruit, often referred to as seed after drying, and leaves have value as flavor. The dried fruits, used as a spice, are often confused with ajwain. The stem is sometimes used like celery for salad.

It is the root that is important as a spice and for making essential oil. Freshly dug cut roots are washed, sliced to 1–1.3 cm thickness, and carefully dried. If oven-dried, the temperature should be 50–55°C.

### Essential Oil

The literature on the components of lovage root oil is somewhat sketchy. Terpineol is the major component (Farrell 1990). It is present to the extent of 0.3–1.0%. A very

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old analysis of herb oil from France gives the physical characteristics as follows (Guenther 1950).

| | |
|---|---|
| Optical rotation | +0°40′ to +1°20′ |
| Refractive index | 1.5502–1.5591 at 20°C |
| Specific gravity | 1.034–1.057 |
| Solubility | 1 mL dissolves in 1–2 mL 80% alcohol |

According to the FCC, lovage oil obtained from the lovage root has a yellowish-greenish-brown to deep brown color and the characteristic aromatic odor and taste of lovage. It is soluble in most fixed oils and slightly soluble, with opalescence, in mineral oil. It is relatively insoluble in glycerin and propylene glycol. The oil becomes darker and more viscous under the influence of air and light.

Its physical characteristics as defined by the FCC are as follows.

| | |
|---|---|
| Optical rotation | –1° to +5° |
| Refractive index | 1.536–1.554 at 20°C |
| Specific gravity | 1.030–1.057 |
| Solubility | 1 mL dissolves in 4 mL of 95% alcohol, sometimes with slight turbidity |

There is very little production of oleoresin. Because of the medicinal properties of its nonvolatile constituents, oleoresin would be a convenient form for use as a food flavoring. Additionally, there is report of the presence of coloring components, which give a crimson-red color to alcohol extract.

## Uses

Lovage extractives have potential for use in processed foods such as soup, baked goods, cheese spreads, and sauces. It is a minor component of flavoring used for tobacco, liqueurs, cordials, confectionary, and medicinal preparations. It is effective in pharmaceutical preparations for stimulating secretion of gastric juice and for reducing salt in body fluids (Farrell 1990).

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Lovage root oil | 2651 | 8016-31-7<br>84837-06-9 | 172.510 | – |
| Lovage extract | 2650 | 8016-31-7 | 172.510 | – |
| Lovage leaf oil | – | 8016-31-7 | – | – |

## References

Farrell, Kenneth T. 1990. *Spices, Condiments and Seasonings*, 2nd edition. New York: Chapman and Hall, pp. 124–126.

Guenther, Ernest. 1950. *The Essential Oils*. Malabar, FL: Robert Krieger Publishing, vol. 4, pp. 649–654.

# 73 Mace

## *Myristica fragrans* H (*Myristicaceae*)

## Introduction

The nutmeg tree yields mace, which is a bright red lacey cage covering the nutmeg shell. Its history is intertwined with that of nutmeg.

## Plant Material

Since mace is derived from the tree that produces nutmeg, the details about the plant are the same as those for nutmeg (see Chapter 78 on nutmeg). The distribution is also the same as that of nutmeg and therefore these details are not repeated.

Mace is the soft, reticulated aril of nutmeg. It has a bright scarlet color and very delicate flavor, though it is somewhat similar to nutmeg. The size of the thin, broken aril is dependent on the size of the round nutmeg. Nutmeg, being a round kernel, needs long hours of sun drying. Color is not important in the case of nutmeg. Mace, being thin and soft, needs delicate handling and drying. It is this need for different handling that has caused the two to be considered as separate spices.

The different grades of mace are: top quality, bright orange-colored “Banda mace”; next in quality, “Java estate mace” which is golden yellow with streaks of red; next, “Siauwa mace,” with lighter color and less aroma; and the lowest grade, “Papua mace.” There are also some lower grades derived from other *Myristica* spices.

The dry yield of mace is only about 3.5% of the nutmeg. Besides the delicate aroma and exotic color, the low yield is a factor in making mace a costlier spice than nutmeg.

## Chemistry

Dry mace has 6.5% protein, 48% carbohydrate, 4% crude fiber, and 24.5% extractables, mainly consisting of triglycerides and essential oil. As in nutmeg, myristicine is the important oxygenated terpene. Water-soluble matter includes leucocyanidin. The fat-soluble color is identified as lycopene, similar to that present in the tomato (Gopalakrishnan et al. 1979).

## Essential Oil

On steam distillation, dry mace gives an essential oil with yield of 8–9% for Sri Lankan and Indonesian samples. Indian mace generally gives a lower yield of 6%.

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**Table 73.1.** Composition of mace oil from Indonesia and Sri Lanka

| **Constituent** | **Mace Oil (Area %)** | |
|---|---|---|
| | **Indonesia** | **Sri Lanka** |
| $\alpha$-Thujene | 3–5 | 3–5 |
| $\alpha$-Pinene | 15–22 | 15–20 |
| Sabinene + $\beta$-pinene | 25–35 | 30–40 |
| $\delta$-3-Carene | 3–5 | 3–5 |
| Limonene | 3–5 | 3–5 |
| *p*-Cymene | 0.5–1.5 | 1–2 |
| $\beta$-Phyllandrene | 2–4 | 2–4 |
| $\alpha$-Terpinene | 5–9 | 4–8 |
| Terpinen-4-ol | 3–6 | 3–5 |
| Safrole | 2–3 | 0.5–1.5 |
| Myristicine | 6–10 | 4–6 |
| Elimicine | <0.5 | 2–4 |

The average composition of Indonesian and Sri Lankan mace oil is presented in Table 73.1. Generally, mace oil is believed to be richer in myristicine, but tests do not substantiate this. Terpene hydrocarbons, pinenes, and sabinene are present at high levels. Because of lower yield and brighter color, it is understandable that mace is costlier than nutmeg. Regarding the essential oil, the difference between mace oil and nutmeg oil is sometimes difficult to tell, though in a recent study, mace oil shows 32.68% myristicine while there is only 13.58% in nutmeg oil. There are also differences in the large number of compounds identified (Malik et al 2002).

As per the FCC description, mace oil is a colorless or pale yellow liquid with the characteristic odor and taste of nutmeg. It is soluble in most fixed oils and in mineral oil, but it is insoluble in glycerin and propylene glycol.

Its physical characteristics as defined by the FCC are as follows.

| | East Indian type | West Indian type |
|---|---|---|
| Optical rotation | +2 to +30° | +20 to +30° |
| Refractive index | 1.474–1.488 | 1.469–1.480 at 20°C |
| Specific gravity | 0.880–0.930 | 0.854–0.880 |
| Solubility | 1 mL dissolves in 4 mL 90% alcohol | |

## Oleoresin

Deoiled mace can be extracted with hexane to obtain the resin, which is mainly triglycerides. All the same, a very small quantity of undistilled high boilers such as sesquiterpenes and oxygenated derivative may be extracted, thus adding value. The resin yield will be as much as 15% without considering oil. The oil content of oleoresin is as per customers' specification and, accordingly, the required quantity of mace oil is added. Because of closeness of analysis and organoleptic characteristics, it is not uncommon to add some quantity of nutmeg oil to mace oil.

## Uses

Like nutmeg oil, mace oil is regarded as an essential baking oil. It is used in all foods where nutmeg oil is used. Mace oil is generally used in more expensive products because of its more delicate flavor. Oleoresin gives a more rounded flavor, especially where much heating is involved.

Mace, like nutmeg, is used in Ayurvedic therapy. For such products, oil will be useful if more refined preparations are to be made.

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Mace oil | 2653 | 8007-12-3<br>84082-68-8 | 182.20 | – |
| Mace oleoresin/extract (including $CO_2$ extract) | 2654 | 8007-12-3 | 182.20 | – |

## References

Gopalakrishnan M.; Rajaraman, K.; and Mathew, A.G. 1979. Identification of mace pigment. *J. Food Sci. Technol.* **16** (6), 261.

Malik, M. Shafiq; Jasra, Abdul Basit; Khan, Javed Iqbal; and Ahmed, Rafi. 2002. Studies on the chemical composition of essential oils of mace and fruit kernel from *Myristica fragrans*. *Proc. Pak. Acad. Sci.* **39** (1), 79–82.

# 74 Mandarin

## *Citrus reticulata* Blanco (*Rutaceae*)

### Introduction

Mandarin oranges are a variety of orange that has a loose peel, popularly referred to as “loose jacket” to distinguish it from the “tight jacket,” of a normal orange, which has a peel that tightly adheres to the flesh. It is also referred to as “kid glove orange.” *Citrus reticulata* Blanco is synonymous with *Citrus nobilis* var. deliciosa Swingle. Mandarin (also spelled mandarine) is a sweet fruit with red-orange skin. In the Philippines, such oranges are named *naranjita*, while Latin Americans call them *mandarina*.

Mandarin oranges are believed to be native to Southeastern Asia, in countries like the Philippines, Japan, Southern China, India, and Indonesia. Although they were cultivated in China 3000 years ago, they came to Europe only in the nineteenth century, and a little later to North America.

In the United States, such oranges are called tangerines. While the terms “mandarin” and “tangerine” are sometimes used interchangeably, the distinctiveness of the two oils is maintained by some experts.

Removal of the segments from these oranges is as easy as removing the peel. It is a fruit used very much as a table variety and in salads, generally after removing the pale, thin skin of the segments. Segments are also canned in syrup after deskinning.

There are many varieties that are popular in different places in the world. However, only the peel oil can become a flavor, which can be used in other foods to improve the organoleptic quality.

### Plant Material

The mandarin orange tree is generally smaller than that of sweet orange. With age it may reach a height of 7–8 m, with a wide spread of branches and leaves. The tree usually has thorns, but its twigs are slender. The leaves may be thin or broad. It has lanceolate leaves with minute, rounded, serrate edge and petiole with narrow wings. The flowers are borne singly or in small group in the leaf axis.

The fruits are oblate, with peels which are bright orange to red in color. The peel is loose and easy to remove with one’s hands. The segments can be separated easily without the squirting of juice. Its seeds are small and slightly elongated but pointed at one end. The inside of the seed is greenish in color. The transverse diameter of an American tangerine orange ranges between 5 and 7.5 cm.

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Mandarins are more cold-hardy compared with sweet oranges, and the tree is more tolerant to drought conditions. However, fruits are tender and easily damaged. Mandarins have several disadvantages for commercial exploitation. The fruits do not have a great capacity to hold on the tree. In addition, the rind is delicate and therefore there is more risk of damage during transporting. The tree generally has a tendency for bearing on alternate years, making yield in a region unpredictable. The fact that it is easy to peel and separate into segments makes it convenient to use as a table variety; therefore, there is also less processing. At processing centers, peels are collected for production of oil.

## Essential Oil

Until recently, in the United States, oil extraction was independent of juice extraction. This is because the juice or the fruit of the loose skin oranges is not quite suitable for canning. Therefore, after the fruits are used as for the table, a small percentage are crushed to obtain an emulsion of oil and juice. This is centrifuged to obtain cold-pressed oil. In recent years, a new process has been devised using flash pasteurization. This has enabled the industry to get a large quantity of oil as a by-product of the juice industry. For this, after the fruits are washed, they are sent to the rotary juice extractor, which cuts them into halves and extracts the juice. The peel is then expressed in a tapering screw press or other specialized press. The effluent is freed of solid debris by sieving, and the oil is separated from the aqueous cell liquid by centrifugation. The oil will have a red-orange color with the typical aroma and flavor of the outer rind of the fruit.

In Sicily and adjoining areas, the fruits are eaten or exported, leaving very little for oil extraction. Oil is recovered from some fruits either by the hand-pressing sponge process or by using a machine. The yield is generally 0.8%. In Brazil, small amounts of mandarin oranges are also extracted after use as fresh fruit by the use of a rasping machine. Here, the whole fruit is scraped against rotating corrugated disks and walls inside a closed drum. The yield is only about 0.2% (NIIR Board 2009).

According to the FCC, cold-pressed mandarin oil is a clear, dark orange, red-yellow, or brown-orange liquid with a pleasant orange odor. Oils produced from unripe fruit often show a green color. The oil is soluble in most fixed oils and in mineral oil, is slightly soluble in propylene glycol, but is insoluble in glycerin. It may contain a suitable antioxidant.

Physical characteristics as defined by the FCC are as follows.

| | |
|---|---|
| Optical rotation | +63° to +78° |
| Refractive index | 1.473–1.477 at 20°C |
| Specific gravity | 0.846–0.852 |

According to the FCC description, cold-pressed tangerine oil is a red-orange to brown-orange liquid with a pleasant orange odor. Oils from the unripe fruit are often green. It is soluble in most fixed oils and in mineral oil, slightly soluble in propylene glycol, and relatively insoluble in glycerin. It may contain a suitable antioxidant.

Physical characteristics as defined by the FCC are as follows.

| | |
|---|---|
| Optical rotation | +88° to +96° |
| Refractive index | 1.473–1.476 at 20°C |
| Specific gravity | 0.844–0.854 |

The principal constituent of mandarin peel oil is limonene. By GC studies, 48 compounds have been identified in tangerine oil (Kugler and Kovats 1963). Seven acids and 24 alcohols have been noted. Out of 16 carbonyl compounds reported, four straight-chain aldehydes, four monoterpene, and two sesquiterpene aldehydes have been noted. Four esters identified include *N*-methyl anthranilate. Two ketones are nootkatone and carvone. Nootkatone is typical of grapefruit aroma. 1,8-Cineole and thymol are present in tangerine oil.

The leaves and twigs on distillation give oil of petitgrain mandarin with a yield of around 0.3%. (NIIR Board 2009).

## Uses

The oil of the mandarin orange is used as a modifier of sweet orange oil meant for the beverage industry. It is also used, like other citrus oils, in different baked products, confectioneries, and as a flavor booster for orange juice- and pulp-based products. It is also valuable in some liqueurs and cordials as well as in perfumes.

Tangerine oil generally resembles sweet orange oil and finds use in products where orange oil is used. With the improved method of juice extraction, tangerine oil is now the distinct aroma used in different products as a flavor.

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Mandarin oil | 2657 | 8008-31-9 | 182.20 | – |
| Mandarin oil, terpeneless | – | 68917-20-4 | – | – |
| Tangerine oil | 3041 | 8008-31-9 | 182.20 | – |

## References

Kugler, E.; and Kovats, E. 1963. Information on mandarine peel oil. *Helv. Chim. Acta* **46**, 1480–1513.

NIIR Board. 2009. *The Complete Technology Book of Essential Oils*. Delhi: Asia Pacific Business Press, pp. 216–227.

# 75 Marigold

## *Tagetes erecta* L (*Compositae*)

## Introduction

Marigold flowers have an attractive yellow to orange color. They are grown in gardens for their flowers, which are sometimes used for making garlands. In India, marigold flower garlands are popular for Hindu temple offerings. It is one of the easiest flowers to grow and can brighten a home garden as no other flower can. Small marigold plants are often used as the boundary of a flower bed or lawn. English writers of old called the flower gold or "rudder." It was later associated with the Virgin Mary and, in the seventeenth century, with Queen Mary. Perhaps these associations have given the flower the name "marigold."

The Portuguese first noted the flower in Central America in the sixteenth century. Several varieties are now known in different regions of the world. African or American marigold (*Tagetes erecta*) grows up to 90 cm and its flowers are nicely shaped with a diameter of 12–13 cm. The flowers are yellow. French marigold (*Tagetes patula*) has red or orange small flowers. The plant grows to a lesser height, 10–40 cm, and its flowers have a diameter of about 5 cm. Signet marigold plants (*Tagetes signata*) have clusters of yellow to orange flowers with a cool lemon scent. There are also varieties of pot marigold that are not true marigold.

From a natural color point of view, *T. erecta* is the most important of the marigold varieties. The flowers are thick with extractable yellow pigments belonging to the carotenoid family. South America, China, and India are the major producers of the pigment.

## Plant Material

The flower of the marigold plant, which is an annual, is used as the raw material for the pigment (see Photo 21). Generally, it is easy to grow, and has a color between yellow and orange. It flowers all through the summer and is relatively immune to insect or microbial attack. Larger flowers with intense color are preferred. Marigold leaves are finely cut and fern-like. Signet marigold leaves are even finer than those of *T. erecta*, which is the major variety used for extraction of color.

## Preparation of Flower for Extraction

The active pigment of marigold is lutein, present only in amounts of 0.1–0.15%, which accounts for nearly 90% of the carotenes present. Therefore, to extract the pigment,

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**Photo 21.** Marigold flower. See color insert.

large volumes of flowers must be processed. Flowers contain slightly over 85% moisture; in order to maintain their freshness, farmers often sprinkle them with water, which makes them even moister.

Harvesting is labor-intensive, as it has to be carried out manually. The pigments are heat-sensitive and therefore very high temperatures cannot be used for drying. And to dry such a voluminous quantity of fresh flowers using hot air would be prohibitively expensive. Therefore, a preliminary process known as silage is employed. During this step, flowers are allowed to rot to the point where the cells break and water oozes out. Flowers are kept in large and spread-out cement tanks with arrangements for water to drain out. A typical silage will consist of 200 tonnes of fresh flowers. In about 15 days, about 12% of the moisture will escape by draining. In 22 days, 13.5% will escape. The mass, partially freed of liberated moisture, is then passed through a squeezing device to further reduce the moisture level. Generally, about 16–20% water will escape.

The flower meal, freed of about 50–55% of the original moisture, is then dried using hot air. The device used is an open dryer with a mesh bottom. The meal is spread over this to a thickness of about 5 cm. Heated air is passed through the bottom. The arrangement is a crude through-flow dryer. The drying results in an extractable mass representing 7–11% of the original weight of the fresh flower. The moisture content of the dry powder will be 12–13%. The xanthophyll content of the meal will be about 10%. Moisture removal at different stages is presented in Table 75.1.

It may be noted that during silage, there is considerable loss of weight due to the escape of soluble solids such as carbohydrates, proteins, and acids with the moisture that flows out.

**Table 75.1.** Moisture and weight reduction during preparation of dry meal from fresh marigold flowers

| | Weight (kg) | Moisture Content (%) | Moisture Loss (% of Fresh Flower) |
|---|---|---|---|
| Fresh flower | 235,714 | 86 | – |
| After 15 days of silage | – | – | 12 |
| Further 22 days of silage | – | – | 13.5 |
| Squeezing | – | – | 16–20 |
| After drying | 28,286 | 10 | 30–35 |

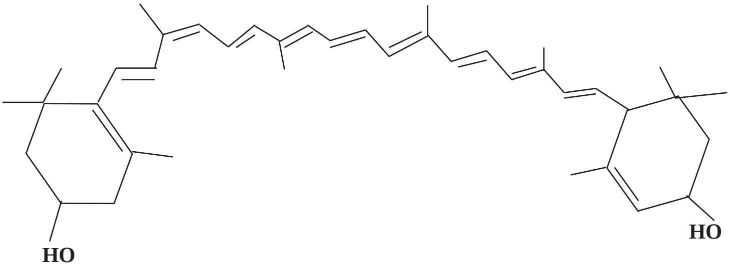

**Figure 75.1.** 9-*cis*-Lutein.

The biggest problem during the dewatering operation is pollution. The drained water during silage and squeezing will have some soluble nutrients, which cause the growth of polluting microbes and a foul smell. In recent years, both China and India entered into marigold extraction. Because of lack of space and pollution, many Indian processors have stopped processing marigold. China, with a large area in some regions and appropriate technology, has developed a monopoly on marigold pigments. Processing in South America, especially in Peru, has also been unsuccessful because of the high cost of labor.

## Chemistry

The pigments in marigold flowers are all oxygenated carotenes (xanthophylls). About 90% of the carotenoid pigments in marigold is lutein (Fig. 75.1). Zeaxanthin represents about 5%. The lutein occurs as esters, and a typical composition is lutein dipalmitate 50%, lutein dimyristate 30%, lutein monoester 6%, and unidentified 9% (Antony and Shankaranarayana 2001). There are also small amounts of distearate, myristate-palmitate, and palmitate-stearate.

Lutein and other xanthophylls are responsible for the color of the flower. Lutein also gets deposited in the yolk of the egg if added to chicken feed. For this use, a large amount of marigold extract is manufactured.

Lutein in marigold is in natural *trans*-isomeric form, but may get converted to *cis* form during some steps of processing. However, both isomers can contribute to ocular health (see section on “uses” below).

## Extraction

The dry meal is extracted with hexane. The successive miscella in the case of batch extraction is combined and solvent distilled off without raising the temperature much above the boiling point of hexane. When large quantities are involved, extraction is carried out using a continuously operating moving chain. The meal will move in one direction and the solvent with progressive enrichment moves in the opposite direction. The extract is a dark brown pasty liquid. It will have a mild odor of marigold and the typical putrid smell due to retting during silage operation. The product becomes loose when warmed to 50–60°C.

The yield of the extract is about 8–10% of the dry meal. The product will have 80–120 g/kg of xanthophylls. The residual solvent is below 3000 ppm.

Because of its putrid smell, the product is useful only for chicken feed. Vacuum distillation results in low residual solvent and some deodorization, but the product is still not suitable for food use. There is a need for standardization of a process involving disintegration of flowers, careful partial drying, and extraction with a mixture of hexane and acetone to get pigment from the cells. Some exploratory trials have shown some promise of creating a product with satisfactory flavor.

## Uses

Marigold extract rich in lutein has a bright yellow-orange color that is useful in a wide range of food products. Presence of lutein is also valuable as a nutraceutical. The color maintains stability during heat processing. For use in food, many standardized forms such as oil-soluble, water-dispersible, spray-dried, and plated on solid matrix are manufactured. These are used in mayonnaise, dairy products, confectionery, and baked items to take advantage of its yellow-orange color.

However, the fine color has not been fully exploited as a natural food colorant (Sowbhagya et al. 2004). Most of the marigold extract now produced is made for use in chicken feed, because of the intense off-flavor as a result of the silage process. It is the belief of the author that if extracts are made by careful drying and extraction with an appropriate solvent system, the use of this natural color will be more widely used in food preparations.

Lutein present in the extract is a valuable nutraceutical. The macular region of the retina is vulnerable to age-related degradation. Lutein, which cannot be synthesized by humans and therefore has to be taken with food, is extremely important for the health of the eye. Lutein is an antioxidant capable of protecting the macular region of the retina from peroxidative damage. Generally, commercial preparations will also contain zeaxanthin and cryptoxanthin.

Marigold extract is widely used in chicken feed to help color the yolks yellow. For standardization of the yellow-orange shade of the yolk, a tremendous amount of saponified marigold extract is used.

## Analytical Method

Xanthophylls are estimated by the AOAC method. Here, xanthophylls are extracted by a mixed solvent and absorbance is measured in a spectrophotometer at 474 nm.

## Identification Numbers

| | FEMA No. | CAS | US/CFR | E-No. |
|---|---|---|---|---|
| Marigold absolute | – | 8016-84-0<br>91770-75-1 | – | – |
| Lutein | – | – | – | 161b |

## References

Antony, J.I.X.; and Shankaranarayana, M.L. 2001. Lutein. *World of Food Ingredients*, April–May, pp. 64–70.

Sowbhagya, H.B.; Sampathu, S.R.; and Krishnamurthy, N. 2004. Natural colorant from marigold—chemistry and technology. *Food Rev. Int.* **20** (1), 33–50.

# 76 Marjoram

## *Marjorana hortensis* M (*Labiatae*)

### Introduction

Marjoram, also called sweet marjoram, is a cold-sensitive perennial herb or undershrub with a fine aroma. Oregano is sometimes referred to as wild marjoram, but it is a different herb; marjoram belongs to the mint family. For a long time, marjoram was known as *Origanum marjorana*, though presently the botanical name *Marjorana hortensis* is used. Although it is a perennial, it is cultivated as an annual.

In Rome, a newly married couple is crowned with marjoram. It is a symbol of honor in Crete. In Greek, the name of marjoram means joy of the mountains and the plant represents happiness. In Sicily, it is believed to have the property of removing unhappiness.

### Plant Material

Marjoram is an erect plant which grows close to the ground and rarely has a height over 30 cm. It is bushy, with grayish-green, oval, hairy leaves. It has groups of flowers in knot-like formations. The dried leaves and floral parts, after field drying, form the herb that is used as a spice and for making extractives. It has a sweet and spicy aroma and a bitter and camphoraceous taste and flavor.

The plant is cultivated in the European countries of France, Germany, the United Kingdom, Hungary, Italy, Spain, and Portugal; North African countries of Morocco and Tunisia; and some countries of South and Central America.

Marjoram leaves on dry basis have over 60% carbohydrates, 7% fat, 13% protein, 18% fiber, and minerals and vitamins. However, the most significant constituent is the essential oil that is responsible for its aroma and flavor.

### Essential Oil

Dry marjoram leaves yield around 1% of volatile oil. The major component of the oil is its sabinene derivatives, which are bicyclic (Novak et al. 2008). GC-MS study of oil from Albania shows 28 volatiles (Jirovetz et al. 2008). Terpinen-4-ol accounts for 14%, $\alpha$-terpinene 9%, and sabinene 8%. From the oil produced in Egypt, 30 major and minor compounds are detected. Terpinen-4-ol, linalool, $\gamma$-terpinene, $\alpha$-terpinene, and sabinene are the major components (El-Nakeeb et al. 2006).

Sweet marjoram oil, according to the FCC, is a yellow or greenish-yellow oil with a warm, fragrant, and spicy note resembling cardamom and lavender. Its taste is sharp

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and slightly bitter. It is soluble in most fixed oils and in mineral oil. It is only partially soluble in propylene glycol and it is insoluble in glycerin.

Physical characteristics as defined by the FCC are as follows.

| | |
|---|---|
| Optical rotation | +14 to +24° |
| Refractive index | 1.470–1.475 at 20°C |
| Specific gravity | 0.890–0.906 |
| Solubility | 1 mL dissolves in 2 mL of 80% alcohol |

## Oleoresin

Well-powdered, dried leaves, when extracted with hexane, give an oleoresin with a yield of 1.5–2%. Depending on the quality of leaves, the volatile oil content of oleoresin will be between 12 and 20% v/w.

It is a dark greenish-brown, somewhat pasty product with a typical thyme/minty aroma and flavor. It is miscible with fixed oil. Dilution with vegetable oil or any other diluent will make it easier to use. It is partially soluble in propylene glycol and insoluble in glycerin. The flavor of marjoram is deceptively potent and care is needed to avoid adding an excessive amount to food. Therefore, the more balanced flavor of the oleoresin is preferred.

## Uses

Marjoram oil can be used as a flavor in liquor, liqueurs, sauces, and condiments. Both the oil and oleoresin can be used in various meat preparations such as sausages, chicken preparations, and special soups. The oil finds use as a fragrance in soaps and perfumes.

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Marjoram oil sweet | 2663 | 8015-01-8<br>84082-58-6 | 182.20 | – |
| Marjoram extract/oleoresin | 2659 | 84082-58-6 | 182.20 | – |

## References

El-Nakeeb, M.A.; Fathy, S.M.F.; and Salma, O.M. 2006. GC-MS analysis, biostatic activities and biocidal dynamics of the essential oil of *Origanum marjorana* cultivated in Egypt. *Alex. J. Pharm. Sci.* **20** (2), 150–156 (*Chem. Abstr.* **147**:207647).

Jirovetz, L.; Bail, S.; Buchbauer, G.; Denkova, Z.; Slavchev, A.; Stoyanova, A; and Schmidt, E. 2008. Chemical composition, antimicrobial activities and olfactory evaluations of an essential marjoram oil from Albania as well as some target compounds. *Ernaehrung* **32** (5), 97–201.

Novak, J.; Lukas, B.; and Franz, C.M. 2008. The essential oil composition of wild growing sweet marjorana from Cyprus-3 chromotypes. *J. Essent. Oil Res.* **20** (4), 339–341.

# 77 Mustard

## *Brassica alba* L, *B. nigra* K, and *B. juncea* L (Cruciforae)

## Introduction

Long before the West started using mustard, the Chinese used it as a seasoning for food. In Europe, it is used as a condiment for salted meat. Many strongly flavored spices were used in winter not only for preserving meat, but also to mask off-flavor due to spoilage. Some were believed to be useful for protecting the digestive system. Ancient Greeks used mustard as seasoning for their meat and fish. Ancient Romans mixed the spice with grape juice, known at that time as “must,” to make what is known as “must ardens” translated as “burning must”; from this the name “mustard” probably originated.

It is possible that Roman soldiers brought the spice to England where it became a valuable ingredient of seasoning. The two main grades are English and French mustard. All over the world, sulfur-containing flavors have been appreciated in specialty foods to give a wasabi-like pungency. Mustard is also an important oilseed and, along with rapeseed, is a major source of fixed oil. The low erucic acid variety of rapeseed, called canola oil, makes it one of the major fatty oils. Because of this use, mustard along with rapeseed became a major crop of the world. This also helped in the spread of mustard flavor to all parts of the globe.

## Plant Material

Black mustard (*Brassica nigra*) and brown mustard (*Brassica juncea*) are generally grouped together and called black mustard. The tiny fruits are pressed to the inflorescence axis. The seed coat shows minute reticulation and adheres to mucilaginous material. The outer skin is covered with a thin cuticle. The spice is cultivated in Europe, although recently there has been a switch over to the white variety.

The light-colored mustard, referred to as white or yellow mustard (*Brassica hirta* or *Brassica alba*) grows on a plant with a hairy stem. The leaves are irregularly pinnate and the flowers are spreading and yellow. The hairy pods have empty, knife-like beaks and contain relatively large and pitted seeds. There is a good deal of mucilaginous material. The mustard plant and dried mustard are presented in Photo 22.

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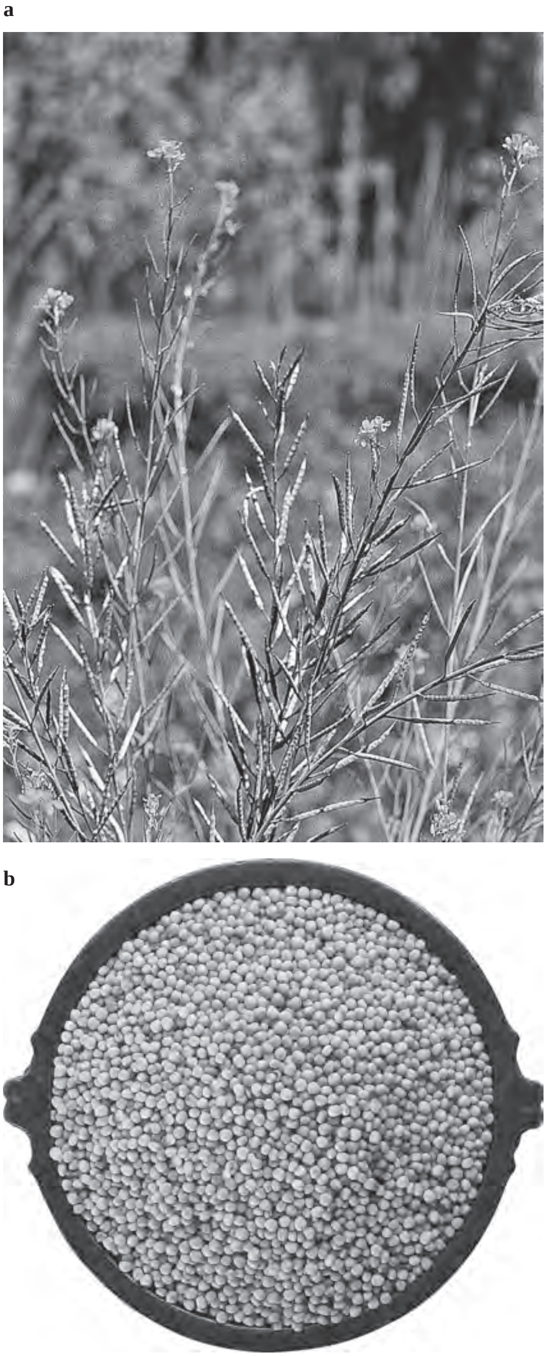

**Photo 22.** (A) Mustard in bloom. (B) Dried yellow mustard. See color insert.

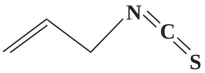

Figure 77.1. Allyl isothiocyanate.

## Chemistry

Mustard seeds are a source of fixed oil and about 30% of the dry seed consists naturally of triglycerides. The seeds are an excellent source of protein which is present in levels of 25–30%. It has about 10% crude fiber and minerals.

Black mustard contains allyl glucosinolate, popularly called sinigrin. When the mustard is crushed, the enzyme myrosinase present in it degrades sinigrin, in the presence of water, to allyl isothiocyanate (AITC) (Fig. 77.1). AITC has a boiling point of 151–153°C, a specific gravity of 1.0175, and solubility of 2 g in 1 L of water at 20°C.

White mustard, on the other hand, contains the glucosinolate known as sinalbin. This, in the presence of water, is acted on by myrosinase to produce 4-hydroxy benzyl isothiocyanate, which has a half-life of a little over 1 hour. This pungent material degrades into 4-hydroxy benzyl alcohol and thiocyanate ion, which are only weakly pungent. Another related glucosinolate, glucobrassicin, when in contact with water and enzyme, also yields a nonpungent isothiocyanate.

## Essential Oil

The essential oil of mustard is formed only after the action of the enzyme myrosinase on the right variety of mustard. Black mustard (*B. nigra*) or brown mustard (*B. juncea*), which contains sinigrin, is a suitable raw material. It is first expelled to remove all the fixed oil. The cake obtained is then treated with water so that the enzyme can act to produce AITC with a small amount of butenyl isothiocyanate. The proportion of cake to water is maintained at 16.5:83.5.

This slurry is then transferred to a steam distillation unit fitted with stirrer and steam jacket. The slurry is preheated to about 60°C for 1 hour and then open steam is admitted so that steam-water distillation takes place. The mixture of oil and water is collected by means of a water-cooled condenser in a closed receiver arrangement for heavier-than-water oil. The mustard oil, which is mainly AITC, is removed. The yield of the oil is only 0.3–0.4%.

The oil generally contains 85% allyl and 10% butenyl isothiocyanate. The specific gravity is over 1. The oil from some types of white mustard is 80% butenyl isothiocyanate and 12% AITC. This may have a lower specific gravity and lower refractive index than the product from black mustard.

Recent development has shown that the spinning cone column (SCC) method, which was developed for aroma recovery from fruit pulp, can be effectively used to separate isothiocyanate-rich essential oil from mustard. All the other operations except distillation are similar. The SCC is a vertical stainless steel cylinder with a central rotating shaft. To facilitate intimate contact, there are two sets of inverted cones. One set is attached to the inside wall of the column and another to the central shaft. The cones attached to the shaft rotate with the shaft while those on the wall are fixed in such a fashion that they are alternate with one another.

The slurry is made to flow from the top to bottom, and stripping steam flows from the bottom to the top. As the steam passes over the thin layer of slurry, it picks up volatiles and is led to the condenser. Volatile-free slurry flows down and can be collected.

From the condenser, a mixture of volatile oil and water are sent through a series of separators. Oil, being heavier, collects at the bottom. Since the oil is very expensive and yield is low, generally, during the last separation, the entire volume of water is kept overnight so that every droplet of volatile oil settles before the water is discarded.

The yield of volatile oil from condensation is better than that from conventional distillation. A new variety of Canadian yellow mustard is believed to be richer in AITC, and with this the yield can be 0.8–1%. Against this, one has to consider the high capital investment needed.

Mustard oil is highly volatile, pungent, and therefore hazardous. It needs special packaging such as aluminum bottles, placed inside a mild steel jacket, protected inside a dealwood box. The operation creates polluted water, which then needs special treatment. There are reports of workers affected by discomfort and illness in the traditional method of manufacturing.

Mustard oil, according to the FCC, is a pale yellow liquid with a sharp, pungent odor and taste. It does not have angular rotation. Good quality oil requires over 93% AITC.

Physical characteristics as defined by the FCC are as follows.

| | |
|---|---|
| Refractive index | 1.524–1.534 at 20°C |
| Specific gravity | 1.008–1.019 |

## Oleoresin

There is very little oleoresin manufacture of mustard oil. Some sporadic but unsystematic efforts have been made. It is not clear whether the preliminary step of expelling and treatment with water to activate the enzyme must be carried out before extraction is performed. If it were possible, it would have resulted in a process that is simple, inexpensive, and relatively safe. But extraction with organic solvent can be tricky when so much water is present in the slurry.

The saturated and unsaturated fatty acid composition can be analyzed using GC-MS (Liu et al. 2001). The lysine content of *Brassica napus* and *B. juncea* is analyzed employing near IR reflectance spectroscopy (Gan et al. 2005).

## Uses

Mustard oil is used in mustard paste and other dishes that need the pungent, volatile flavor of mustard or horseradish. Many Japanese food products use mustard oil.

Many processed meat preparations such as bologna, frankfurters, and salami require mustard flavor. It is also useful in salad dressings, condiments, and soups.

## Identification Numbers

| | FEMA No. | CAS | US/CFR | E-No. |
|---|---|---|---|---|
| Mustard oil (for AITC) | 2034 | 57-06-7 | 172.515 | – |
| Mustard extract | – | 8007-40-7 | 182.20 | – |

## References

Gan, Li; Pan, Zhe; Zhao, Li; Xu, Jiuwei; Zhang, Yu; and Fu, Tingdong. 2005. Analysis of lysine contents by near-IR reflectance spectroscopy in *Brassica napus* and *Brassica juncea*. *Zuowu Xuebao* **31** (7), 944–947 (Chinese) (*Chem. Abstr*. **145**:313310).

Liu, Qian; Li, Zhanjie; Xie, Mandan; and Zhu, Yufan. 2001. Component analysis of fatty acids in mustard seed. *Fenxi Ceshi Xuebao* **20** (3), 49–50 (Chinese) (*Chem. Abstr*. **136**:150051).

# 78 Nutmeg

## *Myristica fragrans* H (*Myristicaceae*)

### Introduction

Nutmeg is believed to be native to the Banda Island of modern Indonesia. Ancient Romans used it as incense for burning. In those days, nutmeg was regarded as a costly spice. In ancient England, there was a belief that nutmeg could ward off diseases, such as the bubonic plague.

During the Middle Ages, Arab merchants sold nutmeg to the people of Italy as an expensive luxury item. In the sixteenth century, after their great expeditions, Portugal took control of the Indonesian nutmeg trade. A century or two later, the Dutch and later the British controlled the trade of nutmeg.

Nutmeg has been mentioned in Indian Vedic literature, and has importance in Ayurvedic therapy. Large-scale commercial cultivation was introduced by the British toward the end of the nineteenth century.

### Plant Material

The fruit grows on a lush evergreen tree with a height of 10–15 m. The leaves grow into a lush round mass over 2–3 m, making the tree an attractive one. The tree is unisexual, with separate male and female trees. Peach-like fruits with a thick rind are borne only on the female tree. The kernel is the nutmeg of commerce, the outside of which is a hard, thin shell. The kernel is slightly oblong with a diameter of 2–4 cm. The dried aril, a yellow to red colored, soft, broken layer that surrounds the shell, is mace, another spice (see Chapter 73 on mace). See Photo 23.

A major producer of nutmeg is Indonesia. In the Americas, the traditional source of nutmeg was the island of Granada. The nutmeg from that region is known as West Indian, while that of Indonesia is called East Indian nutmeg. Today, Sri Lanka and India are substantial producers, but the oil resembles that of West Indian nutmeg.

Dried nutmeg is generally high priced, though a popular grade of raw material for the manufacture of extractives is called BWP (broken, wormy, and punky), which is cheaper.

### Chemistry

Nutmeg contains about 6% protein, 35% fat, nearly 50% carbohydrates, and 4% crude fiber. It has mineral matter and some vitamins, including a small quantity of vitamin A.

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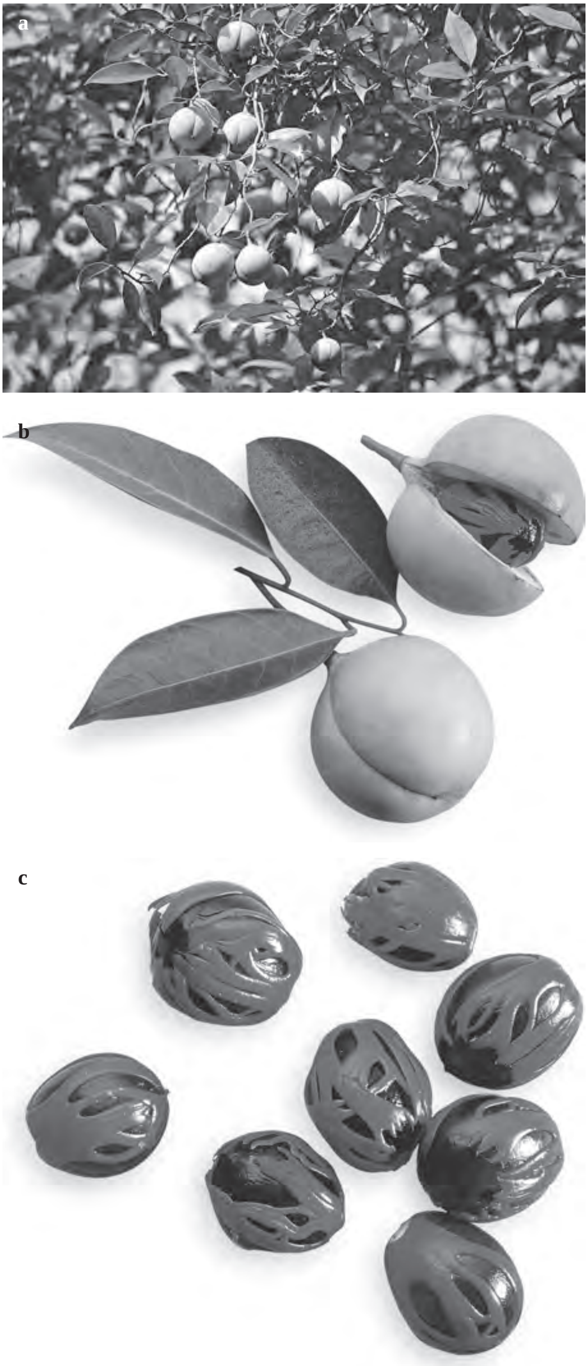

**Photo 23.** (A) Nutmeg fruit on the tree. (B) Opened fruit showing nutmeg covered with mace. (C) Nutmeg with mace over it. See color insert.

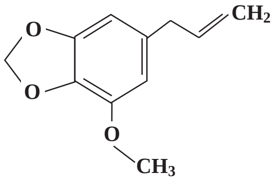

**Figure 78.1.** Myristicine.

The main fatty acid of the fat is myristic acid, a 14-carbon saturated fatty acid. About 75% of the triglycerides are trimyristin. Having plenty of saturated glycerides, the fat of nutmeg is a semisolid product, which, because of its consistency, is popularly called nutmeg butter.

The characteristic constituent of nutmeg essential oil is myristicine, or 3-methoxy-4,5-methylendioxy-allyl benzene (Fig. 78.1).

## Essential Oil

After size reduction to a coarse powder using a roller mill, nutmeg is packed in a stainless steel vessel and steam is passed through the bottom. The yield of oil separated from water on cooling is 6–12%. The quality of oil is measured according to the content of the oxygenated heavy dicyclic terpene myristicine. While West Indian, Sri Lankan, and Indian nutmeg yield an oil with about 2% myristicine, good Indonesian oil has a much higher myristicine content, sometimes as much as 9–10%. In identical conditions, shelled nutmeg gives an oil yield of 9.5% for Indonesian, 8% for Sri Lankan, and 5–6% for Indian nutmeg.

Analysis of Indian, Sri Lankan, and Indonesian nutmeg oil has been carried out, and the results are presented in Table 78.1. Sabinene and pinenes are major components but are not very significant.

Nutmeg oil is an almost colorless to pale yellow liquid with the characteristic spicy and stimulating aroma of nutmeg.

In a study that compared West Indian nutmeg oil with East Indian, it was noted that Jamaican oil shows lower quantities of phenyl propanoids, myristicine, and safrole. In addition, three isomers of ocimene have also been noticed in Jamaican oil (Simpson and Jackson 2002). Nutmeg oil from Nigeria shows 49.09% of sabinene, 13.19% of $\alpha$-pinene, 6.72% $\alpha$-phellandrene, and 6.43% of terpinen-4-ol (Ogunwande et al. 2003). Or combining silica gel column separation with analysis, isovanillin is found in nutmeg oil along with dehydro-diisoeugenol, myristicine, elimicine, and some nonvolatile constituents (Li et al. 2006). In another recent investigation of the oil obtained by solvent-free microwave extraction followed by GC-MS analysis, 42 components representing 98.62% of the oil were revealed. The main volatiles are sabinene (23.93%), myristicine (11.06%), $\alpha$-pinene (9.52%), $\beta$-pinene (8.95%) 4-terpineol, limonene, elimicine, *p*-cymene, and safrole (Zheng et al. 2007). In a study of the oils from nutmeg of East Indian, West Indian, and Papua origins, there are similarities in the composition of volatiles. The aroma-dominating compound in East

**Table 78.1.** Composition of nutmeg oil from three origins

| Constituent | Nutmeg Oil (Area %) | | |
|---|---|---|---|
| | Indonesian | Sri Lankan | Indian |
| $\alpha$-Thujene | 4–6 | 2–5 | 2–4 |
| $\alpha$-Pinene | 14–17 | 12–16 | 13–17 |
| Camphene | 0.3–0.8 | 0.2–0.6 | 0.3–0.8 |
| Sabinene + $\beta$-pinene | 20–30 | 35–45 | 37–45 |
| $\delta$-3-Carene | 1.5–3 | 2–4 | 2–4 |
| Limonene | 2–5 | 3–6 | 3–5 |
| $\beta$-Phellandrene | 3–5 | 2–4 | 4–6 |
| *p*-Cymene | 1.5–3 | 0.5–1.5 | 1–3 |
| $\alpha$-Terpinene | 8–11 | 4–8 | 6–9 |
| Terpinen-4-ol | 6–10 | 5–8 | 5–8 |
| Safrole | 1–2 | 0.7–1.5 | 1.0–1.5 |
| Geraniol | <0.5 | <0.5 | <0.5 |
| Methyl eugenol | 1–2 | 0.3–0.8 | 0.5–1 |
| Myristicine | 6–10 | 2–3 | 1.5–2.5 |
| Elimicine | 0.2–0.8 | 1–2 | 1.5 to 2.5 |

Indian oil is myristicine, in West Indian oil elimicine, and in Papuan oil safrole (Ehlers et al. 1998).

According to the FCC, nutmeg oil occurs as a colorless or pale yellow liquid with the characteristic odor and taste of nutmeg. Two types of oils, East Indian and West Indian, are commercially available. It is soluble in alcohol.

Physical characteristics as defined by the FCC are as follows.

| | East Indian type | West Indian type |
|---|---|---|
| Optical rotation | +8 to +30° | +25 to +45° |
| Refractive index | 1.474–1.488 | 1.469–1.476 at 20°C |
| Specific gravity | 0.880–0.910 | 0.854–0.880 |
| Solubility | 1 mL in 3 mL 90% alcohol | 1 mL in 4 mL 90% alcohol |

## Oleoresin

The deoiled nutmeg has 15–24% nutmeg butter, which is mainly trimyristin. It can be extracted with hexane. Sri Lankan and Indonesian nutmeg plants give a higher yield than Indian. On blending with oil, the oleoresin with appropriate volatile oil content can be made. Generally, 30–40% oil content is preferred but any range between 10% and 90% can be used.

Nutmeg oleoresin has a light yellow to reddish-brown color, the lighter color being obtained if extracted from a shell-free nutmeg.

## Uses

Oil and oleoresins are used in a wide range of meat preparations. They are also used in baked goods, liqueurs, chewing gum, confectionery, and soups. A large amount of oil is used in cola-based soft drinks.

Myristicine is an insecticide that can be described as naturally occurring in the plant world. It has mild neurotoxic effect and is a monoamine oxidase inhibitor. There is scope for future researchers to take advantage of the possible use.

In Ayurvedic therapy, nutmeg is believed to be a remedy for digestive disorders, for dehydration caused by vomiting and diarrhea, and for colds and related disorders. The oil and oleoresin can find use in modern medical compositions designed for the above disorders.

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Nutmeg oil | 2793 | 8008-45-5<br>84082-68-8 | 182.20 | – |
| Nutmeg oleoresin (including $CO_2$ extract) | – | 84082-68-8 | 182.20 | – |

## References

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# 79 Onion

## *Allium cepa* L (*Alliaceae*)

## Introduction

Onions have a long history, as traces have been detected in settlements dating back to 5000 BC. It is believed that the onion originated in West Asia. It is one of the oldest cultivated crops. Cultivation may have taken place around 3000 BC, as evidence suggests that in Egypt, workers who built the pyramids were fed with onions. Egyptians worshipped it as a symbol of eternal life. In Greece, athletes consumed it to purify the blood, and Roman gladiators rubbed it on their muscles to firm them up. Doctors were believed to have prescribed onions for a wide range of purposes such as to regulate bowel movement and male sexual performance as well as to relieve headaches, coughs, snakebites, and even hair loss.

A wide range of foods use onion, which is both a spice and vegetable. Onion is also noted for its ability to cause eye irritation. This drawback encourages development of processed onion products, including extractives, for use as a flavor and for seasoning. In fact, "onion without tears" was the marketing slogan of one of the manufacturers of extractives.

## Plant Material

Onion is a bulb (shown in Photo 24) of a biennial plant. Though it grows underground, it is a shoot portion developed for storing food for the plant, and is not a root tuber. Being widely used, there are several cultivars in different parts of the world suiting the climatic conditions. Agricultural research has enabled the development of onions of different sizes, with colors varying from white to red, and with different total solids. Because of its widespread use as a vegetable and large-scale processing into dehydrated products, only countries that have a great surplus can afford to process it into extractives. Because of the importance of texture quality, especially when onion is used as a vegetable, extractives have a demand only for use as a pure flavor.

According to the Food and Agriculture Organization of the United Nations, China produces nearly 10,000 tonnes and India 5500 tonnes of a total world annual production of 64,101 tonnes. This is followed by the United States, Turkey, Pakistan, Russia, South Korea, Japan, Egypt, and Spain.

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**Photo 24.** Onion; cut pieces show structure. See color insert.

## Chemistry

Onion on dry basis has 70–75% carbohydrates and about 10% protein, minerals, and some water-soluble vitamins, though these nutritional properties will not be relevant when extractives are used.

The flavor of the onion has been studied in detail. The flavor precursors isolated include methyl-propyl and propenyl derivatives of L-cysteine sulfoxide. From these, thiosulfonates and thiosulfinates are formed, which cause the odor when fresh onions are cut or crushed. When onions are boiled, further decomposition results in the formation of di- and trisulfides. Dimethyl thiophenes are formed when the onion is fried. The tear-producing constituent is believed to develop due to splitting of the precursor S-propenyl sulfoxide; the unstable propenyl sulfenic acid may be the tear-producing agent. This decomposes in 90–100 seconds to thiopropanal S-oxide and, subsequently, into propanal.

The reactions leading to flavor and tear-producing agents have been studied by a number of researchers. There are some useful reviews on the subject by Abraham et al. (1976) and Arnault and Aunger (2006).

## Essential Oil

The volatile oil content depends on the variety of onion used. Generally, the Indian variety has a negligible oil content. In some varieties, oil forms on water distillation as a dark brown oil, which has a tendency to crystallize on standing. The yield is 0.01–0.02%. It is reported that oil is produced from some Chinese varieties. The main constituents are *n*-propyl and methyl-*n*-propyl disulfides. Because of the very low yield and high cost, it may be more practical to use oleoresin.

According to the FCC, onion oil occurs as a clear, amber-yellow to amber-orange liquid with a strong, pungent odor and a taste characteristic of onion. It is soluble in most fixed oils, in mineral oil, and in alcohol. It is insoluble in glycerin and in propylene glycol.

Physical characteristics suggested by the FCC are as follows.

| | |
|---|---|
| Refractive index | 1.549–1.570 at 20°C |
| Specific gravity | 1.050–1.135 |

## Oleoresin

The extract can concentrate to two items: the water-soluble constituents and fat-soluble, nonpolar constituents. The former can be obtained by crushing the material, mixing well with water, and decanting the water phase. This step can be repeated, but to keep a strong flavor, it is better to keep to a maximum yield of 15%. The spent residue can be extracted with a nonpolar solvent such as *n*-hexane. It may be necessary to pump solvent from the bottom and take the miscella from the top for greater efficiency. The combined miscella is freed of solvent and this can be added to the water-soluble part to yield a “green” or fresh onion oleoresin, which is water-soluble. Alternatively, hexane extraction can be carried out as the initial step, followed by water extraction. If oil-soluble oleoresin is required, the hexane extractable can be diluted with fixed oil or mono- and diglyceride along with diluents such as propylene glycol to reduce the strength and unit cost. It may be noted that on boiling, the flavor may lose its freshness and hence boiling with water is not desirable.

On roasting, onion gives a very appealing flavor. The above process can be carried our after roasting cut onion pieces at 100–120°C for up to 15 minutes. Here, also, water-soluble and oil-soluble oleoresins can be made as in the case of “green” oleoresin. The strength depends on the dilution. The flavor is contributed by the breakdown of sulfur-containing compounds of onion flavor and volatile oil including simple organic sulfides.

In recent years, some interesting research has been carried out on onion volatile components. Thiopropanal S-oxide, the lachrymatory (tear-producing) factor, has been analyzed in fresh onion juice, and thiosulfinates and zwiebelanes have been quantified. Frozen and freeze-dried onions, on the other hand, lose the lachrymatory factor but, on analysis, are similar in other components (Mondy et al. 2002). From freeze-dried onion, volatiles obtained by steam distillation extraction followed by extraction with dichloromethane yield 24 sulfur-containing compounds representing 36.87% of total volatile chemical (Takahashi and Shibamoto 2008). These volatiles, as well as the aqueous fractions in the distillate, show anti-inflammatory activity. Quercetin and its glycosides represent the flavonols in onion (Lombard et al. 2002; Zielinska et al. 2008).

## Identification Numbers

| | FEMA No. | CAS | US/CFR | E-No. |
|---|---|---|---|---|
| Onion oil | 2817 | 8002-72-0<br>8054-39-5 | 182.20 | – |
| Onion extract/oleoresin | – | – | 182.20 | – |

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# 80 Orange

## *Citrus sinensis* L Osbeck (*Rutaceae*)

### Introduction

The sweet orange is believed to be a natural hybrid of pomelo (*Citrus maxima*) and tangerine (*Citrus reticulata*). This orange originated in South Asia, probably in India and Pakistan. It must also have grown in Southwest China and countries of what was formerly Indochina. Although it was at one time a wild plant, it is now cultivated commercially in different parts of the world. It is believed to have been introduced to Europe in the sixteenth century by the Portuguese, who brought it either from India or from Macao, an island near Hong Kong. Sweet orange, along with lemon, was introduced to the Americas by Columbus during his second voyage. It thrived in the West Indies and in Florida. Extension to California occurred in 1769 when the first mission was established in San Diego. In Brazil, the Portuguese, and in other South American countries, the Spanish, introduced the sweet orange. Before World War II, the countries in which quantity of cultivation was highest, in descending order, were the United States, Spain, Brazil, China, Japan, Italy, Palestine, North and South Africa, Paraguay, and the West Indies (NIIR Board 2009).

Sweet orange is the most widely cultivated and used citrus fruit. Because of natural hybridization and spread to different agro-climatic conditions, there are numerous subvarieties. Along with the sweet orange, there is also bitter orange, classified as *Citrus aurantium*.

The orange is relished both as a sweet fruit and a source of well-liked juice. Orange juice, orange squash, and orange marmalade are popular processed items. All the same, it is the oil in the peel that is valued as flavoring. Among all essential oils, orange oil may perhaps occupy the number one position in quantity now produced.

### Plant Material

Sweet orange is a trim evergreen tree with a rounded, generally uniformly spread crown. The tree grows to a height of 6–9 m and the crown has a diameter of 4–6 m. Its leaves are shiny and leathery, shaped oblong or elliptical. The length of the leaves is about 10 cm. Leaves have petioles with a narrow wing. The orange blooms in spring, and its flowers are white and grow in clusters. When the flowers appear, fruits from the previous season may still be on the tree.

The orange, liked for its sweet and rich taste, is grown all round the world. California produces varieties such as Navel and Valencia. In Brazil around 1820, a

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single mutation produced the navel variety of orange. The mutation resulted in the development of a second orange at the base of the original fruit. They appear to be conjoined twins, but the outside appearance is like that of the human navel, hence the name. Blood oranges are fruits with red streaks and whose juice has a dark color. Scarlet navel is a variety with dual fruit mutations. Because the navel varieties are a result of mutation, the fruits are seedless. Propagation is possible through grafts and cuttings. Valencia is a variety that ripens late in the season and is extremely valuable for juice.

Florida produces vast amounts of orange juice, leaving the peel to be used for extraction of oil. French Guinea in Africa is another region that produces a great quantity of sweet orange. The greatest increase in production occurred in the first half of the twentieth century. Brazil had a long history of orange cultivation, beginning in the sixteenth century. But it was only just before World War II that Brazil became a major producer and exporter of the fruit, juice, and peel oil. Spain's major area of cultivation is a narrow land between Malaga and Castellon on the Mediterranean coast. The Valencia variety is highly popular. An orange called Naranjito, meaning little orange, wearing the colors of the Spanish team, was the official mascot of 1982 soccer World Cup held in Spain.

Palestine, with its ideal weather conditions, is a major producer of oranges. It is reported that some trees there grow 2000 fruits per season. The Japanese industry increased during World War II, when it was necessary for the country to be self-sufficient. In India, oranges are quite popular, but extraction of oil by cold pressing is done only by major juice processors.

Bitter orange is an evergreen tree with a glabrous trunk. It grows to a height of 10 m. It has long but far from sharp spines, and fragrant flowers. Its fruits are bitter and sour.

## Essential Oil

Essential oil in the orange rind is separated by puncturing the oil cells or by pressing, during which both oil and juice come out. From this mixture, lighter oil can be separated by centrifugation from the heavier aqueous phase. A substantial quantity of oil is also distilled after the rind is separated from the edible inside.

In the United States, the earliest method of removing oil was to press the whole fruit to obtain the juice and oil as an emulsion and then separate the two by centrifuge. But this process has several disadvantages. Much of the oil gets trapped in the spongy peel. Some oil hydrocarbons get trapped in the juice, causing quality variation in the juice due to oxidative changes to the terpene hydrocarbons.

In recent times, highly sophisticated machines separate juice and pulp from the washed and cut citrus fruits, leaving the peel for separation of oil. Some of the machines developed are the Brown Automatic Citrus Fruit Juice Extractor and the FMC Whole Fruit Extractor. After the juice and pulp are removed, the remaining peel is pressed either between two rollers or by a tapering screw press, to remove all the oil through cold pressing. The clean oil is separated from aqueous phase by centrifugation.

In many orange-growing regions, the collection of oil used to be done by hand-operated processes such as the sponge method or the spoon scraping method. In the sponge method, the pulp is removed manually from a cut fruit and the oil from the peel is expressed by means of pressure exerted by hand. In French Guinea, the surface of the fruit with peel is scraped with a sharp spoon and the oozing oil collected into the spoon. In Japan, the fruits were cut into four pieces and the pulp removed by hand. The peel was immersed in warm water and then pressed between two stainless steel rollers moving at 20–30 revolutions per minute. This was then squeezed through canvas bags to remove solid particles.

In Brazil and in European countries such as Spain and Italy, early extraction methods were also hand-operated. Gradually, mechanization was introduced. This included moving pins to puncture the cells, mechanical rotating spindles to scrape the oil held in hand, and mechanical raspers to remove the flavedo from the whole fruit. Today, sophisticated machines are used all over the world; Brazil is now the leader in orange processing. The main products are the juice and the pulp; oil is a by-product.

Only certain principles of extraction are described here. For more detail, readers are advised to refer to specialized books on citrus processing.

Bitter orange peel contains essential oil, which is obtained by cold pressing. Leaves and small twigs of this orange give on distillation orange petitgrain oil with a yield of 0.2%. Freshly picked flowers of the orange tree, on steam distillation, produce orange neroli oil. On poor storage of orange oils, the hydrocarbon limonene is oxidized, giving a camphoraceous odor.

Terpeneless oil is produced by removing the terpene hydrocarbons such as limonene. In this way, oxygenated terpenes, which give the fine aroma and flavor, are concentrated. At the same time, oxidizable limonene is removed. Deterpenation is carried out by vacuum fractional distillation.

The main constituent of orange oil is limonene, which usually accounts for 90% of the oil. The oil also contains aldehydes, coumarins, acids, esters, and other oxygenated derivatives. Bitter orange oil also contains mainly limonene. In many respects, the chemical composition is similar but for its bitter constituents. Some flavonoids such as naringin and neohesperidin present in the peel are intensely bitter.

Volatile compounds and methyl esters of different oranges like blood orange, sweet orange, and bitter orange have been analyzed (Moufida and Marzouk 2003). Limonene is the most abundant constituent. Also identified were 18 fatty acids, mainly unsaturated acids, in the juice.

Using dialysis/pervaporation system; ultrafiltration/dialysis, and vacuum distillation, Auerbach (1995) has prepared folded orange oil. Limonene has been decreased from 95.60% to 76.40%, while total oxygenated compounds have increased from 1.90% to 19.50%. While limonene is the dominant component of orange oil, Lawrence (2009) has compiled recent investigations that detail the composition with respect to minor components. Those who wish to study the composition of orange oil in detail will do well to study this review.

Cold-pressed orange oil, according to the FCC, is an intensely yellow, orange, or deep orange oil with the characteristic odor and flavor of the outer part of the sweet orange fruit. It is miscible with dehydrated alcohol and with carbon disulfide and soluble in glacial acetic acid. The FCC allows the presence of antioxidants but recommends not to use orange oil that contains a terebinthine odor.

Physical characteristics recommended by the FCC are as follows.

| | |
|---|---|
| Optical rotation | +94° to +99° |
| Refractive index | 1.472–1.474 at 20°C |
| Specific gravity | 0.842–0.846 |

When a sufficient quantity of orange peel is accumulated, the peel is subjected to steam distillation to produce distilled orange oil, which, according to the FCC, is a colorless to pale yellow liquid with a mild citrus and floral odor. It is soluble in most fixed oils, in mineral oils, and in alcohol with haze. It is insoluble in glycerol and propylene glycol but an antioxidant can be added.

Physical characteristics are as follows.

| | |
|---|---|
| Optical rotation | +94° to +99° |
| Refractive index | 1.471–1.474 at 20°C |
| Specific gravity | 0.840–0.844 |

Cold-pressed bitter orange oil, as per FCC description, is a pale yellow or yellow-brown liquid with the characteristic aromatic odor of Seville orange and an aromatic and bitter taste. It is miscible with absolute alcohol and an equal volume of glacial acetic acid. It is soluble in fixed oils and in mineral oils. It is slightly soluble in propylene glycol and relatively insoluble in glycerol. It is affected by light and its alcohol solutions are neutral to litmus. It may contain a suitable antioxidant.

Physical characteristics as defined by the FCC are as follows.

| | |
|---|---|
| Optical rotation | +88° to +98° |
| Refractive index | 1.472–1.476 at 20°C |
| Specific gravity | 0.845–0.851 |

## Uses

Orange oil may be one of the most widely used natural flavors. It is used in a wide range of products such as confectionery, boiled sweets, cookies (especially in those with cream), ice creams, dairy products, and even chocolate-based sweets. It has use in orange-flavored soft drinks, popular worldwide. Another important use is as a flavor booster in orange juice- and pulp-based food products such as juice, syrup, and marmalade.

Bitter orange oil is also used in some of the above. In addition, it finds use in liqueurs, condiments, and relishes. Neroli and petitgrain oils are used as a lower priced citrus flavor and also in cosmetics and toiletries.

Limonene, which comes out during deterpenation, is a starting material for the manufacture of carvone, which is a flavoring chemical. Naringin and neohesperidin are also used for making some artificial sweeteners.

Orange oil also has anti-inflammatory and antimicrobial activities and is therefore used in medicinal preparations. Orange oils including neroli and petitgrain oils are also used as a flavor in some medicines.

## Identification Numbers

| | FEMA No. | CAS | US/CFR | E-No. |
|---|---|---|---|---|
| Orange oil, bitter, cold-pressed | 2823 | 68916-04-1<br>72968-50-4 | 182.20 | – |
| Orange oil, distilled | 2821 | 68606-94-0 | 182.20 | – |
| Orange oil, folded | – | 8028-48-6 | 182.20 | – |
| Orange oil, sweet, cold-pressed | 2825 | 8028-48-6 | 182.20 | – |
| Orange oil, terpeneless | 2822 | 8008-57-9 | 182.20 | – |
| | | 8028-48-6 | | – |
| Orange peel oil, sweet, terpeneless | 2826 | 68606-94-0<br>94266-47-4 | 182.20 | – |
| Orange terpenes | | 8028-48-6 | 182.20 | – |
| Orange, terpenes, natural | | 68647-72-3 | | – |
| Orange water, bitter | | 72968-50-4 | | – |

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# 81 Oregano

## *Origanum vulgare* L (*Labiatae*)

### Introduction

Oregano herb is more spicy after it is dried than when it is green and fresh. In ancient Europe, medical men felt that the herb could cleanse the brain and give better vision. It was also considered to be an antidote to the bite of poisonous spiders and scorpions.

Oregano is widely used in Greek, Spanish, and Turkish cooking. Italians have been using it in pizza for centuries. In early 1950s, due to the great mania for pizza all over the world, the production and sale of oregano went up. In the southern Philippines, oregano is used to mask the odor of beef, giving it a refreshing flavor.

Hippocrates, father of modern medicine, valued oregano as an antiseptic and curative for digestive and respiratory disorders.

### Plant Material

Oregano belongs to the mint family. It is native to Mediterranean countries and nearby Central Asian countries. Its close resemblance to marjoram leads to some confusion.

The plant is an erect perennial herb that grows to a height of 20–30 cm. It has tiny leaves that contribute toward its pleasant pungent aroma. The stem is reddish, the leaves greenish, ovate, and opposite. The color of the dried herb is pale grayish-green.

Oregano contains some triglycerides, proteins, and minerals. But its most significant constituent is the essential oil, which gives the dried herb its aroma and flavor.

### Essential Oil

The fresh herb gives an essential oil with a yield of 0.15–0.4%. As the oil is lighter than water, distillation poses no special problems. Oil of oregano may be confused with oil of sweet marjoram, but their great difference in optical rotation makes it easy to identify them.

In various studies, an essential oil yield of 3–4% on a dry basis has been reported. The principal components are carvacrol and thymol (Berghold et al. 2008; Stoilova et al. 2008). Many other terpenes and a large amount of sesquiterpenes are also reported.

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Spanish-type oregano oil, according to the FCC, is a yellowish-red to dark brownish-red liquid having a pungent spicy aroma reminiscent of thyme. It is soluble in most fixed oils and in propylene glycol. It is soluble with turbidity in mineral oil but is insoluble in glycerin. Phenol content should be 60–75% by volume.

Physical characteristics as defined by the FCC are as follows.

| | |
|---|---|
| Optical rotation | –2 to +3° |
| Refractive index | 1.506–1.512 at 20°C |
| Specific gravity | 0.935–0.960 |
| Solubility | 1 mL dissolves in 2 mL of 70% alcohol |

## Oleoresin

Powdered dry oregano herb, when extracted with hexane, gives an oleoresin with 3–4% yield. The volatile oil content of the product will be around 30% v/w.

Mediterranean oregano oleoresin is a dark greenish-brown viscous liquid with a strong thyme-like odor and mildly bitter taste. Oleoresin in the case of oregano is important, because of the large amount of sesquiterpenes that may not all distill with steam. Additionally, it contains many valuable nonvolatile constituents, some of which are antioxidants. The compounds reported are urosolic acid, oleanolic acid, protocatechnic acid, tilianin, sagittatoside, daucosterol, $\beta$-sistosterol, and stigmasterol (Wu et al. 2000).

## Uses

Oregano flavor is valued in European-style cooking. It goes well with sauces and tomato preparations; in meat preparations and roasts made from pork, beef, lamb, veal, chicken; cheese spreads; soups; in a wide range of vegetable preparations; and in all kinds of pizza. Both oil and oleoresin are very convenient to use in processed versions of the above foods.

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Oregano oleoresin/extract | 2827 | 8007-11-2 | | – |
| | | 84012-24-8 | 182.10 | |

## References

Berghold, H.; Wagner, S.; Mandl, M.; Thaller, A.; Muller, M.; Rakowitz, M.; Pasteiner, S.; and Boechzelt, H. 2008. Yield, content and composition of the essential oil of 5 oregano strains (*Origanum vulgare* L) depending on the developmental stage. *Zeitschrift fuer Arznei Gewuerzpflanzen* **13** (1), 36–43 (*Chem. Abstr.* **149**:219356).

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Wu, Rui; Ye, Qi; Chen, N.; and Zhang, G. 2000. Chemical constituents of *Origanum vulgare* L. *Tianran Chanwu Yanjiu Yu Kaifa* **12** (6), 13–16 (*Chem. Abstr.* **135**:2915).

# 82 Paprika

## *Capsicum annuum* L (*Solanaceae*)

## Introduction

Paprika is a faintly pungent, brightly colored chili that is grown as an annual plant. The same species produces the hot chili (red pepper). Chili is a gift of the New World to the Old World. When Spanish explorers went to the Americas, they were fascinated by the attractive, red-colored fruits. In colder climates of Europe, only brightly colored and milder chilis, such as paprika, thrive, unlike in the hotter climate of Asia where the strong and spicy varieties grow well.

Paprika is an important crop of Hungary and other neighboring Central and Eastern European countries. High-grade paprika to be used as such is also produced in Spain, Morocco, the United States, South Africa, and Israel. These are highly valued for their color and flavor, and used in fresh, dried whole, or dried and powdered forms. Extraction-grade paprika is lower priced and not so much valued for its appearance other than its red color and typical flavor.

Paprika has gained importance through the discovery of its ascorbic acid (vitamin C) content by the Hungarian scientist Albert Szent-Gyorgyi, for which he earned the Nobel Prize in 1937. In fact, capsicum fruits have a higher content of ascorbic acid than citrus fruits.

## Plant Material

The plant is an annual herb with a woody stem with branches. A single white flower ends up becoming a fruit, which is initially green but becomes red when ripened. There are different shapes, such as long and tapering with a length of 10–15 cm or roundish and thick with a relatively flat end like that of a bell pepper. Hungarian paprika is rich red in color with a shape that is tapering and pointed, while the Spanish variety is less appealing in appearance with a roundish shape.

Spanish paprika was at one time an important raw material for oleoresin. The Spanish extraction industry extended the raw material production to North African countries such as Morocco. Paprika produced in Zimbabwe and South Africa dominated the market for a while as a good raw material but has not made much progress in recent years. Similarly, Mexico started in the oleoresin industry with raw material grown locally, but the industry did not progress very well. The United States is a

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**Table 82.1.** Capsaicin and color content of paprikas from different regions

| Variety | Capsaicin Content (%) | ASTA Color of Chili | Yield of 100,000 cv O/R | Absorption Ratio of O/R |
|---|---|---|---|---|
| Byadege | 0.1 | 198.8 | 6.5 | 0.975 |
| Tomato Chili (India) | 0.08 | 133.4 | 4.0 | 0.982 |
| Wonder Hot (India) | 0.07 | 118.5 | 3.1 | 0.998 |
| South Africa | 0.03 | 221.0 | 6.3 | 0.968 |
| Zimbabwe | 0.007 | 288.0 | 7.6 | 0.960 |
| China I | 0.08 | 107.0 | 3.5 | 0.981 |
| China II | 0.04 | 212.4 | 7.1 | 0.980 |
| China III | 0.05 | 164.2 | 5.3 | 0.978 |
| Spain (low grade) | 0.02 | 100.7 | 4.4 | 0.974 |
| Peru | 0.06 | 188.0 | 5.7 | 0.974 |
| Ethiopia | 0.06 | 161.4 | 5.2 | 0.965 |
| Mozambique | 0.05 | 171.0 | 4.4 | 0.960 |
| Afghanistan | 0.09 | 177.7 | 5.5 | 0.974 |
| Azerbaijan | 0.04 | 156.0 | 4.7 | 0.962 |

O/R = oleoresin; 1 ASTA unit of color = 40.2 cv.

steady producer of oleoresin, mainly for its own use. In recent years, India, China, and Peru have emerged as producers of raw material for paprika oleoresin. Indian material has some capsaicin, but by successfully fractionating this out, India has emerged as a major supplier of oleoresin. Not only did the oleoresin resemble that of sweet paprika, but recovery of capsaicin also gave some economic advantage. China, with its vast area for cultivation, ideal cold climate, and encouragement given by the government to the extraction industry, may rise to the top of paprika oleoresin world. The extraction industry in Peru showed promise but the growth is uncertain.

India has two main varieties: Byadege and Tomato Chili. Both have perceptible levels of capsaicin and allied compounds of dihydrocapsaicin and *nor*-dihydrocapsaicin (for its chemical structure, see Chapter 25 on capsicum). A recent introduction to India is the Wonder Hot variety, which has a low yield of oleoresin but contains more of the red pigments.

The analysis of raw material from different countries is presented in Table 82.1. The units of color absorption ratio and others are explained later in the section on "units of color." In each category, there are top-, medium-, and low-grade varieties especially based on color. The values should therefore be considered as trends rather than as absolute values. It can be seen that low levels of capsaicin are present in paprika from Zimbabwe, South Africa, China (II and III), Spain, and Azerbaijan. In comparison, Indian varieties have a high level of capsaicin. In the matter of color content, Byadege compares favorably to samples from outside India. But the absorption ratio of Byadege is low, indicating a lower level of red pigments. Wonder Hot in particular and Tomato Chili both have a good absorption ratio. But lower yields of oleoresin and color make both of these expensive as raw material. By introducing fractionation to remove pungency, Byadege is now one of the most important raw materials of oleoresin paprika in the world.

## Chemistry

Generally, dry paprika pods contain 15% protein, 8% fat, 55–58% carbohydrate, and a fiber content of 20–22%. It is a rich source of ascorbic acid and also has small amounts of B vitamins and vitamins A and E. Paprika has no essential oil.

The most important constituents of paprika and its oleoresin are the xanthophylls, which are oxygenated carotenes. From earlier studies (Govindarajan 1987), the various constituents present can be summarized and presented as in Table 82.2. While carotenes are yellow in color, the oxygenated derivatives have orange and red coloration. Among these, the red pigments capsanthins and capsorubins are very important. Not only are these red pigments responsible for the appealing red color of the products, but they also get deposited in egg yolks of chickens that consume it as part of their feed. The chemical structures of the color compounds are presented in Figure 82.1 (Fisher and Kocis 1987). A Hungarian study about the development of pigments in maturing paprika pods shows 34 carotenes accounting for 1.3 g/100 g on dry basis. Of this, capsanthin accounts for 37%, zeaxanthin 8%, capsorubin 3.2%, and β-carotene 9%. For more details of the pigments in paprika, the review by Deli and Molnar (2002) is useful.

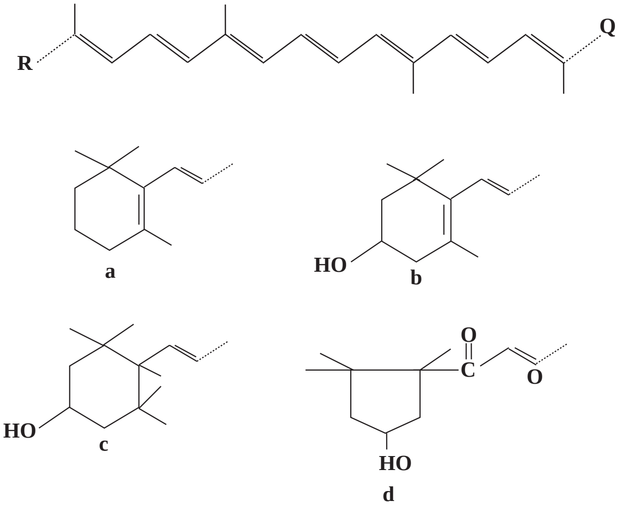
## Units of Color

The strength of oleoresin paprika is expressed as "color value" (cv). This value is empirical, originally intended to represent the highest dilution at which color is just

**Table 82.2.** Carotenoid pigments in paprika

| Component Present at Different Maturity | Color on TLC Plate | Relative Amounts as % in Saponified Extracts of Ripe Paprika |
|---|---|---|
| Chlorophyll a | Green | |
| Chlorophyll b | Green | |
| β-Carotene | Yellow | 11.6–18.6 |
| β-Carotene 5–6 epoxide | Yellow | |
| β-Carotene 5,6, 5′6′ diepoxide | Yellow | |
| β-Cryptoxanthin | Orange | 4.2–12.3 |
| β-Cryptoxanthin, mono- and diepoxide | Yellow | |
| Mutotoxanthin | Yellow | |
| Lutein | Orange | |
| Zeaxanthin | Orange | 2.3–6.5 |
| Antheraxanthin | Yellow | 1.6–9.2 |
| Violaxanthin | Yellow | 7.1–9.9 |
| Luteoxanthin a | Yellow | |
| Luteoxanthin b | Yellow | |
| Auroxanthin | – | |
| Neoxanthin | Yellow | |
| Cryptocapsin | Orange | 1.8–5.1 |
| Capsanthin | Red | 31.7–38.1 |
| Capsanthin epoxide | Red | 0.9–4.2 |
| Capsanthin isomers | Red | |
| Capsorubin | Red | 6.4–10.3 |
| Capsorubin isomer | Red | |

TLC, thin layer chromatography.



|  | R | Q |  | R | Q |
|---|---|---|---|---|---|
| **Capsanthin** | b | d | **Cryptocapsin** | a | d |
| **$\beta$-Carotene** | a | a | **Zeaxanthin** | b | b |
| **Violaxanthin** | c | c | **Antheraxanthin** | b | c |
| **Cryptoxanthin** | a | b | **Capsanthin epoxide** | c | d |
| **Capsorubin** | d | d |  |  |  |

**Figure 82.1.** Carotenoid pigments of paprika.

noticeable under standard conditions. But this subjective determination is now replaced by spectrophotometric reading at 460 nm. The color of paprika fruit is generally expressed as ASTA units; 1 ASTA unit is equal to 40.2 cv.

Nearly 40% of the paprika oleoresin produced is used for blending in chicken feed where red pigments are valuable. The red pigment and *trans*-capsanthin expressed as percentage of the total carotenoids estimated by spectrophotometer and HPLC, respectively, are significant. But a simple way of finding the level of red pigments is by spectrophotometric determination of the absorption ratio, which is the ratio of absorption at 470 nm over absorption at 455 nm. The higher the value, the higher the content of red pigment. A value of 0.96 shows a low level of red pigments.

## Oleoresin

Since the seeds do not contain color, they are removed. Fine powdering gives a better yield. But to avoid channeling, it is best to make the powder into pellets when extraction is carried out in a vertical percolator in batch countercurrent method. Continuous extraction, with a chain moving the powder, yields good results without pelletizing. In Spain, China, and countries other than India, the extraction solvent used is hexane. The miscella is then freed of the solvent to obtain oleoresin with a yield of 7–8% of oleoresin with 100,000 cv.

Indian paprikas, like Byadege, have some pungency and a capsaicin content of around 0.1%. Extraction is carried out using a mixture of acetone and hexane (25:75). The oleoresin so obtained will contain capsaicin along with color. This is then washed free of capsaicin using aqueous methanol or ethanol containing 20–30% water. It is possible to remove most of the capsaicin to obtain an oleoresin containing less than 200 ppm of capsaicin. Such an oleoresin is comparable to one produced using sweet paprika of Spain. The usual yield of oleoresin with Byadege is 5–6% of oleoresin of 100,000 cv. The capsaicin recovered is a valuable by-product. As already mentioned in Chapter 25 on capsicum, this capsaicin-rich fraction, often referred to as the color-pungent fraction, may show poor dispersibility in fixed oil. Therefore, it can be used in regular capsicum oleoresin in low proportions.

It is this innovation of the partitioning of capsaicin during the extraction of paprika, which is somewhat hot, that made India the dominant supplier of oleoresin paprika, although China is beginning to surpass India.

Oleoresin paprika is a clear, dark red, oily liquid, nearly free of hotness and without any off-flavor of rancidity or mustiness. The most traded grade is 100,000 cv followed by 40,000 cv. It is traded in smaller quantities in other color values from 20,000 to 160,000 cv.

As already mentioned for chicken feed grade, the red pigments should be high as they are the ones deposited in egg yolk. Generally, the acceptable limit of *trans*-capsanthin is above 38% of the total carotenes. That would mean that oleoresin paprika of 100,000 cv should have over 24 g of *t*-capsanthin/kg of oleoresin. The levels of the $\beta$-carotene and capsanthins are given in Table 82.3.

Generally, antioxidants are used to extend the shelf life of the color. In earlier days, processors used to add ethoxyquin as a cheap antioxidant. However, due to toxicity, this is now discouraged. Rosemary with its natural antioxidants is widely accepted (see Chapter 86 on rosemary). A very efficient antioxidant is tocopherol. Phenolic compounds in the following order have been found to be effective antioxidants: BHT, $\alpha$-tocopherol, *epi*-gallocatechin gallate, quercetin, rosmarinic acid, and 3-caffeic acid (Cuvellier and Berset 2005).

Paprika color is relatively stable to light compared with other natural colors such as curcumin, but the oleoresin requires storage in an environment free of light and heat. Heat treatment above 100°C will destroy some pigments.

**Table 82.3.** Analysis of paprika raw materials for carotenes and capsanthins

| **Variety** | **$\beta$-Carotene % (Area %)** | ***t*-Capsanthin % (Area %)** | ***C*-capsanthin % (Area %)** |
|---|---|---|---|
| Byadege (India) | 10–13 | 35–38 | 14–17 |
| Tomato (India) | 8–10 | 37–40 | 16–18 |
| Wonder Hot (India) | 5–8 | 38–43 | 18–22 |
| Chinese | 7–11 | 38–42 | 11–14 |
| South African | 11–13 | 39–41 | 12–14 |
| Zimbabwe | 10–12 | 35–38 | 15–17 |

## Analytical Method

The color as ASTA units is estimated using the ASTA method of measuring the absorption at 460 nm of oleoresin at specified dilution. Oleoresin manufacturers follow the method standardized by the Mayonnaise Salad Dressing (MSD 10 method) manufacturers. In this method, 1 g of oleoresin is diluted to 10,000 with acetone read at 462 nm. The absorption so obtained is multiplied by a factor of 66,000.

The red percentage of paprika oleoresin is determined by finding the absorption at 495 nm and at 422 nm and using the following formula:

$$\%\ \text{Red} = \frac{\text{Absorption at 495}}{\text{Absorption at 422}} \times 72.5 - 24.5.$$

The percentage of *trans*-capsanthin is calculated by the ratio of the area of *t*-capsanthin to the total area, when oleoresin is passed through an HPLC silica column using an eluting mixture of hexane and acetone 80:20. The absorption ratio is given under “units of color.”

## Uses

Paprika oleoresin is used as a natural color in a wide range of foods such as meats, seafoods, vegetables, soups, dressings, and sauces. Being a natural color, it can also be used in dairy products where use of synthetic color is discouraged. In a wide range of specialized meat products, such as sausages, frankfurters, and bolognas, the paprika color is found very attractive. Being essentially a spice oleoresin, it can be used to standardize tomato ketchup color, especially when poorly colored tomatoes are used.

One of paprika’s major uses is to mix it with chicken feed to yield a reddish yolk. Such eggs are used in parts of Japan, Korea, and Mexico. Saponification of the xanthophylls improves the ability to impart color to yolk (Galobart et al. 2004).

Capsanthin and capsorubin with 3-hydroxy-k-end group show strong quenching activity of singlet oxygen and inhibition of lipid peroxide. The pigment exhibits anti-lung cancer effect and can be a good chromopreventive agent in carcinogenesis (Maoka et al. 2004).

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Paprika oleoresin | 2834 | 84625-29-6 | – | 160 c |
| Carotenes and $\beta$-carotene | – | – | – | 160 a |

## References

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# 83 Parsley

## *Petroselinum crispum* Miller (*Umbelliferae*)

## Introduction

Parsley is used in European, American, and Middle Eastern cookery. Like coriander leaf, parsley is also used in various preparations. However, the intensity of flavor is milder for parsley than for coriander. Parsley is believed to have originated in Sardinia.

Early medical men, such as Dioscorides and Theophrastus, mentioned parsley's medical uses. The herb used as seasoning has curly leaves, different from the flat-leafed variety *Petroselinum neapolitanum*. There is also a variety that is cultivated for its thick roots known as Hamburg root parsley, used mainly in Central and Eastern Europe. However, these varieties of parsley are not generally made into extractives.

## Plant Material

Parsley is a cool weather plant, and so it is cultivated in temperate countries. In subtropical regions, the plant grows well at high altitude where the temperature remains low. The main growing areas are Mediterranean Europe, Algeria in North Africa, and the states of Louisiana and California in the United States. It is also cultivated in Western Europe, Canada, Japan, and Middle Eastern countries.

The plant is biennial with a green stem and many branches. The height of the plant is 60–65 cm. The leaves are sometimes divided and sometimes very curly. The herb, on drying, assumes a pale green color with a pleasant, spicy aroma. The flavor is tangy, sweet, and typically spicy.

The parsley has an essential oil, which is responsible for its fine flavor. It also has fatty oil, which has petroselenic acid up to 75% and has industrial use. Dried parsley has 22% protein, 52% carbohydrates, 5% fat, 10% fiber, and minerals, especially calcium and potassium.

## Essential Oil

Parsley herb oil is obtained from the aerial parts containing immature fruits. The yield is only 0.25%. The volatile oil obtained from the flowering top has excellent aroma characteristics but the yield is very low, only about 0.06%.

On the other hand, if the plant is allowed to grow, the fruit becomes mature. On drying, this is referred to as parsley seed. On distillation at commercial scale for 40–45 hours, parsley seed oil is obtained with a yield of 2.5%.

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The essential oil from the parsley herb contains apiole, which is a phenolic ether and contributes significantly to the flavor. It also has terpene hydrocarbon, *α*-pinene, and a small amount of myristicine. Some oxygenated compounds are also present in the oil from the herb.

Prakash (1990) reviewed the various investigations and reported the presence of myristicine, *α*-pinene, small amounts of aldehydes, ketones and phenols, and *β*-phellandrene. A large number of less volatile components have also been reported (Kasting et al. 1972), which may not be significant in volatile oil, but could be important in oleoresin.

A study of herb oil in Egypt using GC and GC-MS shows myrcene (23.75%), *β*-phellandrene (19.47%), and myristicine 8.79% (El-Nikeety et al. 2000). Other compounds have been detected, including 5-undecen-3-yne, cyclohexene, 1-methyl-4-(5-methyl-1-methyene-4-hexenyl), and 2-pyridinamine-4-methyl. Storage studies prove that the best conditions for storage of the oil are in a dark glass or aluminum bottle kept at freezing temperature.

The seed oil has 0.5–1.5% *α*-pinene, 3–5% *β*-pinene, 1–2% myrcene, 35–40% limonene, and 15–20% apiole. The seed has apiin, which is a glyceride of apigenin with sugar moities glucose and apiose.

Parsley seed volatile oil has a slight greenish tint when made in a commercial plant. It has a spicy aroma with a slightly bitter taste.

Parsley herb oil, as per the FCC, is a yellow to light-brown mobile liquid. It is soluble in fatty oils, in mineral oils, and in alcohol with haziness. It is only slightly soluble in propylene glycol and is insoluble in glycerol.

Physical characteristics of parsley herb oil as defined by the FCC are as follows.

| | |
|---|---|
| Optical rotation | +1 to –9° |
| Refractive index | 1.503–1.530 at 20°C |
| Specific gravity | 0.908–0.940 |

Parsley seed oil, according to the FCC, is a yellow to light-brown oily liquid with solubility characteristics similar to those of the herb oil. Physical characteristics as defined by the FCC are as follows.

| | |
|---|---|
| Optical rotation | –4 to –10° |
| Refractive index | 1.513–1.522 at 20°C |
| Specific gravity | 1.040–1.080 |

## Oleoresin

After grinding and extracting the dry herb with acetone, the oleoresin is obtained. The yield is about 4% and oleoresin contains 2–6% volatile oil. The oleoresin is an oily, viscous material with a spicy aroma and bitter taste. It is generally used after dilution for convenience of handling.

On extraction of the seed with solvents such as ethylene dichloride or a mixture of acetone and hexane, an oleoresin is obtained with a yield of 12–14% and volatile oil content of about 18%.

Extraction of the deoiled seed powder with hexane gives a resin with a yield of about 12%. The required quantity of previously produced volatile oil can be blended with this.

Parsley seed oleoresin is an oily liquid with dark brown color and a background green shade. It has pleasant, spicy aroma and slightly bitter taste.

## Uses

Parsley is used in various meat preparations, salad dressings, snacks, and baked foods. It is also well liked in some beverages and condiments. Both the oil and the oleoresin are convenient for processed foods of the above description. Parsley is reported to cause skin reactions, though this can be avoided through use of extractives, which do not contain allergens. The herb is recognized as having many medical qualities, some of which are present in the oleoresin.

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Parsley leaf oil | 2836 | 8000-68-8 | 182.20 | – |
| Parsley seed oil | – | 8000-68-8 | 182.20 | – |
| Parsley seed extract/oleoresin | 2837 | 8000-68-8<br>84012-33-09 | 182.20 | – |

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# 84 Peppermint

## *Mentha piperita* L (*Labiatae*)

## Introduction

Mint has a long history and in earlier days the most popular mint was peppermint. Although it is not used as much as spearmint, it is well known as a simple flavor of popular candies, with a particular emphasis on its cooling effect. Before the present sophisticated products became common, simple peppermint candies were quite popular with children.

Medical men such as Dioscorides and Pliny recommended peppermint for various ailments. In the olden days, mint twigs were used to welcome victorious gladiators (Farrell 1990). Romans and Jews used to grow the plant in connection with their houses of worship.

Peppermint is native to Mediterranean countries. Like Japanese mint, peppermint has a large percentage of menthol. The "pepper" part of the name is probably derived from the pungent taste of this mint.

## Plant Material

As in other mints, in peppermint the dried aerial part forms the herb from which the essential oil is obtained. The United States is an important producer of peppermint, though it is also cultivated in many countries of Europe, South America, and Asia, and in Australia.

Commercially grown peppermint has two varieties: English or black mint, and white mint. Black mint is a hardy plant whose yield is higher and is therefore more commercially important. There is very little cultivation of white mint, but the quality of oil obtained from this variety is considered superior. Black mint has a violet-brown stem, while white has a green stem. Both of these varieties are otherwise similar.

The stem is erect, branched, quadrangular, and naked or rarely covered with trichomes (Aktar et al. 1988). Leaves are opposite, petiolate, ovate to oblong, and lanceolate. They are 3–7 cm in length, serrate at the edges, glabrous or pubescent along their dossal veins, and punctuated with small oil globules. The surface of the leaf is glabrous and dark green in color. The color of the flower is light purple and flowers are arranged in terminal spikes. The calyx is glabrous and dotted and the corolla is purple, glabrous, and about 5 mm in length.

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Harvesting of the aerial part should be carried out when the plant starts to bloom (Prakash 1990). This will ensure a maximum yield of oil and menthol. The oil recovery suffers rapidly after the full bloom stage, due to the shedding of leaves. In fact, the loss of oil is greater when harvesting is delayed rather than when it is premature. The first formed chemical is the ketone menthone, which is transformed to menthol. The oil content increases up to a certain stage and then decreases. During this time, free menthol content increases. Hence, the time of harvest is critical.

Drying has to be carefully carried out to reduce loss of oil. Direct sun drying may result in a loss of as much as 24% due to evaporation and resinification (Prakash 1990), so the drying is done in shade when the loss can be restricted to well below 10%. Usually, a satisfactory partial drying can be obtained in 4–5 days. Processing of the dry herbage is more economical and convenient as the yield is obtained faster due to weakening of oil cells.

On steam distillation, peppermint oil can be obtained from the herb with a yield of 0.8–1%. Although peppermint has a large proportion of menthol, for making pure crystals of menthol, Japanese mint is more suitable. (For the chemical structure of menthol, refer to Chapter 62 on Japanese mint.) Almost 50% of the oil is made of l-menthol, which is responsible for the cooling effect. Next in importance is menthone. However, a recent Vietnamese study (Nguyen 2003) reported that the main constituent is l-menthone, which is present to a level of 47.60%. Menthone accounted for 24.10%, menthofuran 6.07%, 1,8-cineole 5.55%, and pulegone 4.22%. In another study (Orav et al. 2004), variations in composition of peppermint oils produced in different regions of Europe were examined. The yield obtained varies between 0.8% and 3.3% from the dried herb. A total of 46 compounds have been identified, representing more than 90% of the oil. The main components are menthone (11.2–45.6%), menthol (1.5–39.5%), isomenthone (1.3–15.5%), menthyl acetate (0.3–9.2%), limonene (1.0–5.9%), and *trans*-sabinene hydrate (traces to 6.2%). There are differences between samples from different regions. The ratio of menthol to menthone is found to vary between 0.04 and 2.8, and 1,8-cineole and limonene between 0.3 and 5.0. From the oils of Greece and Hungary, menthol is seen as the predominant constituent (37–40%). Russian peppermint oil contains only 1.5% menthol but has high menthone (38.2%), isomenthone (15.5%), and pulegone (13.0%). In Estonian oil, both menthol (31.6–35.8%) and menthone (37.9%–39.5%) are seen in high percentage. In an Iranian study, after hydrodistillation, menthol (36.24%) and menthone (32.42%) are also found to be the major constituents (Behnam et al. 2006). Studies also show weak antifungal activity for the essential oil.

Peppermint oil from the semiarid conditions of South India contains menthol (40.08%) as the major component; other constituents are limonene, menthone, menthofuran, pulegone, and menthyl acetate, among 62 peaks in all and 25 major peaks (Kaul et al. 2001).

According to the FCC, peppermint oil is a colorless to pale yellow liquid with the strong, penetrating odor characteristic of peppermint and a pungent taste together with a sensation of coolness when inhaled into the month. It can be rectified by distillation. It is soluble in alcohol and most vegetable oils but insoluble in propylene glycol.

Physical characteristics of peppermint oil as defined by the FCC are as follows.

| | |
|---|---|
| Optical rotation | −18° to −32° |
| Refractive index | 1.459–1.465 at 20°C |
| Specific gravity | 0.896–0.908 |
| Solubility | 1 mL dissolves in 3 mL of 70% alcohol |

## Uses

Mint leaves are widely used for garnishing preparations of Asia, Asia Minor, Europe, and America. In the production of processed foods, it is more convenient to use the oil.

Peppermint oil is an all-time favorite flavor for chewing gum, confectionary, ice cream, and sauces. It also has use in dental preparations and medical preparations for digestive disorders. Because of its cooling sensation, it is used in tobacco products. For the same reason, it is used in nonalcoholic beverages, soft drinks, and cookies (such as cream biscuits).

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Peppermint oil | 2848 | 8006-90-4 | 182.20 | – |
| | | 98306-02-6 | | – |
| Peppermint oleoresin/extract | 2848 | 8006-90-4 | – | – |
| Peppermint water/absolute | – | 98306-02-6 | – | – |

## References

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Farrell, Kenneth T. 1990. *Spices, Condiments and Seasonings*. New York: Chapman and Hall, pp. 133–136.

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# 85 Red Sandalwood

## *Pterocarpus santalinus* L (*Fabaceae*)

## Introduction

Red sandalwood is a magnificent tree whose trunk has an attractive natural food colorant. The tree is very important in Ayurvedic therapy because of its medical significance. It is an expensive wood very highly valued for making furniture and handicraft items. Its heavy, thickly packed wood is rated along with other valuable woods such as teak and rosewood. It is a tree that takes years to grow to full maturity, and conservationists are concerned about the population. It is now a protected plant and therefore, in recent times, its availability for extraction purposes has become a problem. For this reason, the pigment of red sandalwood has become less and less popular. A better program for nurturing the trees, tree planting, and exploitation of the chips and raw dust created as by-products during handicraft making can give an extended life to the pigments of red sandalwood, known as santalin. The pigment was studied in mid-nineteenth century by Pelletier and later marketed by E. Merek from 1960 (Verghese 1986).

## Plant Material

Red sandalwood is a large, attractive deciduous tree. It grows to over 10 m in height with a well-developed trunk and branches. The trunk has black-brown bark deeply cleft into rectangular plates. The heart wood is dark purple colored (Warrier 1995).

The tree has compound leaves, each with three to five leaflets. The leaflets are broad, elliptical, and obtuse, with pale green undersides. The surface of leaves is covered with fine hair. Its flowers are yellow, with simple or sparingly branched axillary or terminal recemates. The fruits are oblique pods which narrow into a stalk and are winged. The central hard portion contains the seed, which is reddish brown and smooth.

Both the wood and fruit are considered medicinally important. Small pieces of the wood have a good claret red color due to the natural pigment. In powder form, it gives off a faint odor resembling that of orris root.

The tree is very hardy and regenerates well. It grows on rocky or dry hills of 250- to 700-m altitude and sometimes on precipitous hillsides in hot dry climate, preferably with good drainage to avoid waterlogging.

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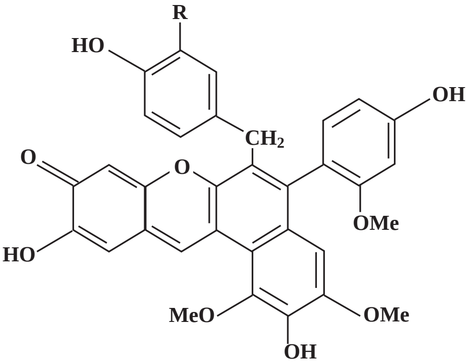

**Figure 85.1.** Santalin. Santalin A: R = OH; santalin B: R = OMe.

## Chemistry

The pigment consists of santalins A and B (Fig. 85.1). Santalin B has an additional methyl group compared with santalin A. There is an allied compound designated as santalin C whose structure is uncertain (Verghese 1986). The wood has essential oil and tannic acid.

## Extractive

The santalins are generally required to be a solid crystal powder. For trade purity, the measure at 475 nm absorbance should not be less than 1 when crystal powder is made into 0.01% solution in ethanol. This requires not only extraction but also avoidance of lipids and water-solubles.

The dry wood is made into small pieces and then coarsely powdered in a hammer mill. After being loaded into a vertical batch percolator, a washing with hexane is done by pouring solvent on top and allowing it to percolate by gravity. The lipid extract is taken out and disposed of after recovery of the solvent. The lipids, mainly essential oil, represent about 1%. The remaining powder is freed of hexane and then extracted with methanol by gravity percolation until the washings do not have any noticeable color. The combined methanolic miscella is freed of the solvent. The resinous matter is then boiled with water. The water extract is removed and disposed of. This process is repeated so that the residue obtained is a crystalline solid with good characteristic color and absorption value as described above. Experience shows that about four washings will yield a solid santalin of required strength. The solid is then dried and ground as per customers' specification.

For ease of handling, sometimes santalin in liquid form is needed. This is made by adding an equal weight of propylene glycol after solids appear on removal of methanol but before water washings.

Santalin crystals soften at 223–268°C depending on purity, but at 270°C they turn into a carbonaceous mass, as they decompose on melting.

## Uses

Red sandalwood extract is used as a natural color in foods and alcoholic beverages. Unrefined color has always been used in India. Until recently, the color was very much in demand in Europe for use in fruit products, beverages, and candies. However, the European Commission has not accorded it an E-number. This fact, along with the restriction of its use in India due to conservation of the tree, may make this attractive color less and less available.

Ayurvedic therapy attributes many useful medical properties to red sandalwood such as antipyretic and anthelmintic. Made into paste, it is applied to relieve inflammation, eye swelling, and boils. For bleeding piles, the powder is mixed in milk and ingested. The wood paste is regarded as a coolant and skin purifier.

## Analytical Method

The empirical method generally used by the industry is by measuring the absorbance at 475 nm. A value of 1 in a solution in ethanol at 0.01% strength is regarded as a satisfactory crystal powder.

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Sandalwood red | – | 84650-41-9 | 172.510 | 166 |

## References

Verghese, James. 1986. Santalin—a peerless natural colourant. *Cosmet. Toiletries* **101**, 69–71.
Warrier, P.K. 1995. *Indian Medicinal Plants*. Madras: Orient Longman, vol. 4, pp. 384–387.

# 86 Rosemary

## *Rosmarinus officianalis* L

## Introduction

The history and romance of rosemary are as fascinating as the herb itself. It has value as a flavor, fragrance, medicine, and, in recent years, antioxidant.

There is a story from a source at Trinity College library, Cambridge, that Queen Philippa's mother, Countess of Hainault, sent the first plant to England. Rosemary has since thrived there. In Spain, people consider it to be the bush that gave shelter to the Virgin Mary while traveling to Egypt, and in honor of that they refer to it as Romero, the pilgrim's flower, from which the popular name arose. In the Mediterranean countries, it is believed to give protection from witches and other evil spirits. All parts of the plant are considered useful to give protection from some disease or other and to generally uplift the health and spirits.

Ancient people used rosemary with the belief that it would strengthen memory and act as an emblem of fidelity. It is used at wedding and funerals. Rosemary was also cultivated in the kitchen garden as a symbol of the dominant influence of the mistress of the house. In Shakespeare's *Hamlet*, Ophelia distributes rosemary flowers as a symbol of remembrance. Rosemary leaves were used to flavor tea and wine. As for its medical benefits, rosemary is included in many recipes suggested for various diseases.

## Plant Material

Rosemary is a small evergreen shrub cultivated in Mediterranean countries such as Spain, Portugal, Italy, Yugoslavia, Turkey, Tunisia, and Algeria, as well as in the United States. The heavily branched plant grows to about 2 m. Its leaves are needle-like with a length of 2–3 cm, shaped like curved pine needles. The plant has small, light blue flowers.

Rosemary is propagated by seeds, cuttings, and division of roots. The healthiest plants are reported to be grown from seeds. The best condition for growth is light, somewhat dry soil. It prefers a bit of shade. When dried, the herb assumes a brownish-green color and has a tea-like aroma. However, when crushed, the aroma is more pleasant with a spicy and camphoraceous note. The taste is fragrant, spicy, and pungent, with a bitter note.

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## Chemistry

Dried rosemary has 4.5% protein, 17.5% fat, 47.5% carbohydrates, and 19% crude fiber. It has 6% ash, which represents calcium, phosphorus, and iron. It has vitamin A, ascorbic acid, and some B vitamins.

Rosemary has about 1–2% essential oil. In recent years, rosemary extract has become valuable as an antioxidant. Chen et al. (1992) have extracted oil with different solvents and studied the effectiveness of the various compounds acting as antioxidants. They include carnasol, rosmanol, carnosic acid, rosmaridiphenol, and urosolic acid. Rosmarinic acid, present in lesser quantities than carnosic acid, has gained importance due to its various biological properties including antimicrobial, anti-inflammatory, and antioxidant properties. Rosmarinic acid is a strong, water-soluble antioxidant used in seafood, extracts of natural color, cosmetic preparations, and packaged food. It is an orange-red powder that also dissolves in organic solvents. It is an ester of caffeic acid with 3,4-dihydroxyphenyl lactic acid. The structures of carnosic acid and rosmarinic acid are presented in Figures 86.1 and 86.2, respectively. One of the ways to obtain rosmarinic acid at a higher concentration is by extraction with supercritical $CO_2$.

## Essential Oil

The dry herb is first ground to powder using a hammer mill and then passed through a roller mill. In the latter, the particles are pressed so as to facilitate the entry of steam or solvent. After the herb is loaded in a stainless steel still, steam at low pressure is passed for 18 hours. The oil removed from the Florentine flask receiver will amount to about 1.5%.

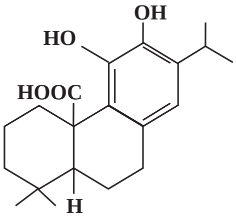

**Figure 86.1.** Carnosic acid.

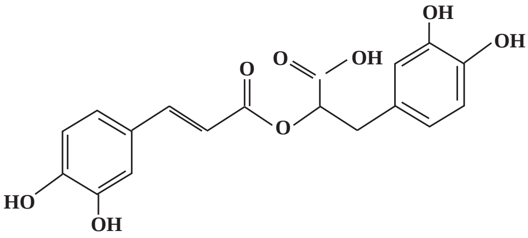

**Figure 86.2.** Rosmarinic acid.

Rosemary oil is a colorless to pale yellow oil with a warm, camphoraceous flavor. Oil is usually distilled from the upper portion of the plant's shoots, but the oil obtained from only the flowering top as per the British Pharmacopoeia is superior.

One study with 24 cultivars revealed that there are 34 chemical constituents to rosemary oil (Tucker and Marciarello 1986). A recent study reveals that its major components are $\alpha$-pinene (40–45%), 1,8-cineole (17.4–19.4%), camphene (4.7%–6.0%), and verbinone (2.3–3.9%) (Atti-Santos et al. 2005)

According to the FCC, rosemary oil is a colorless or pale yellow liquid with the characteristic odor of rosemary and a warm, camphoraceous taste. It is soluble in most vegetable oils but insoluble in alcohol and in propylene glycol.

Physical characteristics as defined by the FCC are as follows.

| | |
|---|---|
| Optical rotation | −5 to +10° |
| Refractive index | 1.464–1.476 at 20°C |
| Specific gravity | 0.894–0.912 |
| Solubility | 1 mL dissolves in 1 mL 90% alcohol |

## Oleoresin

Rosemary powder, after suitable drying, can be extracted to obtain the resin portion. With hexane, the yield is 3–4%. But with acetone, the yield can be as high as 13–14%. To this, previously collected oil can be blended. Rosemary oleoresin is a viscous liquid with a greenish-brown color and with characteristic herbal aroma.

While two-stage extraction, as above, is useful for obtaining oleoresin as flavor or fragrance, the present-day emphasis is on its value as an antioxidant. For this purpose, direct extraction is more useful as there is loss of nearly 50% of the carnosic acid content during the steaming required to obtain essential oil. For use as an antioxidant, the presence of oil is not significant. By direct extraction with hexane, a yield of 5–6% of extract with a carnosic acid content of around 20% is possible.

Generally, hexane extract yields a carnosic acid content of 18%. This can be boosted to double this strength by extraction with 30% aqueous methanol. Such a product is nearly a solid, which requires powdering. It can also be suitably diluted with additives or a weaker extract to obtain a liquid form, which is more convenient to use. Other constituents such as carnosic acid, urosolic acid, and rosmarinic acid also have antioxidant properties.

## Uses

Rosemary oil has use both in flavoring and fragrance. Because of its better balance, oleoresin is more convenient for use in foods. Rosemary flavor is used traditionally in Mediterranean cooking. When processed foods are made, it is more stable and practical to use oil and oleoresin.

In recent years, the most important use of rosemary is as an antioxidant. Carnosic acid at 3–5% is now the most effective natural antioxidant, after BHT and BHA, which are synthetic. Rosemary extract is used in paprika oleoresin as an antioxidant. Rosmarinic acid has biological properties such as antimicrobial, anti-inflammatory, and antioxidant characteristics.

## Analytical Method

Carnosic acid–containing extract is dissolved in methanol and injected into an HPLC C18 column with a mobile phase of acetonitrile and acidified water (with 0.5% acetic acid) in the ratio of 70 : 30. The detection wavelength is 230 nm and is calculated against a standard carnosic acid (Sigma-Aldrich). Rosmarinic acid is determined using the above column and solvent system of acetonitrile and acidified water (with 0.03% trifluoroacetic acid) in the ratio of 25 : 75. The detection wavelength is 280 nm and calculated against standard rosmarinic acid (Sigma-Aldrich). The AOAC does not give a method.

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Rosemary absolute | 2992 | 8000-25-7 | | – |
| Rosemary oil | 2992 | 8000-25-7<br>84604-14-8 | 182.20 | – |
| Terpeneless oil | – | 68917-54-4 | | – |
| Rosemary oleoresin/extract | 2992 | 84604-14-8 | 182.20 | |
| Rosemary water | – | 84604-14-8 | | – |

## References

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# 87 Saffron

## *Crocus sativus* L (*Iridaceae*)

## Introduction

Saffron is often called the “golden spice.” It gives a rich color and exquisite flavor. Dried saffron is generally regarded as the most expensive spice. It is comprised of the dried stigma and style top of a flower. One kilogram of dry saffron requires 50,000–100,000 stigmas; this gives an idea of the high cost involved.

It is possible that saffron was first used for its intense coloring ability. Later, Greeks and Romans used it for its fine scent quality in their luxurious baths. Oils with the aroma of saffron and other expensive spices were used by Egyptian pharaohs to anoint their bodies (Farrell 1990). By the end of the eighth century, Moors after their conquest of Spain brought saffron to Spain and Europe. Spain is an important producer of this expensive spice.

It is believed that the history of saffron cultivation runs over 3000 years. The precursor of the presently cultivated plant is *Crocus cartwrightianus*. A new mutant emerged when cultivators selectively bred plants with long stigmas. Some believe that saffron was documented by Assyrians in the seventh century BC.

Use of the spice in the treatment of several diseases during the last four millennia has been noticed in recovered records. In paintings dating from 1500 BC, the use of saffron as a medicine can be seen. There are records that Cleopatra used saffron in her bath to make her more desirable. Perfumers, physicians, and even ordinary people of the Mediterranean used saffron in ancient times as well.

## Plant Material

The saffron plant is a relatively small one, growing to a height of less than 12 cm. It has an erect thin stem and an underground corm or bulb. Domesticated saffron is usually not seen in the wild, mainly because its reproduction requires human assistance. The plant as we know it was developed by artificial selection in search of longer stigmas. The plant has become sterile. It has purple flowers, but the flowers do not produce germinating seeds. The plant has 5–12 narrow green leaves that grow nearly vertical to a length of about 40 cm.

Replanting is done by cutting up the underground corm, which consists of small, brown, starch-storing globules with a diameter of 4–5 cm when fully grown. The corm

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**Photo 25.** Saffron. See color insert.

survives for one season and then is cut into 6–10 cormlets. Each of these can grow into a new plant. The corms have fibrous roots. Each flower has a three-pronged style. Each style ends with a crimson stigma, usually 25–30 mm in length.

The saffron plant can grow in arid or semiarid lands of Mediterranean or North American regions. However, some irrigation is required. In regions such as Kashmir, which get good rainfall, irrigation is not mandatory. Saffron can survive the hot summer breeze as well as cold winters with frost and short periods of snow cover, though persistent damp or hot weather is harmful to the crop. It grows poorly in the shade and therefore it is best to plant it on slopes that face toward sunshine.

Planting is usually finished by the month of June. After summer, when the plant is dormant, the corms start growing the aerial parts, especially the leaves. By early autumn, the buds appear and by mid-autumn the flowering starts. Saffron blooms during a short period of 1 or 2 weeks. Harvest time is therefore busy. Further, the flowers, which appear at dawn, wilt during the day. So during a short time, the tedious process of harvesting by hand has to be carried out. One kilogram of flowers yields 72 g of fresh saffron, which, on drying, accounts for 12 g of dry saffron (see Photo 25).

Spain is the main saffron-producing country. Saffron is also grown in many other European Mediterranean countries, and in India, Iran, and China.

## Chemistry

The average composition of dry saffron is: moisture 15.6%, carbohydrates 13.35%, fixed oil 5.63%, essential oil 0.6%, crude fiber 4.48%, and ash 4.27% (Pruthi 1976). Higher levels of essential oil (1.37%) and fixed oil (13.4%) have also been reported.

The spice contains more than 100 volatile components that contribute toward its aroma. A large number of nonvolatile compounds, mostly carotenoid in nature, have been reported. These include zeaxanthin, lycopene, and $\alpha$- and $\beta$-carotenes. The specific yellow color of saffron is due to $\alpha$-crocin (Fig. 87.1), which is a digentibiose ester of *trans*-crocetin. The aglycone itself is water-soluble. Glyceride is therefore more hydrophilic and can be used to conveniently color water-based food products.

Another significant constituent of saffron is picrocrocin (Fig. 87.2), which is responsible for the spice's bitterness. It is an ether of safranal and a $\beta$-D-glucose moiety. When saffron is treated with heat, as in drying, picrocrocin yields free safranal and glucose. Safranal is volatile and is responsible for some of saffron's desirable flavor. Safranal is less bitter than the glycoside and is the major constituent (70%) of

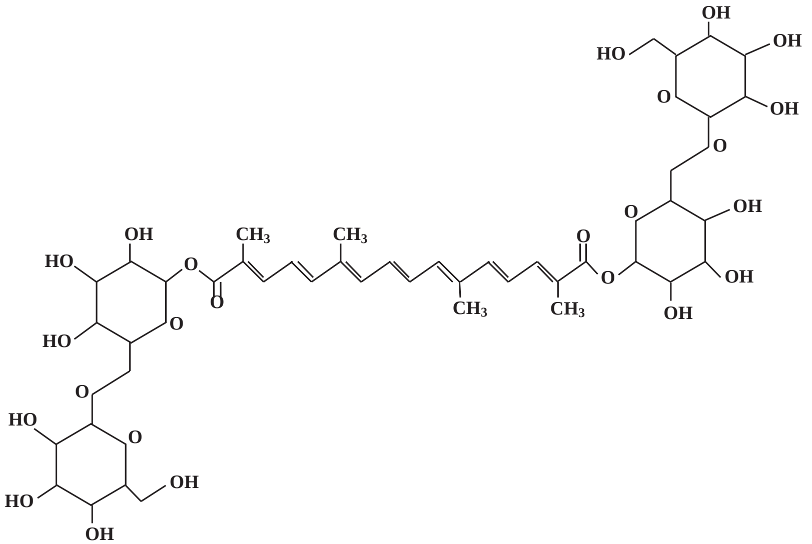

**Figure 87.1.** $\alpha$-Crocin.

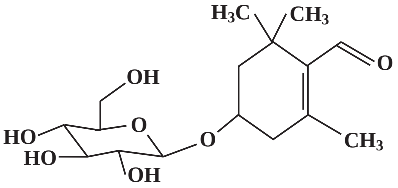

**Figure 87.2.** Picrocrocin.

the volatile fraction of the spice. An equally important aroma chemical is 2-hydroxy-4,4,6-trimethoxy, 2,5-cyclohexadien-1-one. Even though this constituent is present at a lower dose than safranal, it is a dominant contributor to the aroma which is "hay-like."

Changes to the aroma and coloring constituents subsequent to gamma irradiation for sterilization and preservation have been studied (Zareena et al. 2001). No significant qualitative changes are seen on irradiation, although a trained panel detects slight deterioration at 5 kGy. The effects of time and temperature of drying on safranal content have been studied (Gregory et al. 2005); drying at a high temperature of 80–90°C for 20 minutes, followed by continued drying at 43°C, gave better retention of safranal.

## Extractives

Because of the prohibitive price of saffron, it is not practical to make it into either essential oil or oleoresin. Reports indicate that very little extractives are made. It gives a volatile oil with a yield around 1%. The oil contains hydroxy-trimethoxy-cyclohexadien-one and safranal, the characteristic aroma compounds. With many nonvolatile constituents such as crocin (the dye), picrocrocin, and many carotenoids, it may be more realistic to make an extract. But here also the high cost of the spice is prohibitive. Nevertheless, the spice itself is a good flavoring and coloring material.

## Uses

Being an expensive flavor item, saffron is typically used only in exotic dishes made for special occasions. It is especially suitable for coloring and flavoring rice preparations and candies. Spanish *paella*, Indian *biryani*, Scandinavian baked goods, and special meat preparations of the United Sates and Europe are some of the dishes in which this expensive spice is used. It also makes an excellent additive to beverages, ice cream, confectionery, baked goods, and meats, if the price warrants its use. The high cost of saffron encourages people to use substitutes like turmeric or safflower in foods (sometimes claiming to be using saffron).

However, for connoisseurs who appreciate the exquisite flavor of saffron, with its metallic honey and hay-like notes, there is no substitute. It is nevertheless said that saffron is an acquired taste.

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Saffron extract | 2999 | 84604-17-1 | 182.20 | – |

## References

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# 88 Sage

## *Salvia officinalis* L (*Labiatae*)

## Introduction

Until relatively recently, sage was more prominently known as a medicinal herb than as a seasoning material. The name of the genus, *Salvia*, is taken from *salvere*, the Latin word for “to save.”

The herb sage has a rich history of exotic uses, such as to ward off evil, as an antidote for snake venom, and to increase the fertility of women. Romans attributed many curative properties to the herb. In the Middle Ages, it was cultivated in monastery gardens because of its curative properties. There are several cultivars of sage that are medicinally useful. However, the one used for flavoring purposes is the herb being described here.

## Plant Material

Sage is believed to be indigenous to European Mediterranean regions; the best quality sage comes from the Dalmatian Islands of Yugoslavia. Apart from many European countries of Mediterranean region, it is also cultivated in the United Kingdom, Portugal, Turkey, and the United States. The latter, however, imports some sage from Yugoslavia and Albania.

The sage plant has a somewhat woody and white stem with a height of about 30 cm. It has oblong leaves that are grayish to silvery green in color and numerous flowers, which are typically purple but sometimes bluish or whitish. The plant belongs to the mint family. The leaves of the young plant just before full flower set have the best flavor and the largest amount of essential oil. To retain its natural color and aroma, the herb is dried in the shade.

When crushed, the leaves of the herb give an aromatic and spicy aroma. Its flavor, which is herbaceous and balsamic, combines a bitter and astringent taste.

## Essential Oil

Ground dry sage of Moroccan origin gives a yield of 1.1% with 32 hours of commercial steam distillation in a stainless steel unit. The steam pressure is kept very low to obtain a slow distillation rate. The yield is reported to vary with region, climatic conditions, and season of picking.

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The terpene hydrocarbons noted in sage include α- and β-pinene, camphene, myrcene, and limonene. There is also over 20% of 1,8-cineole and camphor, besides some β-caryophyllene. The major component reported is thujone.

Egyptian sage oil has 28 volatiles, the most prominent of them being camphor (25%), α-thujone (22%), and β-thujone (18%) (Edris et al. 2007). 1,8-Cineole and α-thujone are the major constituents in the hydrodistillate of Tunisian sage (Fellah et al. 2006). Using GC-MS, more than 50 compounds have been identified. These include 1,8-cineole, fenchone, linalool, linanylacetate, sabinene, sabinyl acetate, and α- and β-thujone (Jirovetz et al. 2006).

According to the FCC, Dalmatian-type sage oil (*Salvia officinalis*) is a yellow to green-yellow liquid with warm, camphoraceous, and thujone odor and flavor. It is soluble in most fixed oils and in mineral oil. It is slightly soluble in propylene glycol but it is practically insoluble in glycerin.

Physical characteristics as defined by the FCC are as follows.

| | |
|---|---|
| Optical density | +2 to +29° |
| Refractive index | 1.457–1.469 at 20°C |
| Specific gravity | 0.903–0.925 |
| Solubility | 1 mL dissolves in 1 mL 80% alcohol |

As per the FCC, Spanish-type sage oil (*Salvia lavandulaefolia* or *Salvia hispanarium*) is a colorless to slightly yellow oil with camphoraceous odor that has a cineole top note. It is soluble in most fixed oils and in glycerin. It is soluble, usually with opalescence, in mineral oil and in propylene glycol.

Physical characteristics as defined by the FCC are as follows.

| | |
|---|---|
| Optical rotation | –3 to +24° |
| Refractive index | 1.468–1.473 at 20°C |
| Specific gravity | 0.909–0.932 |
| Solubility | 1 mL dissolves in 2 mL of 80% alcohol |

## Oleoresin

Deoiled sage herb, on extraction with hexane, yields 2.2% of resin, which can be blended with previously obtained volatile oil to desired specifications.

Direct extraction of ground dry sage with hexane gives an oleoresin with a yield of 5% and with a volatile oil content of around 10%. Extraction with a mixture of hexane and acetone (30 : 70) gives a yield of 7%, but the volatile oil content decreases to 6–7%.

Sage oleoresin is a dark brown, viscous liquid with a floral odor combined with mint aroma and mild sweetness.

## Uses

Sage is used in a wide range of meat preparations. It is indeed a widely used herb, especially in Western cooking. The leaves are sprinkled in vegetable preparations and cheeses. For processed foods of the above description, both oil and oleoresin are very valuable.

Its varied medicinal properties make sage oleoresin a favorite ingredient. The oleoresin also has good antioxidant properties. Sage oil also has use as a fragrance material in household insecticide and cleaning preparations.

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Sage oil | 3001 | 8022-56-8 | 182.20 | – |
| Sage oil, Spanish | 3003 | 8016-65-7<br>90106-49-3 | 182.20 | – |
| Sage oil, Dalmatian | – | 8016-64-6 | | – |
| Sage oleoresin/extract | 3002 | 8022-56-8<br>97952-71-1 | 182.20 | – |
| Sage absolute, Spanish | – | 8016-65-7 | | |

## References

Edris, A.E.; Jirovetz, L.; Buchbauer, G.; Denkova, Z.; Stoyanova, A.; and Slavchev, A. 2007. Chemical composition, antimicrobial activities and olfactory evaluation of *Salvia officinalis* L (sage) essential oils from Egypt. *J. Essent. Oil Res.* **19** (2), 186–189.

Fellah, S.; Diouf, P.N.; Petrissans, M.; Perrin, D.; Ramdhane, M.; and Abderrabba, M. 2006. Chemical composition and antioxidant properties of *Salvia officinalis* L oil from two culture sites in Tunisia. *J. Essent. Oil Res.* **18** (5), 553–556.

Jirovetz, L.; Buchbauer, G.; Denkova, Z.; Slavchev, A.; Stoyanova, A.; and Schmidt, E. 2006. Chemical composition, antimicrobial activities and odour descriptions of various *Salvia* sp. and *Thuja* sp. essential oils. *Ernaehrung (Vienna)* **30** (4), 152–159.

# 89 Savory (Sweet Summer)

## *Satureja hortensis* L (*Labiatae*)

## Introduction

Savory (summer or garden savory) is a spice which has been used in Europe for a very long time. There are two varieties: summer and winter savory. The former is the main variety cultivated, although leaves of both are used for seasoning. Summer savory is considered better.

Savory is often referred to in ancient literature. It is believed that Romans introduced it to the British Isles where it has become a popular item in the gardens. Its fine flavor was so well appreciated that it was included in many medieval dishes described more than a thousand years ago. Before the European conquest of the East when major spices like pepper became more available, herbs like savory had a great deal of importance in culinary practices. Early medical men also described many curative properties for savory.

## Plant Material

Summer savory is an annual plant that grows to a height of about 1 m. It has a strong taproot. Leaves are linear (1–1.5 cm long), elliptical, and opposite, with deep-pitted glands. Flowers are small, being axillary cymes, and colored white with small red to violet patches.

When dried, the herb assumes a brownish green color and forms the raw material for extractives. It has a fragrant, spicy aroma with mild medicinal note; its taste is mildly peppery. The dry herb has about 7% protein, 55% carbohydrates, 15% crude fiber, minerals, and some B vitamins. It has essential oil.

Savory has curative action for colic and flatulence and can act as an expectorant. It is an ideal flavor to be added to medical preparations, but its principal use is a food flavor.

## Essential Oil

The oil obtained by steam distillation is a yellow-brown, mobile liquid with an aroma resembling that of thymol. Studies on the constituents of the volatile oil have been well reviewed by Prakash (1990). The studies include oil from different regions. While a number of familiar terpenes and their oxygenated derivatives were reported, it is

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extremely difficult to summarize the results and give them as a simple composition of the oil. Studies in the last decade are few.

In one recent investigation of the savory herb available in Poland, the yield of volatile oil obtained is between 2.3% and 3.8% (Lis et al. 2007). Besides carvecrol (39–52%), γ-terpinene is present (31–39%). Analysis of Crimean savory shows 33 identified components, with carvacrol, *p*-cymene, and 1,8-cineole in significant amounts (Misharina et al. 1999). There are no reports available about savory oleoresin production.

## Uses

With its typical aroma, savory oil is a good flavoring for liqueurs, bitters, and other special alcoholic beverages, baked goods, and even confectionery.

## Identification Numbers

| | FEMA No. | CAS | US/CFR | E-No. |
|---|---|---|---|---|
| Savory summer oil | 3013 | 8016-68-0<br>84775-97-3 | 182.20 | – |
| Savory winter oil | 3016 | 8016-68-0 | 182.20 | – |
| Savory summer oleoresin | 3014 | 8016-68-0 | 182.20 | – |
| Savory winter oleoresin | 3017 | 90106-57-3 | 182.20 | – |

## References

Lis, A.; Piter, S.; and Gora, J. 2007. A comparative study on the content and chemical composition of essential oils in commercial aromatic seasonings. *Herba Polonica* **53** (1), 21–26 (*Chem. Abstr.* **149**:174595).

Misharina, T.A.; Golovnya, R.V.; and Beletskii, I.V. 1999. Determination of volatile components in the essential oil of summer savory by capillary gas chromatography. *J. Anal. Chem.* **54** (2), 198–201.

Prakash, V. 1990. *Leafy Spices*. Boston: CRC Press, pp. 89–93.

# 90 Spearmint

## *Mentha spicata* L (*Labiatae*)

## Introduction

Spearmint is the most popular and commonly used mint variety. Large manufacturers such as Wrigley and Cadbury Adams have made the flavor a great favorite of the young by adding spearmint to their wide range of chewing gums, which are popular in the United States, Canada, Australia, and Europe. In recent years, spearmint-flavored Mentos candies have been promoted all over the world, including Asia.

Even before its use in these well-known confectionery items, spearmint was a popular flavor in toothpaste for its freshening effect. A special cultivar of spearmint is quite popular in Morocco. It has a clear pungent note along with mild aroma and is used as a tea there. It is also used in some nonalcoholic beverages such as iced tea. It is believed that spearmint infusion may be beneficial in treating women having male characteristics, including growth of hair on the face and body. It probably helps by controlling the level of free testosterone in the blood, but this finding has not been confirmed.

## Plant Material

At one time, the United States was the major producer of spearmint, with cultivation spread throughout the states of Indiana, Michigan, and Oregon. Today, Washington State is a good producer. Spearmint is also produced in Europe and has recently taken hold in India.

Spearmint is a perennial plant which attains a height of 30–60 cm. It is an erect plant with branches. Leaves are sessile, smooth, lanceolate or oval-lanceolate, and sharply serrate. The leaves are 6–7 cm long, smooth on the upper surface and grandular on the lower surface (Aktar et al. 1988). The flowers are long, narrow, and have sharp points resembling a spear, hence the name "spearmint." Calyx teeth are hirsute or glaborous with corolla of about 3 cm in length. The stem of the plant may be with or without hair. In the United States, there is a closely related mint, *Mentha cardiaca* SF Gray. This is called Scotch spearmint and cultivated to a limited extent. The Central Institute of Medicinal and Aromatic Plants in Lucknow, India, has introduced improved clones of both spearmint and Scotch spearmint collected from the United States.

Spearmint thrives in loamy soil, which is mixed with farmyard manure. Propagation is by plant division. Although the spearmint plant produces leaves for a number of years, for healthy growth and good yield, it is better to plant it again each year.

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## Essential Oil

The aerial part of the plant consisting of the leaves and flowering tops represents the herb from which spearmint essential oil can be steam-distilled. On an average, the yield of oil is 0.6%. The oil is colorless, yellow, or greenish-yellow with a characteristic appealing aroma and flavor, which is believed to improve with age (Prakash 1990). The aroma is described as fresh, penetrating, minty, sharp, but pleasantly aromatic with a touch of herbaceous note.

The main constituent is l-carvone, which is also present in caraway oil and dill oil. Unlike Japanese mint, spearmint does not have a large percentage of menthol. Chemical studies of a sample from Bangladesh show 73.29% carvone, 7.59% *d*-limonene, and 3.83% dihydrocarvone (Chowdhury et al. 2007). Similarly, an analysis of Scotch spearmint oil shows 69.3% and 66.7% of l-carvone in two varieties (Liu et al. 2005). Limonene is also noted in substantial quantities. In a sample from Iran, among the 28 components noted, carvone is present only to the extent of 22.40%; linalool (11.25%) and limonene (10.80%) are also noticed (Hadjiakhoondi et al. 2000). In a Chinese study, carvone is not seen as a main component (Xu et al. 2003). The principal components among 39 are piperitenone oxide, 1,8-cineole, *dl*-limonene, $\beta$-myrcene, and $\beta$-pinene. However, Chen et al. (2003) in another Chinese study found carvone, limonene, and dihydrocarvone as the main constituents.

Lawrence (2008) has reviewed the analytical data of a large number of studies from all over the world. His own data from the United States show that the carvone content is between 58.47% and 69.44%. To study in detail many minor components present, the reader is referred to the review.

The FCC describes spearmint oil as a colorless, yellow, or green-yellow liquid having the characteristic odor and taste of spearmint.

Physical characteristics as defined by the FCC are as follows.

| | |
|---|---|
| Optical rotation | −48° to −5° |
| Refractive index | 1.484–1.491 at 20°C |
| Specific gravity | 0.917–0.934 |
| Solubility | 1 mL dissolves in 1 mL of 80% alcohol |

Oleoresin is not generally made in the case of spearmint. However, FEMA and CAS numbers have been allotted to the extract, indicative of its production. Some flavonoids and phenolic compounds including rosmarinic acid have also been reported (Zheng et al. 2006).

## Uses

Spearmint oil is a valuable flavoring material for chewing gum, confectionery, baked sweet foods, desserts, jellies, and a variety of other sweet items. Mint-flavored chewy and hard candies are extremely popular.

Spearmint oil is one of the most widely used flavors for toothpaste because of its effective mouth-freshening qualities. For the same reason, it is used in mouthwashes and dental preparations.

## Identification Numbers

| | FEMA No. | CAS | US/CFR | E-No. |
|---|---|---|---|---|
| Spearmint oil | 3030 | 84696-51-5 | 182.10 | – |
| Spearmint oil (terpeneless) | – | 8008-79-5 | | – |
| Spearmint oil Scotch | – | 91770-24-0 | | – |
| | | 8008-79-5 | | – |
| | | 91770-24-0 | | |
| Spearmint extract | 3031 | 84696-51-5 | 182.20 | – |

## References

Aktar, Husain; Virmani, O.P.; Sharma, Ashok; Kumar, Anup; and Misra, L.N. 1988. *Major Essential Oil-Bearing Plants of India*. Lucknow, India: Central Institute of Medicinal and Aromatic Plants, pp. 167–181.

Chen, Jing-wei; Wu, Zhen; Yan, Peng-fei; and Wang, Yu-ling. 2003. Study of chemical constituents of essential oil from *Mentha spicata* L. *Harbin Shangye Daxue Xuebao, Ziran Kexueban* **19** (1), 72–74 (*Chem. Abstr.* **141**:203287).

Chowdhury, Jasim Uddin; Nandi, Nemai Chandra; Uddin, Minhaj; and Rehman, Majibur. 2007. Chemical constituents of essential oils from two types of spearmint (*Mentha spicata* L) and *M. cardiaca* L introduced in Bangladesh. *Bangladesh J. Sci. Ind. Res.* **42** (1), 79–82.

Hadjiakhoondi, Abbas; Aghel, Nasrin; Zamanizadeh-Nadgar, Nasrin; and Vatandoost, Hassan. 2000. Chemical and biological study of *Mentha spicata* L essential oil from Iran. *J. Fac. Pharm.* **8** (1 & 2), 19–21 (*Chem. Abstr.* **135**:97190).

Lawrence, Brian M. 2008. Progress in essential oil. *Perfumer Flavorist* **33** (4), 36–38.

Liu, Shaohua; Qin, Qingyun; Yang, Weihao; and Zhang, Xiangmin. 2005. Analysis on chemical constituents of essential oils from Scotch *Mentha spicata*. *Zhongcaoyao* **36** (4), 505–506 (Chinese) (*Chem. Abstr.* **146**:189884).

Prakash, V. 1990. *Leafy Spices*. Boston: CRC Press, pp. 49–57.

Xu, Pengxiang; Jia, Weimin; Bi, Liangwu; Liu, Xianzhang; and Zhao, Yufen. 2003. Studies on chemical components of the essential oil from *Mentha spicata*. *Xiangliao Xiangjing Huazhuangpin* (**4**), 14–16 (Chinese) (*Chem. Abstr.* **141**:265544).

Zheng, Jian; Gao, Huiyuan; Chen, Guangtong; Yang, Xiaoke; Wu, Bin; and Wu, Lijun. 2006. Chemical constituents of the active parts of *Mentha spicata* II. *Shenyang Yaoke Daxue Xuebao* **23** (4), 212–215 (Chinese) (*Chem. Abstr.* **146**:468845).

# 91 Star Anise

## *Illicium verum* Hooker (*Magnoliaceae*)

## Introduction

Star anise is a star-shaped fruit with a flavor similar to that of aniseed. China is the major producer. There are many legends regarding the star shape and fine aroma in Chinese folklore. In recent times, it is becoming quite popular in cuisines all over the world.

## Plant Material

Star anise is the dried fruit of an evergreen tree that grows to a height of 10–15 m with a trunk thickness of 25 cm. Its leaves are 10–15 cm long and 3–5 cm in breadth. The leaves have an elliptical shape and pointed ends. Flowers are borne singly, which are either white or red in color. The reddish-brown fruit is star-shaped with eight points and opens on maturation and drying. Each follicle is boat shaped, hard, and wrinkled, and contains a smooth, hard, dark-colored seed. The follicle has an anise-like aroma. The seeds also have an aroma but at a lesser intensity. The spice is traded as star-shaped whole fruit. It is not generally available in ground form, perhaps because the aroma may be lost. In China, it is harvested between March and May.

The spice is indigenous to Southern China and Northern Vietnam. It is popular in the cuisines of Asia, especially those of China. It is an ingredient of hot curry powder in India. (See Photo 26.)

Star anise is also credited with some medicinal properties. As a remedy for rheumatism, it is taken like tea. It is also chewed after meals as an aid to digestion, although some people feel that as a remedy for colic it is not advisable. Shikimic acid, which is used for making antiflu drugs, is derived from the constituents of star anise, mainly anethole. Japanese star anise (*Illicium anisatum*), which is a close relative of Chinese star anise, is reported to cause neurological and gastrointestinal toxicity (Ize-Ludlow et al. 2004).

Decorticated seeds separated from the star contain 55% of fixed oil, the oil has a saponification value of 194.5, iodine value of 88.4, and acetyl value of 8.4. The main fatty acids are oleic 63.2%, linoleic 24.4%, stearic 7.9%, and myristic 4.4%.

## Essential Oil

On steam distillation, dried star anise yields 3–3.5% volatile oil. As in aniseed, the main constituent of the oil is anethole, which is present to a level of 85–90% (see Chapter 16 on aniseed).

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**Photo 26.** Star anise. See color insert.

Physical characteristics reported for such oil are as follows.

| | |
|---|---|
| Optical rotation | −2° to +1° |
| Refractive index | 1.5530–1.5582 at 20°C |
| Specific gravity | 0.978–0.987 at 25°C |

According to a recent study using GC-MS, the components of the star anise are found to be *trans*-anethole (94.37%), methyl chavicol (1.82%), and *cis*-anethole (1.59%) (Singh et al. 2005). A recent Chinese study based on supercritical fluid extraction and solvent extraction followed by GC-MS examination shows several peaks, with anethole as the main compound (Wang et al. 2007).

## Uses

The Chinese use star anise in meat preparations, especially in pork and chicken. Star anise oil can replace the spice in processed food. It can also be used in savory and sweet preparations made in other parts of the world where aniseed and its oil are used.

Star anise oil can find use in medicinal preparations for stomach and digestive ailments. It can also be a good source of anethole, which has additional uses (see Chapter 16 on aniseed).

## Identification Numbers

| | FEMA No. | CAS | US/CFR | E-No. |
|---|---|---|---|---|
| Star anise oil | 2096 | 8007-70-3 | 182.10 | – |
| | | 84650-59-9 | | – |
| Star anise extract | 2096 | 8007-70-3 | 182.10 | – |

## References

Ize-Ludlow, Diego; Ragone, Sean; Bernstein, Jeffrey N.; Bruck, Isaac S.; Druehowny, Michael; and Garcia Pena, Barbara M. 2004. Chemical composition of Chinese star anise (*Illicum verum*) and neurotoxicity in infants. *JAMA* **291** (5), 562–563.

Singh, Gurdip; Maurya, Sumitra; de Lampasona, M.P.; and Catalan, Cesar. 2005. Chemical constituents, antimicrobial investigations and antioxidant potential of volatile oil and acetone extract of star anise fruits. *J. Food Sci. Agric.* **86** (1), 111–121.

Wang, Qin; Jiang, Lin; and Wen, Qibiao. 2007. Study on chemical components analyzed by GC-MS and antioxidation of star anise extracts. *Zhongguo Tiaoweipin* (**3**), 38–42 (English) (*Chem. Abstr.* **149**:103057).

# 92 Sweet Flag (Calamus)

## *Acorus calamus* L (*Araceae*)

## Introduction

Sweet flag (also called calamus) has been historically regarded as a symbol of male love. The name is associated with a case of male to male attachment in Greek mythology. This aspect was symbolized by English poets in the nineteenth century. It has been suggested that the similarity of the spadix to the human penis is the reason for this symbology. In Japan, the sharp sword-like leaves of the plant represent a Samurai's fighting spirit. The name "sweet flag" is derived from its sweet aroma and the wavy edge of the leaves, which resemble a fluttering flag.

Calamus has been important in medicine and, to a lesser extent, in perfumery. In ancient Israel, calamus oil was used as an anointing oil in places of worship. In Egypt and some Asian countries, calamus had a reputation as an aphrodisiac. In Europe, the rhizome was added to wine and other specialty beverages. In North America, native Americans found it to be a stimulant. When chewed to a paste and applied to the face, calamus was supposed to suppress excitement and fear while fighting. Making a warm infusion and gargling or chewing a piece of rhizome is a good remedy for sore throat. In Ayurvedic therapy, it is regarded as a rejuvenating substance. Sweet flag has a long and interesting history of use in various traditional herbal treatments.

## Plant Material

The sweet flag plant is a semiaquatic, rhizomatous, perennial herb. It is generally seen by the side of ponds and in marshy places. The plant has long, sword-like, thick leaves with a wavy edge. The leaves grow from the rhizome and therefore there is no distinguishable stem.

The leaves are green and thickened in the middle. The flowers are light brown and densely packed in sessile cylindrical spadix. Its fruits are oblong turbinate berries with a pyramidal top. The seeds are few and pendant from the apex of the cells (Warrier 1994). The rhizome is the valuable part of the plant. It is much branched, cylindrical or slightly compressed, and almost as thick as the middle finger. The external color is light brown or pinkish brown. The inside is white and somewhat spongy.

Usually, the dried, rod-like rhizome is cut transversely into cylindrical bits of 1–1.5 cm in diameter. The upper surface shows triangular leaf scars. The pieces exhibit a strong odor and a characteristic acrid and aromatic taste.

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## Essential Oil

Disintegration of dried rhizome and steam distillation gives a yellow aromatic volatile oil with a yield of 1.5–4.6%. The optical rotation reported is rather high, at +9 to +35°, with refractive index being 1.500–1.508 (Pruthi 1976). In older reports, the constituents reported are *β*-asarone, *cis*-methyl isoeugenol, asaryl aldehyde, calamene, linalool, calamol, calameone, eugenol, methyl eugenol, azulene, pinene, cineole, and camphor. *β*-Asarone, at 76%, is the major component (Leung and Foster 1996). In fact, in Chinese oil, *β*-asarone is reported at 85%. *β*-Asarone is reported to be carcinogenic. Some other minor constituents reported include sesquiterpenes, acoragermacrone, acolamone, and isoacolamone. Acoradin, 2,4,5-trimethoxy benzaldehyde, 2,5-dimethoxy benzoquinone, and some nonvolatile constituents are also seen in the rhizome.

In this author's lab, the yield obtained in commercial production is 2.8%. The dry rhizome is reduced in size by pulverization in a hammer mill, followed by passing through roller mill. This is then steam-distilled using low pressure for 35 hours. Because sweet flag oil is heavy, better results are obtained in a small still capable of loading only 200 kg, where the total height is about 1 m, rather than a large still where the total height is over 2 m. The oil obtained is a yellowish to brownish slightly viscous oil with refreshing pleasant aroma.

The physical characteristics as defined by the FCC are as follows.

| | |
|---|---|
| Optical rotation | –0°.45′ to +1°.15′ |
| Refractive index | 1.5430–1.5525 |
| Specific gravity | 1.0350–1.1050 |

Studies using GC-MS show that sweet flag rhizome contains *β*-asarone (47.53%), L-calamenene (9.75%), isocalamendiol (5.41%), and pre-isocalamendiol (3.53%). However, the oil from the root has some different components. The root oil shows calamene (20.00%), aristolene (15.71%), acoradiene (14.19%), and *cis*-isoelemicin (9.51%) (Gong et al. 2007). In another analysis using GC-MS, 36 chemical constituents are identified, which account for 98.05% of the volatile oil (Zhang et al. 2007). The volatile oil (3.5%) is obtained by supercritical carbon dioxide extraction; on analysis, this reveals acorenone (13.4%), isoacorone (11.6%), sesquilavandulol (11.0%), dehydroxy isocalamendiol (7.7%), and *β*-asarone (5.5%) (Marongiu et al. 2005).

There is very little demand and production of sweet flag oleoresin. 2,4,5-Trimethoxy benzaldehyde has been isolated from petroleum ether extract (Hossain et al. 2008). This has very good pesticidal properties when tested against the flour beetle and rice weevil.

## Uses

Calamus oil has limited use as a food flavor. It is primarily used for its medical qualities.

*β*-Asarone is reported to be carcinogenic and therefore calamus and its oil were banned for use in food in 1968 by the U.S. FDA. However, the Indian Spices Board has included calamus in the list of safe spices.

The greatest use of calamus oil is as a fragrance ingredient in various cosmetics and toiletries. The root oil is used in hair tonics and antidandruff preparations.

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Calamus oil | – | 8015-79-0<br>84775-39-3 | – | – |

## References

Gong, Xianling; Dian, Linghui; Zhang, Lijian; and Cai, Chun. 2007. Study on chemical constituents of volatile oil in rhizome and root of *Acorus calamus* L. *Zhongguo Yaofang* **18** (3), 176–178 (Chinese) (*Chem. Abstr.* **149**:351138).

Hossain, Md. Shahin; Zaman, Shahed; Haque, A.B.M. Hamidul; Bhuiyan, Mohammed P.I.; Khondkar, Proma; and Islam, Md. Robiul. 2008. Chemical and pesticidal studies on *Acorus calamus* rhizomes. *J. Appl. Sci. Res.* **4** (10), 1261–1266.

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Marongiu, Bruno; Piras, Alessandra; Porcedda, Silvia; and Scorciapino, Andrea. 2005. Chemical composition of the essential oil and super critical $CO_2$ extract of *Commiphora myrrh* (Nees) Engl. and *Acorus calamus* L. *J. Agric. Food Chem.* **53** (20), 7939–7943.

Pruthi, J.S. 1976. *Spices and Condiments*. New Delhi: National Book Trust, pp. 215–217.

Warrier, P.K. 1994. *Indian Medical Plants*. Madras: Orient Longman, pp. 51–54.

Zhang, Yan-ni; Yue, Xuan-feng; and Wang, Zhe-Zhi. 2007. GC-MS analysis of chemical constituents of *Acorus calamus* volatile oil. *Zhongchengyo* **29** (1), 124–126 (Chinese) (*Chem. Abstr.* **147**:455793).

# 93 Tamarind

## *Tamarindus indica* L (*Leguminosae*)

## Introduction

The fruit of the tamarind tree is a very valuable flavor that is used in Indian cooking. It serves the role of acidulant. Of all the acidic flavoring materials used, tamarind is one of the most popular, particularly in South India where it is the essential ingredient in dishes such as *sambar* and *rasam*.

Although India is the major producer of tamarind, it is believed that it was first native to East Africa, especially Sudan. It was introduced to India many years ago, though the circumstances are shrouded in uncertainty. Because of this, many people erroneously believe that tamarind is indigenous to India. This belief is strengthened by the fact that India is the major producer of the crop.

After the discovery of the New World, tamarind was introduced to the American continent. In Mexico, tamarind grows wild. It also grows in countries in South and Southeast Asia such as Thailand, Indonesia, and Sri Lanka.

## Plant Material

The tamarind tree grows well in semiarid or somewhat humid tropical lands. It can withstand cold to some extent, but intense cold will be injurious to it, especially at a very young stage. It is a slow-growing, large tree with a height of about 25 m and a spread of 8–10 m. With its bright dense foliage, the tree is an attractive one. The trees that grow in America are generally smaller in size.

The leaves are evergreen, feathery, and pinnate. There will be 10–20 small leaflets of about 1 cm in length. The leaflets close when sun goes down. In very dry areas during very warm conditions, there can be some shedding of leaves. The five-petaled flowers are 2–3 cm in size and borne in small racemes, and have a yellow color with streaks of orange or red. The flower bud looks pink due to the outer color of the sepals, of which there are generally four. These are shed when flower actually opens.

The fruits are elongated, 10–15 cm in length, about 2 cm in width, and slightly curved. The irregularly curved fruits are formed in large numbers along young new branches. The fruit is covered with a fawn-colored shell and has five or six bulbous projections. As the pods mature, the inside is filled with juice. The juice becomes pulpy and changes color from light fawn to reddish-brown. The pulp further hardens to a pasty mass when the fruit fully matures and ripens. Across the pulpy mass, there are some hard strands of long fiber growing longitudinally. The pulp is edible and

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**Photo 27.** Tamarind fruits on the tree. See color insert.

forms the main part of the spice. It is sweet and intensely sour, naturally containing sugar and acid.

The pods will contain large, flat, glossy, chocolate-colored, hard seeds embedded in the edible pulp. Generally, the number of projections on the long fruit indicates the number of seeds inside. Indian tamarind fruits are generally big and long, with six to nine seeds, while those from American countries are short, with only three to six seeds. Photo 27 shows Indian tamarind fruits on the tree.

Rootstocks are propagated by seeds, though grafting is also sometimes adopted. Germination takes place in about a week's time. Tamarind grows into a large tree, and this fact should be kept in mind while planting. Trees bear fruits in 6–8 years, though grafted seedlings produce fruits earlier.

Tamarind thrives in a variety of soil; its preferred soil is well-drained and slightly acidic. Tamarind is adapted to dry conditions but watering in its young stage will be beneficial for growth.

Deshelled fruits consist of 55% pulp, 33% seeds, and 12% fiber. A typical analysis of tamarind pulp with 18% moisture will be 9.8% tartaric acid, 38.2% total sugars, 2.8% pectin, and 19.2% crude fiber (Pruthi 1976).

Tartaric acid is the characteristic acid of the pulp. Of the free sugar, 70% is glucose and 30% fructose, with only traces of sucrose.

The pulp is sold in different ways. Mostly it is made into a lump of some shape with seed and fiber not removed. A more refined product is pulp freed of seeds and fiber.

## Extract

Tamarind has no essential oil. However, its juice concentrate is becoming popular for use in both the household and in industry.

Tamarind juice is refined by boiling with water and removing the pulpy component. This is strained through a cloth or a sieve to remove seed and fiber. The processes of boiling with water and straining are repeated two to three times, until all juice matter is removed. The collected juicy extract is concentrated by evaporating water in an open steam kettle. Generally, the extract is concentrated to get a total soluble solid of 60–70° Brix, measured in a refractometer. The concentration can also be made with a vacuum process to get a finer product, but the cost will be higher.

The extracted juice is also made into granular coarse powder through the use of binding agents such as starch; this will be easier to handle in the household, as the powder will be free of stickiness and will be free-flowing. There are some variations in which concentrated juice is dispensed so that the acidulant is supplied in a more convenient way, free of seeds and fiber.

In Thailand and Indonesia, extraction is carried out with aqueous alcohol after tamarind pulp is left to ferment for a short time. Alcohol and most of the water are evaporated away to obtain a concentrate of above 60° Brix. The flavor will be slightly different.

## Seeds/Kernel

The inside of the seed is a rich source of starch, which is used in textile sizing. The jute industry also uses this for sizing, as it is relatively cheap. The starch also has potential for use in rubber and latex processing as a creaming agent and in food texturing.

## Uses

Concentrated aqueous extract of tamarind pulp, freed of seed, fiber, and grit (popularly called “tamcon”) is used in both the household and in industry as an effective sour flavor. In Thailand and India, soft sour-sweet ball-shaped confectionery items are gaining in popularity. A few thousand tonnes are exported from India to the Middle East, the United States, and Europe for use in various sauces such as Worcestershire sauce. For people of South and Southeast Asia settled in the West, concentrated extract allows the enjoyment of tamarind-based savory dishes.

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Tamarind extract | – | – | 182.20 | – |

## Reference

Pruthi, J.S. 1976. *Spices and Condiments*. New Delhi: National Book Trust, pp. 217–219.

# 94 Tarragon

## *Artemisia dracunculus* L (*Compositae*)

### Introduction

Tarragon, also called "dragon's-wort," does not have a long history. It was Ibr Baithar, a botanist and medical man from Arabia, who first drew attention in the thirteenth century to its fine flavor qualities. Later, the French made use of this herb in their cookery. It is also the flavor of a carbonated beverage popular in Russia and nearby countries such as Armenia, Georgia, and Ukraine.

### Plant Material

Tarragon was originally cultivated commercially in Russia but later spread to Southern European countries, Asia, and North America. The Russian variety is considered harsher, while the French is more delicately flavored.

Tarragon is a perennial shrub. It assumes a height of 1–1.5 m in height with slender and many-branched stems. It has bright green leaves, which are lanceolate, 3–8 cm in length and 2–6 cm in breadth. The flowers are 2–4 mm in diameter and grown in clusters of thirty to forty. The tiny flowers have a greenish-yellow to light yellow color. The plant is propagated by root cuttings or division.

Dried tarragon herb has 24% protein, 45% carbohydrate, 7% fat, and 7% fiber. It has minerals, small amounts of vitamin A, and some B vitamins.

### Essential Oil

References to tarragon oil are sparse. The oil is pale yellow with a greenish tint. The dried leaves of tarragon yield the essential oil, at 0.3–1.3% (Prakash 1990). Methyl chavicol is its main constituent (Pruthi 1976), though phellandrene and ocimene are also present.

Physical characteristics of the volatile oil are as follows.

| | |
|---|---|
| Optical rotation | +2 to +9° |
| Refractive index | 1.5028–1.5160 at 20°C |
| Specific gravity | 0.9 to 0.981 at 15°C |
| Solubility in alcohol | 1 mL dissolves in 6 mL of 80% alcohol |

$\alpha$-Pinene, camphene, $\beta$-pinene, limonene, *cis*- and *trans*-ocimene, methyl chavicol, *p*-methoxy cinnamaldehyde, 4-carene, $\alpha$-phellandrene, and linalool have been reported

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in the volatile oil (Thieme and Tarn 1972). Using GC-MS, Vestrowsky et al. (1981) have found a large number of terpene hydrocarbons and oxygenated derivatives. The major ones are sabinene (38.81%), methyl chavicol (17.26%), and methyl eugenol (28.87%). However, in Russian tarragon oil, the identified compounds are elemicin, *trans*-isoelemicin, eugenol, methyl eugenol, and *trans*-methyl isoeugenol (Brass et al. 1983). Some analyses have reported that methyl chavicol is present at levels of over 70% (Prakash 1990).

Extraction with hexane yields an oleoresin, which is a viscous liquid with dark green color. The volatile oil content depends on the raw material and can range between 8% and 16%. Both the volatile oil and oleoresin containing volatile oil have an anise-like odor typical of the herb.

## Uses

Tarragon is considered to be a fine flavor in French cuisine. It is used in meat, fish, and egg preparations. Fresh tarragon herb is also used for flavoring vinegar used in cooking.

Tarragon is an excellent flavor for a number of vegetable preparations, meats, sauces, and soups. The extractives are an ideal flavoring additive if the above items are made into processed food. Volatile oil is very convenient in the production of tarragon vinegar.

## References

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Prakash, V. 1990. *Leafy Spices*. Boston: CRC Press, pp. 95–98.

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# 95 Tea

## *Camellia sinensis* L (*Theaceae*)

### Introduction

Tea is a plant product consisting of the leaves and bud of a plant also called tea. Tea is often consumed as a hot brew. It is believed that after plain water, tea is the most consumed beverage in the world. While there are many specialized varieties, the most important ones are green and black tea.

Tea originated in Southeast Asia, at the point of confluence of Northeast India, North Burma, Southwest China, and Tibet. From there, the plant has been introduced to more than 50 countries. The Chinese have been using green tea as a beverage for many thousands of years. Green tea is popular in other Asian countries such as Japan, Korea, Taiwan, Thailand, and Vietnam.

Assam in India developed black tea by introducing a step of fermentation followed by a heat treatment, during which dark pigments are formed. The same process is followed in South India, Sri Lanka, and Kenya. The British were instrumental in the development of black tea. It was also in India that high-altitude tea known for its strong aroma was developed, mainly in Darjeeling in Northeast India and Nilgiris in South India. In recent years, Africa and South America have started to produce tea in significant quantities.

Importation of tea into England started in the mid-seventeenth century. Although Americans drink coffee more, tea is also popular in the United States. The Boston Tea Party was an act of defiance by the American colonists on new taxation proposals by the British. On December 16, 1773, American citizens threw crates of British East India Company tea from ships into the Boston Harbor.

### Plant Material

Tea is an evergreen plant growing mainly in tropical and subtropical regions. The plant, if allowed, can grow to a tree with a height of 9–15 m. For convenience in harvesting leaves, it is pruned and maintained at a height of around 1 m. The leaves are simple and alternate, and have a shape of elliptic-ovate or lanceolate with a serrated border. It is usually glabrous and leathery (Warrier 1994). It has white flowers, which grow in groups of one to four and have some fragrance. The fruits are depressed, three-cornered capsules with three seeds.

The plant requires about 125 cm of rainfall annually. High-quality tea grows best at elevations up to 1500 m. At high elevations, plant growth is uniform and slow, which

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encourages formation of a good aroma. The young leaves and bud, constituting 3–5 mm of plant material, are called flushes. Only flushes are picked as raw material for tea. During harvesting time, a plant will grow a new flush every 7–10 days.

## Chemistry

Both black tea and green tea contain around 3% caffeine, an alkaloid that stimulates the central nervous system upon consumption. Tea also has other related xanthine alkaloids such as theobromine, theophylline, xanthine, and dimethyl xanthine. For the structure of caffeine, see Chapter 41 on coffee.

Although tea leaves have some carbohydrates, proteins, fats, and small amounts of vitamins, the characteristic group of compounds of the tea leaves are polyphenols, which are responsible for its astringent taste. In recent years, polyphenols have gained importance as a valuable antioxidant that can help people to maintain health and prevent diseases caused by oxidative damage to cells. The most important of these is (–)epigallocatechin gallate, which accounts for around 10% of 25–30% of total polyphenols. Others present are (–)epicatechin gallate, (–)epigallocatechin, (–)epicatechin, (+)catechin, and (+)gallocatechin. It also has some flavonols, leucoanthocyanidins, free amino acids, and organic acids.

From the pioneering work of E.A.H. Roberts in the 1950s and 1960s, we have a fair understanding of tea's polyphenol makeup and the changes that occur during black tea manufacture. The phenolics are first converted to orthoquinones by the action of polyphenolase present. Subsequent reactions during the firing end in the formation of bisflavonols and theaflavin, and subsequent development of dark-colored thearubigins, which contribute to the color of black tea. Recently, ethyl pyrrolidinonyl teasinensin A, a new polyphenol having *N*-ethyl-2-pyrrolidinone moiety, has been isolated from black tea (Takashi et al. 2005).

The taste of black tea is a combined effect of polyphenols, amino acids, caffeines, theaflavins, and thearubigins. For aroma, some of the simple oxygenated terpenes, esters, alcohols, aldehydes, and ketones are important. For green tea, the taste is primarily astringency caused by different catechins, including epigallocatechin gallate, which is also recognized as a valuable antioxidant in green tea.

The volatile oil of green tea has been studied using GC-MS, and several compounds have been reported, among them linalool, geraniol, citronellol (Yang et al. 2002), 4-methyl-1-(1-methyl ethyl)-3-cyclohexan-1-ol, 1-methyl-4-(1-methyl ethyl)-1, 4-cyclohexadiene, eucalyptol, and (+)-4-carene (Liang et al. 2003).

## Extractives

Instant tea or soluble tea is made by hot-water extraction of either black or green tea. Instant tea is used as a convenient form to make the hot beverage. But it is also valuable for making cold tea drinks. Since the temperature is low, the extractives should be cold water-soluble. This is carried out in black tea by first making an aqueous extract and then wintering at 5°C to remove sediments by filtering, using an appropriate nylon filter cloth of 100–250 micron, or by using a super centrifuge. The extract can be made into a spray-dried powder.

In the case of green tea, blackening during extraction may occur. To prevent this, fresh green tea is simultaneously steamed and squeezed in a screw press to obtain a blanched extract in which enzymes are killed. For use in cold beverages, the extract is chilled to 5°C to precipitate sediments. This is then passed through a super centrifuge to remove heavier particles. The product can be spray-dried.

One of the major uses of green tea extractives is as a beverage rich in antioxidants. For this purpose, extraction can be carried out using 50% aqueous ethyl alcohol. It also requires winterization to remove sediments. The extract freed of alcohol is chilled to 5°C and filtered. The clear extract is either spray-dried or preserved by adding alcohol so that its strength is 20–25% of the liquid.

## Uses

Tea is one of the most popular hot beverages. Spray-dried extracts are used in cold drinks such as lemon tea. It is also used in some alcoholic beverages, frozen dairy desserts, candy, baked goods, and puddings (Leung and Foster 1996).

Green tea is now recognized as a nutraceutical with antioxidant properties; therefore, tea extract is used in health foods.

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Tea extract (including absolute) | – | 84650-60-2 | 182.20 | – |
| Caffeine | 2224 | 58-08-2 | 182.1180 | – |

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# 96 Thyme

## *Thymus vulgaris* L (*Labiatae*)

### Introduction

The dried leaves and flowering top of *Thymus vulgaris* form the herb known as thyme. There are many members of the *Thymus* family that find use as flavoring in some regions, but their production and use are limited.

Ancient Egyptians used thyme for embalming. Ancient Greeks felt that thyme was symbolic of bravery and used it in their baths and as incense in their places of worship. Romans also revered it as a purifier and used it to flavor specialty foods such as cheeses and alcoholic beverages. In the Middle Ages, Europeans believed that keeping a sprig of thyme nearby while one slept helped to prevent nightmares. Women used to consider it a privilege to hand over a small branch of thyme to warriors to help them face battles with courage. Dioscorides, the Greek physician, believed thyme could help clear the throats of people affected by asthma.

### Plant Material

Thyme is of Eastern origin, from countries such as China and Indonesia. It is now cultivated in Europe, North Africa, Australia, North America, China, and Russia.

The best conditions for its growth are warm, sunny weather and well-drained soil. Propagation can be through seeds, cuttings, or by division of the root. The plant has the ability to withstand freezing intervals and even some drought conditions.

Thyme is a perennial creeping shrub. It does not grow to a great height, generally less than half a meter. It has pale branches and narrow sessile leaves. Purple flowers appear in clusters.

Fresh thyme is sold as a sprig consisting of a small twig of woody stem with paired leaves and a cluster of small flowers. The leaves and flowering tops are used as a fresh leafy spice. But the whole aerial part, after drying, becomes the herb, which is the raw material for extractives. On analysis, dry herb shows 7% proteins, 5% fat, 44% carbohydrates, and 24% fiber. It has minerals, vitamin A, ascorbic acid, and B vitamins.

### Essential Oil

Thyme herb on size reduction and steam distillation yields 2–3% of essential oil. The oil is a colorless, yellow, or yellowish-red mobile liquid with the characteristic

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**Table 96.1.** Analysis of thyme oil from different regions

| **Reference** | **Mirza and Baher 2003** | **Asllani and Toska 2003** | **Raal et al. 2005** | **Porte and Godoy 2008** | **Sakovic et al. 2009** | **Jaafari et al. 2007** |
|---|---|---|---|---|---|---|
| Region | Iran | Albanian | Europe | Brazil | Yugoslavia | Morocco |
| Thymol % | 39.1 | 21.38–60.15 | 0.9–75.7 | 44.7 | 48.9 | 42 |
| Carvacrol | – | 1.5–3.04 | 1.5–83.5 | – | – | 85 |
| *β*-Caryophellene | 11.1 | 1.3–3.07 | 0.5–9.3 | – | – | – |
| *p*-Cymene | 10.5 | 7.76–43.75 | 4.3–34.4 | 18.6 | 19.0 | 23 |
| Terpinen-4-ol | | | Traces to 3.8 | | | |
| *γ*-Terpinene | | 4.2–27.62 | 0.9–19.7 | 16.6 | | |

pleasant odor of the herb and a mildly pungent, persistent taste. The volatile oil is also described as a pale yellowish-red liquid with a rich, aromatic, warming, herbaceous odor, yielding a sweet, phenolic, somewhat medicinal sensation on evaporation (Farrell 1990). The taste is described as warm, spicy, full-bodied, and herbaceous.

Several analyses have been carried out in recent years on thyme from different regions. The results given in Table 96.1 show that the main constituents are thymol, carvacrol, and *p*-cymene.

A study of European thyme (Raal et al. 2005) showed that thymol dominates in oils from Holland (65.5%) and Estonia (75.7%). Greek oil has a lot of carvacrol. Armanian oil has lower thymol content (17.0%), but is rich in neral and citronellol (32.5%), borneol (4.3%), citronellal (4.0%), 1,8-cineole (4.0%), methyl eugenol, and thymol acetate (7.5%). Brazilian oil has been noted to have 39 constituents, representing 95.1% of the oil, of which 28 have been identified (Porte and Godoy 2008). A sample from Yugoslavia showed antimicrobial activity (Sakovic et al. 2009). Further studies of the composition of thyme oil collected from Italy and Germany and those produced in Lithuania, Brazil, Jordan, and Cuba were compiled by Lawrence (2008). Gamma irradiation or e-beam ionization is found to have no effect on the oil composition.

According to the FCC, thyme oil is a colorless, yellow, or red liquid with thyme's characteristic pleasant odor and pungent, persistent taste. It is soluble in alcohol, in propylene glycol, and in most fixed oils.

Physical characteristics as defined by the FCC are as follows.

| | |
|---|---|
| Optical rotation | –3° to –0.1° |
| Refractive index | 1.495–1.505 at 20°C |
| Specific gravity | 0.915–0.935 |
| Solubility | 1 mL dissolves in 2 mL of 80% alcohol |

Thymol is the main characteristic constituent of the oil, with a melting point between 49 and 51°C. Thymol occurs as a white crystal soluble in water, alcohol, propylene glycol, and most vegetable oils.

## Oleoresins

Commercial extraction of powdered, dry thyme with hexane gives an oleoresin with 2.5% yield. The volatile oil content is 35–40%, though this can be diluted to the specifications of the customer. Thyme oleoresin is a yellowish-brown, viscous liquid with an herbal odor typical of the herb and with a spicy flavor with mild bitterness.

Thyme oleoresin is also described as dark green to brown, somewhat viscous, and at times semisolid, with an oil content of 50% v/w (Farrell 1990).

## Uses

Creole and French cuisine use thyme; for processed foods of this type, the oleoresin is convenient. Thyme is also used in salad croutons, fried chicken, poultry stuffing, and dressings (Farrell 1990). It can blend well in specialty sauces, soups, and preparations of meat, vegetables, and seafood.

Thymol, the main ingredient in thyme oil, has use in medicines and cosmetics. Thymol is also used in beverages, soups, baked goods, and confectionery.

## Identification Numbers

| | **FEMA No.** | **CAS** | **US/CFR** | **E-No.** |
|---|---|---|---|---|
| Thyme oil | 3064 | 8007-46-3<br>84929-51-1 | 182.20 | – |
| Thyme extract | – | 8007-46-3 | 182.20 | – |
| Thymol | 3066 | 89-83-8 | 172.515 | – |

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# 97 Tomato

## *Solanum lycopersicum* L (*Solanaceae*)

### Introduction

The tomato is a fruit primarily used as a vegetable. It is not very sweet but has a fine flavor with some sourness. These qualities make it a favorite item in the kitchen. Its botanical name is synonymous with *Lycopersicon lycopersicum* and *Lycopersicon esculentum*. *Lyco* means “wolf” and *persicum*, “peach”; it is named after the wolf because it was wrongly thought of as toxic due to its membership in the *Solanaceae*, or nightshade, family.

The tomato is a gift from the New World to the Old World after the European conquest of America. The progenitor of this fruit is probably an herbaceous green plant with small green fruits growing in the highlands of Peru. The Aztecs and other civilizations used the tomato for cooking as early as 500 BC. It was Cortez, the Spanish conquistador, who may have been the first to transfer the small yellow tomato to Europe after he captured the Aztec city of Tenochtitlan, now Mexico City, in 1521. However, others believe that Christopher Columbus took the tomato to Europe in 1493.

But it is only in recent years that the fruit was gained its reputation as a producer of valuable pigment. Lycopene, the characteristic color constituent, is also regarded as a valuable nutraceutical.

### Plant Material

The tomato plant is a perennial plant, which has a weak woody stem and grows to a height of 1–3 m. The leaves are pinnate with a length of 10–25 cm and with five to nine leaflets on the petiole. Each leaflet has a serrated border. Both the stem and the leaves are hairy. The flowers are yellow, 1–2 cm in diameter, and are borne in a cyme of 3–12.

Tomatoes are grown all around the world as a popular vegetable. In different agro-climatic conditions, there are many variations in the characteristics of the plant and fruit. According to FAO statistics, world production in 2007 was over 126 million tonnes, of which China accounts for over 33.6 million tonnes, the United States 11.5 million tonnes, Turkey 9.92 million tonnes, India 8.59 million tonnes, and Egypt 7.55 million tonnes. A considerable quantity of this is made into ketchup, which is undoubtedly the most consumed sauce in the world. Only a small percentage of

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**Figure 97.1.** Lycopene.

tomatoes go into production of carotene color. Naturally, the red variety is most popular for this purpose.

## Chemistry

Lycopene is the principal pigment of the tomato, accounting for 80–90% of the total carotenoids (Fig. 97.1). Though it is a hydrocarbon, it is intensely colored. It has no carbon rings at the ends as in $\beta$-carotene and is an aliphatic compound with 13 double bonds, all of which are *trans*. Lycopene is stable like other carotenes but on storage needs protection from light. It is oil-soluble in very dilute concentrations, as it tends to crystallize at even slightly above 100 ppm.

Lycopene is also produced synthetically. It comes as dark red to violet crystals.

## Extractives

Tomato lycopene extract is made by using red tomatoes and solvents such as ethyl acetate or hexane. Such tomatoes rich in carotenes will have 200 ppm of lycopene. The combined miscella is freed of the solvent by evaporation to obtain a rich lycopene extract (Emerton 2008).

Lycopene and $\beta$-carotene from ripe tomato pulp and skins are extracted using supercritical carbon dioxide at pressures between 2000 and 4000 psi and temperatures at 40–80°C. With the proper combination of operative conditions, it is possible to obtain a product with 87% lycopene and 13% $\beta$-carotene (Cadoni et al. 1999). By addition of 5% ethanol as cosolvent, 53.93% of lycopene is extracted by supercritical carbon dioxide with a flow rate of 4 kg/hour, at 55°C and 300 bar pressure (Baysal et al. 2000).

Rozzi et al. (2002) extracted lycopene from tomato skins, which, along with seeds, are the waste of tomato processing. Experiments with temperatures between 32 and 86°C and varying pressures show that lycopene extraction increases with a higher temperature and pressure, resulting in an extraction of 61% of lycopene.

Recently, an environmentally friendly solvent, ethyl lactate, has been suggested as an excellent solvent for extraction of both *trans*- and *cis*-lycopene. Use of an antioxidant such as $\alpha$-tocopherol during extraction increases the efficiency of extraction and the extract's nutritional value (Ishida and Chapman 2009).

## Analytical Method

The FCC describes a spectrophotometric method for determination for synthetic lycopene, by dissolving it in cyclohexane and measuring at 476 nm.

## Uses

Tomato extract provides nearly pure lycopene as it accounts for 80–90% of the carotenoids present. It has been given an E-number and can be used as a natural color. Being a hydrocarbon with 13 double bonds, it has intense color and good oil solubility. Oil suspensions are used in extruded foods, baked products, cheese, butter and other spreads, pasta, soups, gravies, and sauces (Emerton 2008).

Lycopene extract can be made water-dispersible by using an emulsifier such as polysorbate or glyceryl monooleate. Such water-soluble color is used in beverages, ice cream, dairy desserts, candies, meat products, soups, and gravies. The only negative aspect of tomato lycopene is that it may impart a tomato flavor where one is not desired.

## Identification Numbers

| | FEMA No. | CAS | US/CFR | E-No. |
|---|---|---|---|---|
| Tomato extract | – | 90131-63-8 | – | – |
| Lycopene | – | – | – | 160d |

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# 98 Turmeric

## *Curcuma longa* L (*Zingiberaceae*)

## Introduction

Turmeric is a spice valued in the international market more for its bright yellow color than for its flavoring properties. Nevertheless, in India, since ancient times, it has been considered important for its flavoring, coloring, and therapeutic uses. Because of this, it is regarded as an auspicious material and is even used in Hindu religious ceremonies. Turmeric acquired more importance when the Ayurveda, the ancient Indian system of medical practice, was systematically developed by masters such as Caraca and Sasruta.

Like other spices, turmeric also traveled from the Eastern to the Western world, perhaps through the Mediterranean countries. Turmeric is present in the Assyrian list of herbs in 600 BC. It was also found to have been entered in the *Materia Medica* compiled by Dioscorides. In the thirteenth century, Marco Polo mentioned turmeric as growing in the Fokien region of China. He noted its similarity to the color of saffron; hence, in medieval times, turmeric was known as Indian saffron. Although turmeric was considered inferior to saffron as a food color, it is valuable for its therapeutic qualities.

It is believed that the turmeric plant originated in the hills of Western Ghat of Southwest India and spread to other regions of India and Southeast Asia. It is probable that from there it was spread to China, the Caribbean region, and South America by the Spanish. It probably spread later to some regions of Africa via the colonial powers.

For some time, both in East and West, turmeric had importance as a dye for coloring cotton and silk. The dye can be applied without a mordant although the color soon fades, especially on exposure to the sun. Development of synthetic fast dyes sounded the death knell to the use of turmeric as a fabric dye.

Although many South and Southeast Asian countries, as well as other tropical regions, grow turmeric, India remains the major producer. Several cultivars are grown in South India. Some of the major trade types are Alleppey, Erode, Sangli, Rajapuri, and Nizamabad.

## Plant Material

Turmeric is an herbaceous perennial plant (see Photo 28), which grows to a height of 0.5–1 m in height. The leaves are clear green, acute at the ends, and broad. The flowers are pale yellow and arise from two buds at the axil. The rhizome is the main product.

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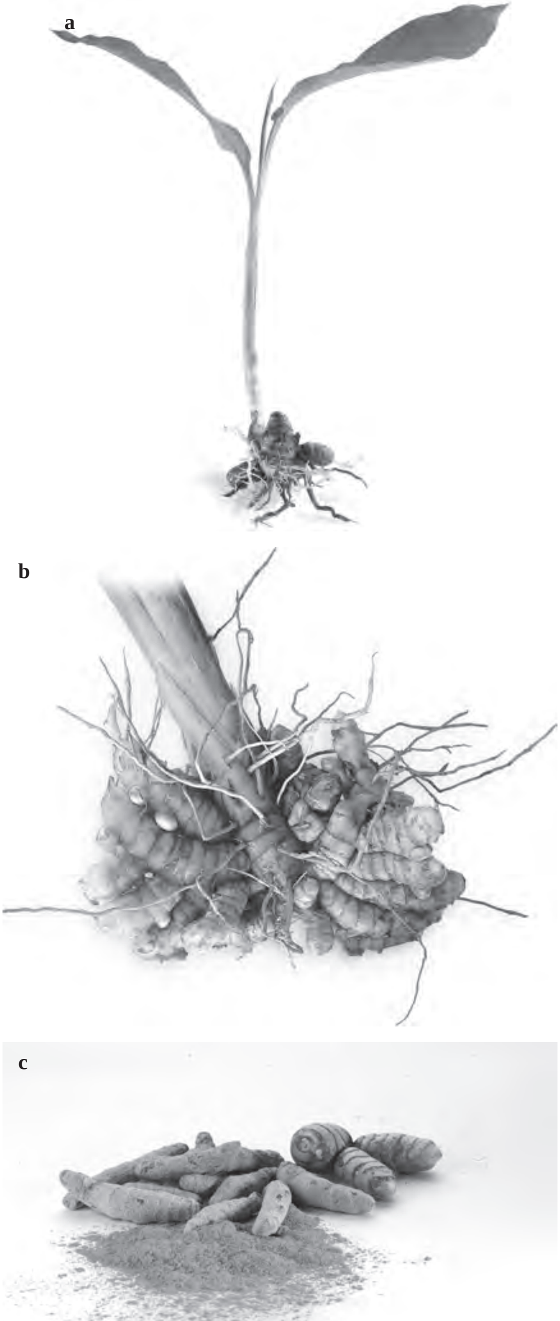

**Photo 28.** (A) Whole growing turmeric plant. (B) Uprooted turmeric. (C) Foreground, powder; left, dried turmeric; right, fresh fingers of turmeric. See color insert.

Propagation is carried out by planting a cut portion of rhizome. Since the plant has to be plucked every year to harvest the valuable rhizome, turmeric has to be treated as an annual plant, needing replantation every year.

The rhizome has two parts: a bulbular primary tuber, known as “mother” turmeric; and some cylindrical, multibranched, secondary rhizomes growing from the mother turmeric, known as “finger” turmeric. Both parts have transverse leaf scars and dents from root scars. There are also true roots emerging from the rhizome.

The dried planting material of the previous season gets weakly attached to the rhizome. While harvesting is done by pulling out the plant, this portion remains stuck in the earth and will not be removed with the rhizome. For a long time, it was not recovered. However, in recent years in the Indian state of Tamil Nadu in some regions farmers are now digging this material out of the earth. It is easy to dry and is the source of the curcumin-rich Pazhangali grade turmeric that oleoresin manufacturers buy. It is not harvested in other regions, where farmers claim that the cost of digging and recovering is not worth it.

Because they contain large amounts of starch, the freshly harvested rhizomes do not dry easily. To facilitate drying, rhizomes are boiled in water for about an hour or so while the starch is gelatinized. If inadequately boiled, when the turmeric finger is broken in half, the juicy extract will form threads between the two pieces. When fully gelatinized, this will not happen. Then the wet rhizomes are sun-dried. On completion of drying, the dried piece will break cleanly. Even though the yellow pigment is sensitive to sunlight, there is no loss during sun drying as the pigments are well protected inside the rhizome.

It is customary to slice mother turmeric into four longitudinal pieces, so that it becomes nearly as thin as finger. Both mother and finger turmeric are used, but the finger turmeric has a slightly higher value. In the export market, there is some demand for polished turmeric fingers. This is carried out by rotating the fingers in a metal drum with rough sidewalls. Polishing gives a bright, appealing yellow color and commands a higher price.

Turmeric, when dry, has an essential oil content of 2–7%, but the oil is not valued for its aroma characteristics. There is some demand for its medicinal value. The active component of turmeric is curcumin, the bright yellow food color, which is present to a level of 1.5–5.5%. Table 98.1 represents rhizomes grown in various important growing areas and their analyses (Krishnamurthy et al. 1976).

## Chemistry

Dry turmeric has 8.6% protein, 8.9% fat, 63.0% carbohydrate, and 6.9% of crude fiber. It has minerals and water-soluble vitamins such as thiamine, riboflavin, niacin, and ascorbic acid at low levels. As mentioned, it also has volatile oil and curcumin pigment.

Typical sesquiterpene compounds known as turmerone are characteristic of turmeric oil. They are ar-turmerone, $\alpha$-turmerone, and $\beta$-turmerone. ar-Turmerone has an aromatic ring, as shown in Figure 98.1. $\alpha$-Turmerone has two additional H and $\beta$-turmerone four additional H, removing one and two double bonds, respectively, from the aromatic ring.

**Table 98.1.** Yields of volatile oil and curcumin

| Cultivar | Volatile Oil (% v/wt) | Curcumin Content (%) |
|---|---|---|
| Waigon | 7.20 | 3.51 |
| Kuchupudi | 5.60 | 4.03 |
| Sugandham | 5.30 | 3.62 |
| Erode | 4.00 | 3.00 |
| Rajapuri | 4.50 | 3.45 |
| Godhvi | 6.00 | 3.49 |
| Tekurpeta | 2.50 | 1.82 |
| Kasturi | 5.80 | 3.44 |
| Miraj 26 | 6.30 | 2.87 |
| Alleppey | 4.00 | 5.44 |
| Duggirala | 3.80 | 2.22 |
| Cuddappa | 3.30 | 2.46 |

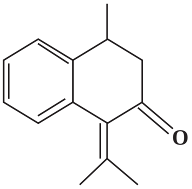

**Figure 98.1.** ar-Turmerone.

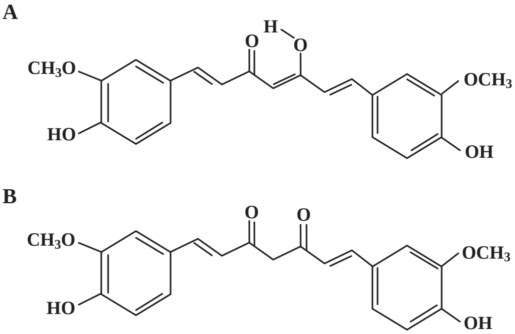

**Figure 98.2.** Curcumin. (A) Enol form. (B) Keto form.

The main pigment is curcumin, whose structure is given in Figure 98.2. This is bis-(feruloyl)methane, which has a slightly reddish, bright yellow color. Curcumin can exist in enol and keto forms. There are two other allied compounds that also have a bright yellow color: *p*-hydroxy cinnamoyl feruloyl methane (demethoxy curcumin) and bis-(*p*-hydroxy cinnamoyl)methane (bis-demethoxy curcumin).

The characteristic yellow color of turmeric is contributed by the three pigments. The usual ratio of these is curcumin 80–85%, demethoxy curcumin 10–15%, and bis-demethoxy curcumin about 5%. As the methoxy group is replaced by hydroxyl group, there is a very slight drop in the reddish tint to the bright yellow color, although on a quick glance the difference is difficult to detect.

Since the three components all have yellow color and similar absorption characteristics, they are referred to together as total curcumin. They have a maximum at 425 nm with an inflection at 445 nm. The three pigments are difficult to separate by ordinary extraction procedure, but can be separated by chromatography.

## Essential Oil

There are many people who believe that turmeric is a dye and not a spice, but in India where for centuries turmeric has been used as an ingredient in curry powder, it has a definite contribution toward the flavor of the food. In the Western world, turmeric is mostly used as a food color, although in the case of mustard paste, for example, turmeric does contribute its own distinct flavor. In world trade, however, turmeric essential oil has very low demand.

Dry turmeric, on coarse grinding and steam distillation, yields turmeric oil, in a range of 2–4%. The oil is a yellowish, mobile liquid with the flat, slightly medicinal aroma typical of turmeric. Because of the need to distill for a long period of time, the deoiled material is not suitable for extraction into oleoresin. This, together with poor demand for the oil, prompts processors to directly extract for oleoresin. For making this into curcumin powder, one of the steps is crystallization. This will cause all the noncrystallizable components including the essential oil, to be removed as the "oil part." The oil part on steam distillation yields volatile oil at a considerably cheaper price. For the limited use of turmeric oil, this recovered oil is sometimes used.

Analytical studies of pure turmeric oil are somewhat scarce. Nearly 60% of the oil is shown to consist of ar-turmerone and $\alpha$-turmerone. Earlier studies indicate that these are present in almost equal proportion. However, other studies indicate a ratio of turmerone and ar-turmerone of 80:20. One study shows this ratio to be 30 : 70, indicating conversion of turmerone to ar-turmerone (Govindarajan 1980). The other major constituent is zingiberene (~25%). Also reported are $\alpha$-phellandrene, cineole, borneol, sabinene, and some sesquiterpene alcohols (9%). In short, it can be said that except for the occurrence of turmerones in large proportions, turmeric oil is similar to ginger oil.

Analysis of commercial true oil and oil recovered from the oil part is presented in Table 98.2. It can be seen that true oil contains more of the turmerones (ar, $\alpha$, and $\beta$), with a consequent lower level for zingiberene. True oil also shows terpene hydrocarbons, alcohols, and cineole in small quantities. Total turmerones ($\alpha$ and $\beta$) account for about 45% versus about 16% of ar-turmerone. The ratio of turmerones to ar-turmeric is 74 : 26; all three put together account for 61% of the total oil as shown by GC analysis. Volatile oil recovered from the oil part shows similarities to true oil, except for a decrease in turmerones and some increase in zingiberene.

## Oleoresin

Extraction of the ground turmeric with solvent and subsequent removal of solvent yield turmeric oleoresin, which has all the essential oils present in the rhizome.

**Table 98.2.** Analysis of true turmeric oil and oil recovered from "oil part"

| Constituent | Turmeric Oil (%) | Oil from Oil Part (%) |
|---|---|---|
| $\alpha$-Pinene | <0.3 | <0.5 |
| Myrcene | 1–3 | 0.5–4 |
| Limonene | <0.5 | 0.2–4 |
| *p*-Cymene | 1–2 | 1–4 |
| 1,8-Cineole | 0.5–1.5 | 1–3 |
| Geraniol | <0.3 | – |
| Eugenol | <0.5 | 0.2–1 |
| $\alpha$-Turmerone | 22–28 | 4–10 |
| $\beta$-Turmerone | 18–23 | 15–20 |
| ar-Turmerone | 12–18 | 1–4.0 |
| Zingiberene | 5–10 | 15–20 |

GLC column: HP Inowax; carrier: $H_2$; detector: FID.
By area %.

Ethylene dichloride, ethyl acetate, acetone, and a mixture of hexane and acetone are all satisfactory solvents. Generally, the yield will be about 10% with a curcumin content of 35%. General demand is for a product with a curcumin content ranging between 25% and 40%, which can be carried out using the right variety of raw material. The oleoresin is a yellow to orange-red, viscous paste with the characteristic aroma of turmeric caused by the volatile oil.

In recent years, there has been demand for crystallized curcumin of about 95% purity. Here, there will be no aroma of turmeric because of the absence of volatile oil. This product is made by dissolving turmeric in the solvent by warming and making a supersaturated solution. On standing for some time, curcumin separates as crude crystals. It is difficult to get crystals from oleoresin made through acetone extraction, but with other solvents the crystals separate.

Crystallization can be repeated for higher strength crystals. Then crystals are filtered, usually using a basket centrifuge, and washed with a small amount of solvent. If the same solvent is used, then there is a chance for a slight loss due to solubilization. If hexane is used, during washing there will be no dissolution. Many solvents are used for crystallization, such as ethylene dichloride, ethyl acetate, ethyl alcohol, and isopropyl alcohol. The choice of solvent depends on the customers' preference. Minute traces of solvent can be detected by GC. There are reports of detection of acetone residues even when it is not used. This is probably generated during the high-temperature distillation in the procedure for estimation (Binu et al. 2007).

The oil part also has value as a natural color, even though the compounds are condensed/polymerized curcuminoids, which do not crystallize, but have a similar color, rather than curcumin.

Condensation of two molecules of vanillin with an appropriate carbonyl unit can produce curcumin. But it has not shown biological activity attributed to natural curcumin and two other allied pigments. In fact, more than a decade ago, attempts were made to produce vanillin from curcumin derived from turmeric. This was with a hope of presenting such vanillin as semi-synthetic, and therefore much better than fully synthetic ones.

## Methods of Testing

Curcumin content is estimated by spectrophotometric ASTA method with maxima read at 415–425 nm. However, this will not give the amount of crystallizable curcumin, which will be only about two-thirds of the total curcuminoid by the ASTA method. The oil part that separates out on crystallization gives absorption at the maxima of curcumin. The crystallizable curcumin has to be determined by actual crystallization and measurement of yield of the dry crystals.

## Uses

Turmeric is used for flavor in a number of Indian and Asian food preparations. Mustard paste also contains the spice. For these, oleoresin is a good replacement.

The food items in which curcumin are used include confectionery, ice cream, beverages, curries, and seafood preparations.

But the greatest use of curcumin is for its nutraceutical properties. Systematic research carried out in the National Institute of Nutrition (Polasa et al. 1991, 1992; Mukundan et al. 1993) has shown that curcumin is an efficient antioxidant and therefore an effective anticancer nutraceutical. Researchers from United States have shown that consumption of curcumin slows down cancer of the breast, prostate, lung, and colon.

The Ayurvedic system of medicine has shown that turmeric has anti-inflammatory and blood cleansing properties. A recent study at UCLA has indicated that consumption of curcumin can help combat Alzheimer's disease (Balasubramanian 2006).

Many cosmetic benefits are attributed to turmeric, mainly due to curcumin. However, turmerone produced by extraction with supercritical carbon dioxide has effective antioxidant and antiaging properties. It is further claimed that turmerone has high bioavailability, enabling an increase in skin tone and improved radiance. In Ayurvedic therapy, turmeric paste is believed to make women's skin smooth and free of hair.

Many advantageous pharmacological effects of turmeric have been reviewed (Aggarwal et al. 2003). It is beneficial for the treatment of prostrate cancer (Dorai et al. 2001), breast cancer (Somasundaram et al. 2002), colon cancer (Chen et al. 2006), and Alzheimer's disease (Balasubramanian 2006).

## Identification Numbers

| | FEMA No. | CAS | US/CFR | E-No. |
|---|---|---|---|---|
| Turmeric oil | 3085 | 8024-37-1 | 182.10 | – |
| Turmeric extract | 3086 | 8024-37-1 | 182.20 | – |
| | | 84775-52-0 | | – |
| Turmeric oleoresin | 3087 | 84775-52-0 | 182.20 | – |
| Curcumin | – | 458-37-7 | | 100 |

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# 99 Vanilla

## *Vanilla planifolia* Andrews, *V. pompona* Schiede, *V. tahitensis* Moore (*Orchidaceae*)

### Introduction

Vanilla was cultivated in Mexico well before European explorers set sail for the New World. In the fifteenth century, the Aztecs invaded and conquered central Mexico. They developed a taste for this fine spice and made the conquered pay them tribute in the form of vanilla beans. The Spanish explorer Cortes introduced the spice to Europe in 1520. Vanilla is believed to have been named after "black flower," as the mature beans turn dark on drying.

European countries tried to grow vanilla beans in tropical countries where they had control, but the efforts to produce beans did not succeed. After considerable investigation, it was found that pollination requires external assistance. This happened in Mexico through a variety of bees and hummingbirds, which enjoy the nectar of vanilla flowers. Hummingbirds' long beaks were able to reach inside the flower to drink the nectar, and in the process the anther was opened, releasing the pollen which in turn fertilized the stigma.

Early documentation of vanilla and its uses was carried out by a Spanish missionary in Mexico in 1560. Even though artificial pollination was introduced in the nineteenth century, it was a 12-year-old French-owned slave, Edmond Albius, who developed the more practical method of pollination, which is even now followed. This involved use of a small stick, usually made of bamboo, which can open the anther almost like the long beak of the hummingbird. This development enabled cultivation and production of vanilla beans in other tropical regions.

Until the middle of the nineteenth century, vanilla beans were mainly cultivated in Mexico. In early nineteenth century, the French took this crop to Reunion Island and Mauritius and then to Comoros, the Seychelles, and Madagascar. Development of a practical pollination method helped in the spread of vanilla production throughout these African islands. Beans produced in this region are known as Bourbon vanilla. Today, Madagascar is the most important producer of vanilla. After saffron, vanilla is regarded as the most expensive spice.

### Plant Material

Vanilla belongs to the orchid family. In fact, in that large family, vanilla is the only variety that is commercially important as a flavoring material. The major species is

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**Photo 29.** (A) Uncured vanilla beans. (B) Cured beans. See color insert.

*Vanilla planifolia*. Two other cultivated varieties are West Indian vanilla, *Vanilla pompona*, and Tahitian vanilla, *Vanilla tahitensis* (Madhusoodanan et al. 2003). *V. planifolia* is an herbaceous perennial vine, which grows as a climber on trees or supports. It is aided by adventitious roots, which are white in color and about 2 mm in diameter. They appear opposite to the leaves. The root proper is in the base. It has a long, cylindrical, succulent, and branched stem. The stem is 1–2 cm in diameter. It has a chlorophyll cover with stomata, so that it can engage in photosynthesis. Its leaves are oblong-elliptic to lanceolate. They are flat, fleshy, subsessile, and alternate, with a length of 10–25 cm and breadth of 3–10 cm. The inflorescence is stout racemose, axillary, and generally simple. The flowers are large, waxy, and pale greenish-yellow. The lower part of the labellum develops into a central column. The tip of the column bears a single stamen with two pollen masses covered by a cap-like hood. The slender stalk-like portion is the ovary, which is 4–5 cm in length.

The formation of the flower is such that self-pollination is difficult because of separation of the stamen from the stigma. In Mexico, where vanilla originated as a commercial crop, pollination is done by a variety of stingless bees or hummingbirds. In all other places and even in some regions of Mexico, hand pollination is the only way to set the fruit.

Hand pollination is carried out by a pointed bamboo splinter, sharpened toothpick, or other similar implement (Madhusoodanan et al. 2003). Using the implement, the hood of the stamen is pushed back and the anther is pressed against the stigma with the thumb, thereby spreading pollen over it. Each flower and stigma receptivity lasts for only a day, and therefore all pollination has to be carried on the same day. The best time for this is in the morning.

The fruit is a capsule and takes 250–280 days to mature, at which point the weight will be around 12 g. The fruits, known as beans, are narrow and cylindrical or three-angled with a length of 10–25 cm and diameter of 0.5–1.5 cm. When plucked, the beans are green in color and without the characteristic aroma. The aroma is developed only after an elaborate curing process.

The beans contain numerous minute black seeds about 0.3 mm in diameter. Under normal conditions, germination of the seeds is difficult. Multiplication is achieved through cuttings of the vine. Today, tissue culture-developed seedlings are employed in commercial cultivation. In most major growing areas such as Madagascar and other African islands, as well as India and China, *V. planifolia* is cultivated.

*V. tahitensis*, as the name suggests, is of Tahitian origin and is cultivated in Indonesia, Hawaii, and some Pacific islands. This variety fetches a lower price. Its main difference is that it has a more slender stem and narrower leaves. Its beans are reddish-brown in color, with a size of 12–15 cm in length and slightly less than 1 cm in diameter. The middle of the bean is broader, tapering toward the ends.

*V. pompona* resembles *V. planifolia*, but the leaves are longer and broader. The flowers are greenish yellow in color and more fleshy. The beans are also fleshier but with a roundish triangular section. The quality of this bean is regarded as inferior to *V. planifolia*.

The major producers of vanilla beans are Madagascar, 6200 tonnes (about 59%); Indonesia, 2399 tonnes (about 23%); and China, 1000 tonnes (about 10%). Others are Mexico, Turkey, Tonga, Uganda, Comoros, French Polynesia, and Reunion, according to an FAO report of 2006.

## Harvesting and Curing

The production, curing, and utilization of vanilla is a highly developed procedure with many variations based on region, agro-climatic conditions, variety and size of the bean, and the local tradition. For detailed information, the reader is referred to various books on the subject. However, the general principles of harvesting and curing are explained in this section. Photo 29 shows harvested and cured beans.

Generally, the vine takes about 3 years to reach the fruit-bearing stage, and will produce for about 12 years. The crop in the first year is likely to be smaller than in later years. About 6–9 months after pollination, the bean starts to develop a yellow color at the tip, which is an indication for harvesting.

The curing processes of Mexico, the Bourbon Island, and other regions that use *V. planifolia* are somewhat similar. In Mexico, vanilla beans are wrapped in blankets and straw mats and placed in ovens for 24–48 hours. In other places, beans are immersed in hot water for a short time, spread in the sun, and turned over periodically to avoid overheating. The beans are then wrapped in blankets, placed in wooden boxes, and allowed to sweat overnight. The spreading in the sun and wrapping are repeated to complete the various enzymatic changes. The beans are stored on racks in holding rooms for a few weeks to further develop the flavor. The overall curing time is 3–6 months. Variations in the conditions are made according to variations in the beans and other factors. To get the best results, beans have to be picked individually making sure that each one is at the proper level of maturity (Nielsen undated).

In Indonesia, where *V. tahitensis* is cultivated, there is a tendency to pick all the beans in a group of vines to save on labor. There can be variation in maturity, and this is reflected in the generally lower quality obtained. The curing process involves use of heat from oil heaters followed by other steps of curing. There have been efforts to improve the process, allowing beans to mature longer on the vine, but, the quality from that region is still regarded as lower than that of Bourbon beans.

In almost every region, there are recommended methods of curing to obtain the best quality beans possible. The final moisture level should be 20–30%. At a higher moisture level, a surface fungus may appear if beans are kept in unhygienic conditions. Occasional opening, wiping if needed, airing, and rewrapping may be required in such situations.

One such process has been developed by McCormicks and Co. (British Patent 1-205-829, 1970). Beans are cut into 1-cm pieces, killed and sweated in an oven at 60°C for 70–78 hours, air oven-dried at 60°C to a moisture level of 35–40%, and then dried in ambient temperature with fanning to obtain a moisture level of 20–25%.

The cured beans are processed in three forms: whole pods, powder, and extract. Whole beans are graded according to length. $A_1$-grade is larger than 15 cm in length. In fact, well-formed, straight beans of 16–17 cm are packaged individually and attractively, to be sold in retail at premium price. A-grade is 13–15 cm, B-grade 10–13 cm, and C-grade smaller than 10 cm. Cut pieces are also sold. The powder form is obtained after grinding, sometimes blended with sugar, starch, or another solid diluent. Extraction is described later.

The above grading system is not universal since pods from different regions are of different sizes. Madagascar beans will range from 16 to 18 cm on average, with some up to 23 cm in length. Le Reunion beans are longer, while Comoros beans are shorter. There is also a system of grading based on appearance. Uniformity in chocolate brown color, absence of defects such as splitting, oily appearance, and delicate flavor are all desirable attributes. Thinness, twisted shape, reddish color, splitting, excessive drying, and poor aroma are all defects that lower the value. Beans from plants other than *V. planifolia* are also rated lower.

## Chemistry

During the curing process, many enzyme-based and chemical reactions take place, resulting in the formation of flavor-giving compounds. The most important is vanillin, which is 4-hydroxy, 3-methoxy benzaldehyde (Fig. 99.1). A minor but important

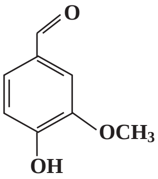

**Figure 99.1.** Vanillin.

component is piperonal (heliotropis), which gives aroma. Besides vanillin, cured beans contain ethyl vanillin, vanillic *p*-hydroxy benzoic acid, *p*-coumaric acid, and some nonvolatile components such as sugars, waxes, fixed oil, and polyphenols. The cured beans contain 20–30% moisture.

## Extraction

Vanilla beans have very little essential oil, though what they do produce has very attractive volatile aroma and flavor. These are sometimes concentrated in extract or essence form. Excessive heat harms the delicate flavor, so ethyl alcohol and supercritical carbon dioxide are the only two suitable solvents. In the case of alcohol, the last traces of solvent are not removed and thereby too much heating is avoided. Supercritical carbon dioxide does not require heating to remove carbon dioxide.

Of the complex flavor mixture, vanillin is the predominant and most important constituent. In addition, there are about 200 compounds present in minute quantities that nevertheless contribute to the aroma and flavor. As defined by the U.S. FDA, a onefold concentrate of vanilla flavor is 13.35 ounces of bean to 1 gallon of alcohol (1 ounce = 28 g; 1 U.S. gallon = 3.79 L). A twofold should contain 26.7 ounces, threefold 40.5 ounces, and fourfold 53.4 ounces to a gallon. To be labeled as an extract, the vanilla flavor must contain 35% of alcohol by volume. Anything less will be labeled as “flavor.” Since the purpose of alcohol is to keep flavor components in dispersion, a concentration over twofold may require more than 35% alcohol. It may be noted that alcohol strength will be lowered by the moisture contained in the cured beans. The vanilla sold in retail is usually single-fold. The stronger ones are used for industrial purposes where large batches of food products are to be flavored (Nielsen undated).

In the United States, blended natural and synthetic vanillas are available as vanilla–vanillin blends. There is also vanilla flavor with other natural flavors (WONF), but it is not clear whether FDA clearance is available for this.

A more practical extraction method is performed on cut, cured vanilla beans. Beans are cut into pieces of 2.5 cm and soaked in 50% aqueous ethanol for 12 days at ambient conditions. After decanting, extraction is performed a second time. Usually, 2 kg of solvent is poured into 1 kg of pieces each time. The combined miscella is carefully freed of solvent by vacuum distillation, keeping the temperature well below 70°C. Vanilla bean extract comes with less than 5% ethanol and 20% moisture. This nearly 80% soluble solid extract is a viscous liquid, soluble in water. It has a dark brown, chocolate color with flavor typical of vanillin, combined with a caramelized rummy note.

Similar extraction using 95% absolute alcohol gives a two-layered product with similar organoleptic characteristics, though slightly less viscous and oil-soluble.

The quality of the vanilla bean depends on more than just vanillin content; other constituents present in the right amounts will increase the flavor appeal of the vanillin present. Generally, the vanillin content of a good cured bean is 1–2% and, in rare cases, even up to 3%. Other chemical components present are *p*-hydroxy benzaldehyde, acetic acid, isobutyric acid, caproic acid, eugenol, furfural, *p*-hydroxy benzyl methyl ether, vanillyl ethyl ether, anisyl ethyl ether, and acetaldehyde (Leung and Foster 1996).

Although vanillin in the beans greatly enhances the quality, its absence does not change the basic vanilla character or render the beans worthless (Ranadive 2006). A number of major, minor, and trace constituents play significant roles in imparting to vanilla its characteristic aroma and flavor. The flavor characteristics of Chinese beans have been studied by extraction with supercritical carbon dioxide followed by analysis using GC-MS; about 30 compounds have been identified (Fu et al. 2002).

## Analytical Methods

The vanillin content is determined by the AOAC method using HPLC. However, the most important aspect of quality evaluation requires sensory evaluation of the organoleptic characteristics.

## Uses

Ground, cured beans are used in various preparations such as confectionery, dairy products, baked items, and beverages. In industrial uses for these items, extracts are generally used. Its single important use is for flavoring ice cream; the most common flavoring for ice cream and dairy products is vanilla extract. Many other flavor preparations invariably contain vanilla, such as chocolate, custard, caramel, and even coffee. In some of such food products, the presence of vanilla is not recognized by consumers, although it may be playing a significant role in overall acceptance. An attempt to add a vanilla flavor to cola-based soft drinks did not meet with much success.

## Identification Numbers

| | FEMA No. | CAS | US/CFR | E-No. |
|---|---|---|---|---|
| Vanilla beans | 3104 | 84650-63-5 | 182.10 | – |
| Vanilla extract | 3105 | 8024-06-4 | 182.20 | – |
| Vanilla oleoresin | 3106 | 84650-63-5 | 182.20 | – |
| Vanilla absolute | – | 8024-06-4 | – | – |
| Vanillin (natural) | 3107 | 121-33-5 | 182.60 | – |

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# Part III
# Future Needs

## Introduction

Part II described a wide range of flavors and colorants of natural origin. With the recent emphasis on the use of natural materials, there is considerable scope for adding more to the list. In fact, a great many plant products are used on a regional basis. Once the flavor qualities of these are recognized, it will not be a complicated job to market them globally.

In fact, activities such as these are an ideal project for students of food and flavor technology. The most important idea to focus on is the development of self-preservable extractives, which are well standardized. Once laboratory studies are done, manufacturing firms can make small lots to test the economic potential and consumer acceptance of these products. Cosmetic and perfumery manufacturers are more adventurous in this respect. There is a constant search for new fragrances, resulting in a large number of products now in use, which were unknown even a decade ago. Food manufacturers and consumers are more conservative in this regard. Of course, one reason for this may be the fact that food is consumed while fragrance materials are only applied externally. However, with well-developed toxicological testing procedures now available, there is no danger of harmful flavors and colors entering a consumer's body, especially if the products are natural. With adverse skin reaction and allergy complications a concern, it would appear that new fragrance materials undergo more rigorous testing than do even flavor ingredients. Besides, if flavors and colors popular in some regions are extended to other parts of the world, there is no need for such fears. It is primarily a question of consumer acceptance. With many materials, the flavor is to a great extent an acquired one. Therefore, long-range programs are needed.

In the case of natural colorants, the greatest problem is the limitation of available materials. Many of the presently available colors are in the yellow to red range. Luckily, these are also well-accepted colors for food. There is still considerable scope to introduce new colorants, which are either water- or fat-soluble. Many of the newly developed natural colorants will also be used by cosmetics manufacturers.

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# 100 Opportunities in Natural Flavors

There are many plant products that are used as natural flavors especially in cookery. Some of them make excellent savory flavors in soups, snacks, dressings, and in ready-made seasonings, provided they are made into usable extractives.

## Allied Spices

Some of the major spices have close cousins that have special flavors. Thus, ginger has related products such as the different types of galangals (Chapters 51–53), and black pepper has long pepper (Chapter 71).

*Allium* species have many members that are utilized in culinary practices. Two well-exploited *Allium* products are garlic and onion, presented in Chapters 55 and 79, respectively. A recent study on the effect of different heat treatments generally used in cooking treatments on various *Allium* products showed interesting changes to their volatile and nonvolatile constituents (Kramer et al. 2006).

**Shallot**, *Allium oschaninii*, originated in Asia and through India it spread to the Mediterranean region. Many people believe that it originated in an ancient city of Ashkelon, in the geographical territory of the present Israel. In taste, it resembles onion but with slightly more sweetness and a milder flavor. It has the some tear-producing quality when cut. Shallots are much smaller than onions (see Photo 30).

Shallots are widely used in the cooking of Southeast Asian countries and in South Asia. Two popular dishes of South India where shallot plays a prime role are sambar and rasam. It is also used in pickles. However, because of poor marketing, shallots are relatively expensive in Europe and in the United States.

Research studies on the shallot are very few. Its tear-producing property is generally assumed to be similar to that of the onion, but there could be subtle differences. It is reported to contain polyphenols of the flavonoid type.

Unlike the onion, shallot does not contribute to the texture of food and its flavor is more delicate. Many people prefer shallot to onion in omelettes mainly because they can enjoy the special flavor without biting into thick pieces. All of these facts point to the possible success of an extract suitably made, which can serve as a unique and welcome flavor in many foods.

**Scallion**, *Allium wakegi*, is known by many names such as spring onion, salad onion, and green onion. Scallion is similar to shallot in flavor but with subtle changes. It does not have a fully developed bulb like other *Allium* products, but has a white,

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**Photo 30.** Shallot. See color insert.

tender, swollen lower end with a green, hollow, upper portion. They have a pungent taste but are milder than onions. They are used either cooked or eaten raw, and used in soups, noodles, and seafood preparations.

**Chives**, *Allium schoenoprasum*, are perhaps the smallest member of the *Allium* species. They are grown in North America, Europe, and Asia. Chives are unique in that they are a plant that has thrived in both the New and Old Worlds. It is an herbaceous perennial plant with a well-formed but small bulb, 2–3 cm long and about 1 cm wide.

Chives are available fresh throughout the year and hence are popular in European cuisines. They can also be dry frozen without much effect on the taste. Like garlic, chive has many sulfur-containing flavoring compounds and is believed to have some medicinal properties. It is rich in vitamins A and C and contains minerals such as iron and calcium. Although chives have been cultivated in Europe from ancient times, chemical studies on the plant are rather limited. There is reason to take up scientific studies so that a well-standardized extractive is available for use in processed foods.

**Garlic chives**, *Allium tuberosum*, are also known as Chinese chives or Chinese leeks. The wild ones are classified as *Allium ramosum*. They have become acceptable in the English-speaking world, but have been popular in China and other Asian countries for quite some time. The plant has strap-like leaves, straight, thin, tall flower stalks, and attractive white flowers. Both stalks and leaves are used in stir-fried foods in China, Japan, and Korea. It is a popular spice for dumplings with eggs, meat, or seafood. Garlic chives are commonly used to make a type of pancake. The flavor has a typical chive taste but with a distinct garlic note. Like other *Allium* cooking ingredients, garlic chives may also play an important role if extractives are made available for processed food industry.

**Leek**, *Allium ampeloprasum*, also referred to as *Allium porrum*, is another member of the onion family. The edible part is the white onion-like bulb and the light green stalk, which is primarily the lower portion of the leaf sheaths. The dark green upper portion is not used.

The leek is known to have been in ancient Egypt and was a favorite food of the Roman Emperor Nero. The leek is the national emblem of Wales and Shakespeare refers to the custom of wearing a leek as an ancient tradition in Henry V.

Leeks can be boiled or fried and gives excellent taste to soups. It is also used raw in salads. While its texture is important, development of a leek extract for use as a natural flavor is worth a try, especially using parts of the plant that are not used in cookery.

The **bell pepper** is the same genus and species, namely, *Capsicum annuum*, as hot chili or paprika. It is valued as a vegetable but has a unique and attractive flavor. In fact, production of synthetic bell pepper flavor has been attempted, though the natural flavor is well worth the trouble. Efforts should be made to use wastage and unused parts of the plant product. It produces very low amounts of capsaicin.

The bell pepper is native to Mexico, Central America, and northern parts of South America. The seeds are believed to have been carried to Europe in 1493, and later spread to Asia and Africa as a very tasty vegetable with mild hotness. Because of its bell shape, it was called bell pepper, though it is sometimes referred to as sweet pepper. In India, it is very common to call the bell pepper “capsicum,” while in Indonesia it is referred to as “paprika.” It is generally used in culinary practices as a green mature fruit before ripening. On ripening, bell pepper may assume a yellow to red color.

On a wet basis, the fruit has 4.64% carbohydrate, 2.40% sugars, 1.7% dietary fiber, 0.17% fat, and 0.86% protein. It has a wide range of vitamins belonging to the B group, ascorbic acid, and a number of minerals. On ripening, it is a rich source of carotenes and lycopenes, all valued as nutraceuticals.

Turmeric also has closely related spices whose flavor is enjoyed regionally (Govindarajan 1980). Some of them are as follows.

***Curcuma aromatica*** grows in most parts of India. Generally, it is cultivated where its more valuable cousin turmeric proper (*Curcuma longa*) (see Chapter 98) is grown. More than just a spice, it has value in cosmetics. A small but steady production of the essential oil is made in South India.

*C. aromatica* is a perennial tuberous herb with an aromatic yellow rhizome. The rhizome looks like that of turmeric but is darker with an olive-green tint. The fingers are longer and thinner. The oil has a pale yellow color with an odor that is quite different from that of turmeric. The yellow shade is due to curcumin, which turns into a volatile fraction during steam distillation.

***Temoe lawak***, *Curcuma xanthorrhiza* R, is similar to turmeric and is popular in Indonesia. The rhizome is mostly valued for its medicinal properties. The rhizome has a very high content of 7–11% v/w of essential oil. It is closely related to *Curcuma domestica* oil. The oil has camphor, *p*-tolyl methyl carbinol, and a large percentage of myrcene.

**Zedoary**, *Curcuma zedoaria* R, is cultivated for its starch and its typical aroma. Rhizome and oil are highly aromatic with a gingery, camphory, bitter note. However, its use is restricted to only a few regions.

**Mango ginger**, *Curcuma amada* R, is a root crop that is more commonly utilized than the others described above. It has a distinct mango flavor and is therefore used in pickling. It also has limited medicinal use.

Analysis shows the presence of hydrocarbons, $\alpha$-pinene, ocimene, and curcumins. Linalool, camphor, cuminyl alcohol, turmarone, and some ketoalcohol have also been reported.

The extractive of mango ginger has an appealing flavor. It has a sweet, bitter, and cooling note with an aroma combining green mango, turmeric, and ginger. The essential oil and oleoresin need more detailed analysis, as they have the potential to be utilized as a natural flavor.

## Masticatory Products

There are some plant products that have become quite popular as a masticatory in different parts of the world. These materials have been able to earn sustained interest mainly because of something special in their flavor. Two such products patronized by local people in South America and Africa are coca leaves (see Chapter 38) and kola nuts (see Chapter 65). How these became wildly popular through a world-renowned soft drink is one of food technology's major success stories of modern times.

**Arecanut**, *Areca catechu*, is the kernel of a palm tree. Also called betel nut, arecanut is an extremely popular masticatory in India and other Asian countries. The fact that a vast industry has developed around this crop speaks volumes on its popularity. The kernel, often referred to as a nut, is surrounded by a husk and therefore externally resembles a miniature coconut. The size of the nut with husk is 5–8 cm in length and 3–6 cm in diameter.

The chemistry of the arecanut has been well studied. When ripe, it has 7–35% polyphenols on dry basis, which give the nut its welcome astringent taste. At an immature stage, the polyphenol level is much higher, going up to 50%. Both (+)catechin and (–)epicatechin have been identified, but the main polyphenol is leucocyanidin, much of which is present as condensed polymeric tannin. Traces of leucopelargonidin also have been reported (Mathew et al. 1969).

The nut also contains an alkaloid, arecolin, present to an extent of 0.1–0.9%. There are also some allied alkaloids at much smaller levels. Research on the chemistry of the arecanut has been limited, although, Wang et al. (1999) published a paper on its catechin content.

There have been reports that chewing the arecanut brings about oral cancer. However, many consumers chew arecanut along with unrefined tobacco. Usually, the chew mix also contains a bit of slaked lime. The carcinogenic property is more likely due to the presence of tobacco and slaked lime. It is believed that an extract of arecanut, mostly made of leucocyanidin derivatives, is as harmless as tea extract.

The catechins of tea, which are flavan-3-ols, are now considered to be an excellent antioxidant. It is quite possible that the flavan-3,4-diols of arecanut are an equally effective antioxidant. The low level of arecoline makes it unlikely to be a harmful chemical. Like most other alkaloids present in foods used as stimulants, it acts on the nervous system, but consumers (especially of earlier generations) love the fine astringent flavor.

In recent years, the popularity of chewing arecanut has decreased, as the younger generation considers the habit to be unfashionable. Despite this trend, processors produce more sophisticated products by blending dry spices and pieces of dessert nuts, and the interest in India is being sustained to some extent.

**Katha**, *Acacia catechu*, is used in India as a masticatory, generally with the chewing mix containing arecanut and betel leaf. *Acacia catechu* is a moderate-sized deciduous tree, 9–12 m in height. Gummy exudate from the wood is brown in color with a brittle, crystal-like structure.

The extract has polyphenols and a good astringent taste. One of the main properties of a polyphenol-rich masticatory is its ability to counter a feeling of nausea; this property is also valuable in a flavor mix.

**Betel leaf**, *Piper betle*, is a climber like black pepper. The fresh leaf is highly valued for its fine herbal aroma, contributed by the essential oil it contains. It is rich in phenol-based terpenes, which give the oil a medicinal note. It contains chavibetol, chavicol, estragole, eugenol, and hydroxy catechol. The volatile oil content of a fresh leaf is 0.12–0.14% (Sharma et al. 1987).

One of the main effects of chewing arecanut and betel leaf is that secretion of saliva is activated. This is a point to be noted for flavor formulation, especially those representing savory flavor.

## Others

**Sarsaparilla**, *Smilax officinalis*, is the root of a plant grown in different parts of the world, especially in the Americas. The name probably comes from the Spanish word *zarga* for "shrub" and *parilla* for "little grape wine." The dried root is used in soft drinks as a flavor, of which root beer and Sioux City sarsaparilla are two examples. It is also made into sweetened drinks in Taiwan, India, and other countries.

There are related plants such as *Aralia nudicaulis* and *Aralia racemosa* that are used as substitutes. The European medical world considers sarsaparilla to be a tonic, diuretic, sweating agent, and blood purifier. However, although it has so much potential, sarsaparilla has not emerged as a flavor usable in different kinds of food, especially as a standardized extract.

Many flavor notes are produced by steps that commonly occur in everyday life. Malting brings about the subtle flavor caused by the biochemical changes that occur during germination of grains. On roasting, flavor improves in the case of dessert nuts and spices. Poppy seed and roasted sesame seed, for example, can yield a good flavor extract. Dried green mango, known as *Amchoor*, is used in northern parts of India as a popular souring agent. If the product is well standardized or, even better, if a concentrate of water or aqueous alcoholic extract is made, it has the potential to be promoted as a natural flavor. Another example is horseradish, a popular condiment in Japan and other parts of the world. It has a pungent, sulfur-containing flavor. It would be worthwhile to produce standardized extractives so that they can be enjoyed in other parts of the world. If one looks around, there are many flavor-contributing plant materials, which are, at present, restricted to only certain regions. Simple operations like ripening, germination, crushing, and thermal treatment may even add other desirable flavor notes to these plants. These are opportunities for the development of novel flavors.

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# 101 Opportunities in Natural Colorants

Sources of natural colorants are rather limited. Almost all edible materials with color, such as some fruits, are already highly priced and therefore are not a usable colorant for other foods. The search must go on for underutilized colorants, even those which are not currently used as food.

## Anthocyanin-Based Colors

Anthocyanins not only have a bright color, but also have excellent water solubility. There are many fruits that are only partially utilized for their coloration. They include black currants, blueberries, and cranberries.

**Black currant**, *Ribes nigrum*, is a fruit native to northern parts of Europe and Asia. It is a small shrub 1–2 m in height. The fruit is an edible berry 1 cm in diameter. It has a very dark purple color with a smooth skin. The plant can produce as many as 5 kg of fruits per season.

Black currant is a fruit well utilized for fruit products, confectionery, and in household cooking. It is a rich source of ascorbic acid, and for this property, it was used in World War I as a source of vitamin C. The anthocyanins present in black currant are delphinidin-3-0-glucoside and rutinoside. The fruit is believed to be a good nutraceutical. An investigation into the anthocyanins and the effect of heat and aging on the color was carried out (Pogorzelski and Czyzowska 1997).

However, the potential of further cultivation and extensive harvesting will have to be explored to make black currant available for use as a natural colorant. The crop became rare in the United States in the twentieth century when the farming of black currant was banned (an outbreak of infestation was considered to be a threat to America's logging industry). With scientific farming and efficient harvesting, the availability of black currant can be extended severalfold so that both the fruit industry and the natural color industry can grow.

The **blueberry** is a flowering plant belonging to genus *Vaccinium* and to the subspecies of *cynococcus*. Several species of *Vaccinium* are grown in different regions.

The blueberry is not a true berry. The fruit is 5–16 mm in diameter. They have a sweet taste with some acidity, causing sourness. Plants are grown in the United States, Canada, and Europe. In recent years, the blueberry has been introduced to the Southern hemisphere, especially in Australia, Chile, South Africa, Argentina, and New Zealand. It is now used in a wide range of fruit products and as a flavorant in cereals, muffins, and snack foods.

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The fruit is rich in anthocyanins, proanthocyanins, and polyphenols (Wang et al. 2008). But harvesting the small fruit is problematic. Nevertheless, if the natural colors of the blueberry are better exploited, there are immense possibilities of extending its cultivation and making its harvesting more efficient.

**Cranberry**, *Vaccinium oxycoccos*, is another fruit crop that has natural coloring components. The fruit grows on a creeping shrub or vines. The fruits are initially white but turn deep red. Its edible fruit has sweetness but also has an intense sourness. The crop is popular in the United States and in some parts of Canada.

Most of the fruits are made into juice, sauce, and sweetened, dried cranberries. It is also made into wine. Cranberries are rich in anthocyanins like cyanidin and peonidin, and other polyphenols such as quercetin. Cranberries are therefore considered to be a nutraceutical, and have great potential as a natural food color.

The fruit of the **mulberry** family (*Morus*) all have an attractive color. *Morus nigra* is a black and *Morus rubra* a red mulberry. The presence of anthocyanins is recognized in these fruits. Investigation to identify the right cultivar, selection of the ideal agro-climatic conditions, and optimization of the extraction procedures are to take advantage of this fruit.

Many of the small-sized fruits, classified as berries, are cultivated and utilized as fruit products. In fact, some of them are used as raw material for extracting color. But the emphasis laid on this latter use is indeed small. There is considerable scope for making natural food color especially from the waste in the processing industry.

## Seminatural Colors

Some colors, such as carmine from cochineal and copper chlorophyllin, are seminatural, as in the extraction there is a minor chemical treatment to effect a significant change. One such potential color is the anthocyanidins from leucoanthocyanidins. Leucoanthocyanidin is a flavan-3,4-diol present in a wide range of plant products, many of them presently not very commercially significant. Leucoanthocyanidins are present mostly as leucocyanidin but are also present in the plant kingdom as leucopelargonidin and leucodelphinidin. On treatment with hot acid, they are easily converted into the corresponding anthocyanidin (for structure of the anthocyanidins, see Chapter 57 on grape). From the chemical structure, it is clear that the change involves a dehydration and a dehydrogenation step. The author has studied leucoanthocyanidins of the arecanut (Mathew and Govindarajan 1964) and cashew nut testa (Mathew and Parpia 1970). During the processing, there are plenty of leucoanthocyanidin materials that are available for conversion. Leucoanthocyanidins are colorless; thus, the plant products that contain them do not command a good price. Raw materials that have colored compounds are generally more expensive. There must be several low-priced tanning materials of condensed tannin type that will contain flavan-3,4-diols. These can be the starting material of anthocyanidins.

Leucoanthocyanidins usually do not occur as glycosides. In any case, treatment with hot acid would hydrolyze any glycoside into aglycone. Hydrochloric acid in an alcohol such as butanol is a good reagent, which when treated at 100°C for 30–40 minutes yields the corresponding anthocyanidin from leucoanthocyanidins. A higher strength of acid and a minute amount of iron as a catalyst gives a higher yield for the reaction (Govindarajan and Mathew 1965). The anthocyanidins come in brilliant pink to red colors. More work is needed to obtain a higher yield and good stability for the color. In fact, anthocyanidins from leucoanthocyanidins are the most promising future source of food color. It would prove very economical since the sources of colorless proanthocyanidins are cheap and abundant in the plant kingdom.

Another source of seminatural food color is flavan-ols such as catechins and leucoanthocyanidin, which, through quinone formation and secondary reactions, give colored compounds. The black pigment of tea is the result of such reactions.

The primary ingredients of a chewing mix known in India as *pan* are arecanut, betel leaf, and wet slaked lime. Calcium hydroxide in the lime, by a change of pH, brings about a significant chemical change to polyphenols, resulting in red-colored saliva and mouth. Women of earlier generations considered the red color produced on lips a beauty symbol, like lipstick of the modern age.

The initial change is quinone formation from flavan-ols in the presence of alkaline pH. This is followed by secondary reactions of an unknown nature to produce the attractive red pigment. This can be reproduced in the laboratory using other alkalis on extracted polyphenols. This reaction can be used to make red pigments as a seminatural food color. There is a need to stabilize the color, however, since on long keeping the color turns dull, probably due to the continued presence of strong alkali.

In the past, the Vietnamese used to make a seminatural black dye for coloring fabric, although with the availability of synthetic dyes, this practice has been discontinued. The dye was made from the fruits of *Diospyros mollis*. They are crushed and treated with cold 1% acetic acid for 3 hours to hydrolyze the glycoside. On treatment with 10% aqueous sodium hydroxide for 30 minutes, filtration, and neutralization with strong hydrochloric acid, the precursor of the dye will be formed as an amorphous solid. This colorless leuco dye, on oxidation by exposure to air, treatment with hydrogen peroxide, or by making it slightly alkaline, turns into a stable black dye. Usually, the filtrations in the process are slow and may need pressure to be sped up.

It is well known that natural indigo plants lost much of their value when synthetic dyes appeared, though now there is good case to revive indigo plantation and extraction of the dye.

## Wood-Based Colors

One of the most attractive food colors is santalin, obtained from red sandalwood (see Chapter 85). The wood of the **jack tree** (*Artocarpus heterophyllus*) also has a color, an attractive yellow one. Because it is used as timber for making furniture and door frames, a fairly large quantity of wood chips and sawdust is produced; these are a potential source of a natural colorant. Similarly, **cashew nut tree** wood (*Anacardium occidentale*) has a reddish-brown color.

Another source of color is the heartwood of **sappan wood**, *Caesalpinia sappan* L, also known as Brazil wood. The wood is light yellow when cut but quickly changes to red. This color can be extracted by water. The heartwood is bitter, astringent, acrid, and attributed to have many medicinal properties in Ayurvedic therapy. No investigation has been carried out to study the color. In South India, it is common to boil water containing wood pieces. The pink-colored water is used for drinking as it is believed to be good for the health.

## Other Colors

With greater emphasis on natural color, there are opportunities for scientists and technologists to discover new sources. Marigold (see Chapter 75) is a flower which has now become a source of color, so there must be other flowers which have color. Once the color is studied and established as a potential source, its propagation can be taken up. In recent years, the sunflower, with its golden yellow color, has been grown for its oil-rich seeds. The petals are not utilized. Even if they are partially withered, there could be some color that can be extracted.

Similarly, fruit waste can be a good source of colorant. If wastes of tomato and grape can be a source of food color, the waste of fruits such as the mango is also worth exploring.

Gardenia fruits, *Gardenia jasminoides*, give yellow-red and blue food color. There has been progress in using this in commercial food products, but there is potential for it to become much more widespread. Some compounds, including crocin and crocetin, have been identified (Chen et al. 2007; Bi et al. 2008).

*Jambul* or *Jamun* (*Jambul syzygium*/*Eugenia jambolana*) is a fruit resembling a berry with an ovoid shape. It turns pink and on full ripening to shining, crimson-black, rich in gallic acid-type tannins. It is valued in traditional medicine. Many useful fruit products can be made out of this, and the presence of anthocyanin and carotene indicate its use as a color (Shahnawaz and Sheikh 2008).

Lovage root (see Chapter 72) has a crimson color extractable with water or alcohol, which has not been examined at length. Kokam (see Chapter 64), especially the red variety, can also yield an extractable color.

Around the world, especially in Asian, African, and South American rural areas, there are colored edible substances whose coloring properties have not been fully investigated. Opportunities for producing novel natural food colors with distinct and attractive hues should be pursued.

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# Index of Systematic Biological Names

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*Natural Food Flavors and Colorants* Mathew Attokaran

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*Natural Food Flavors and Colorants* Mathew Attokaran
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**Photo 2.** (A) Unopened annatto pods. (B) Opened pods with seeds inside.

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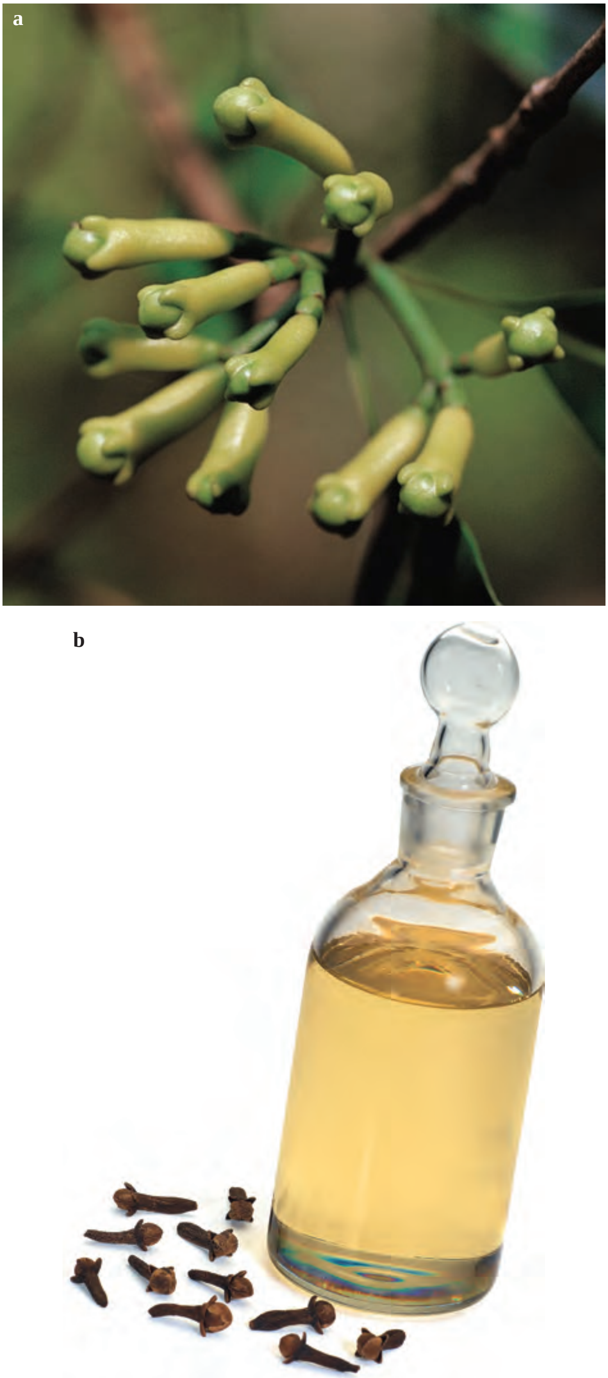

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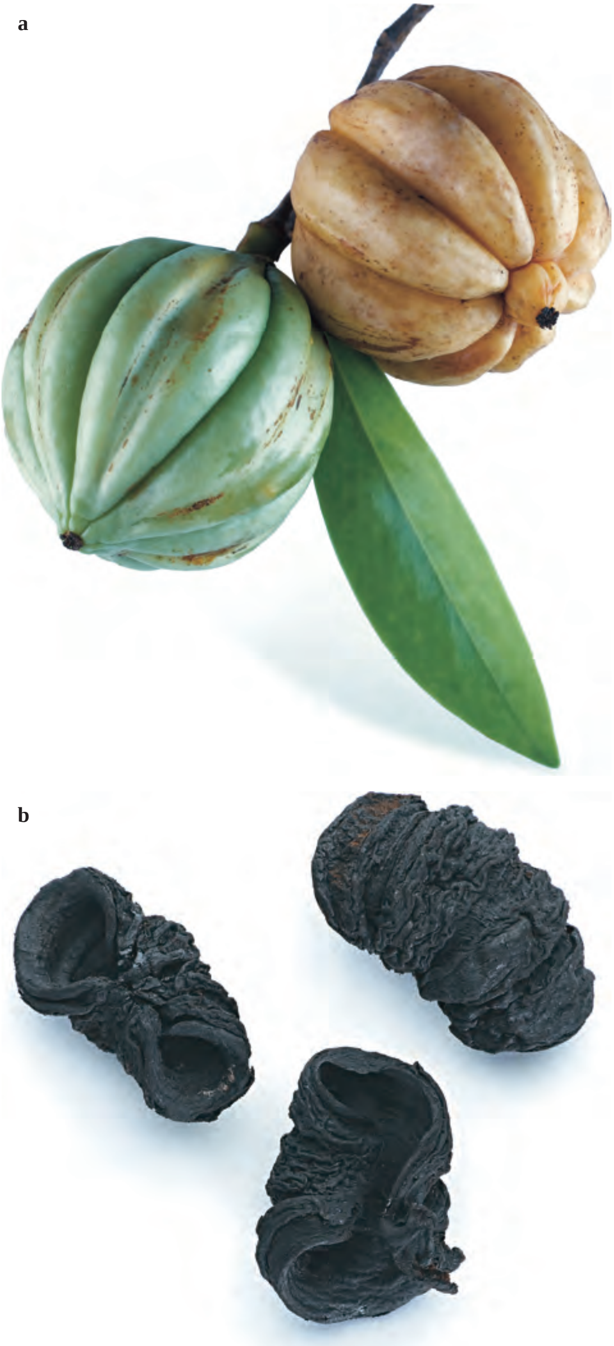

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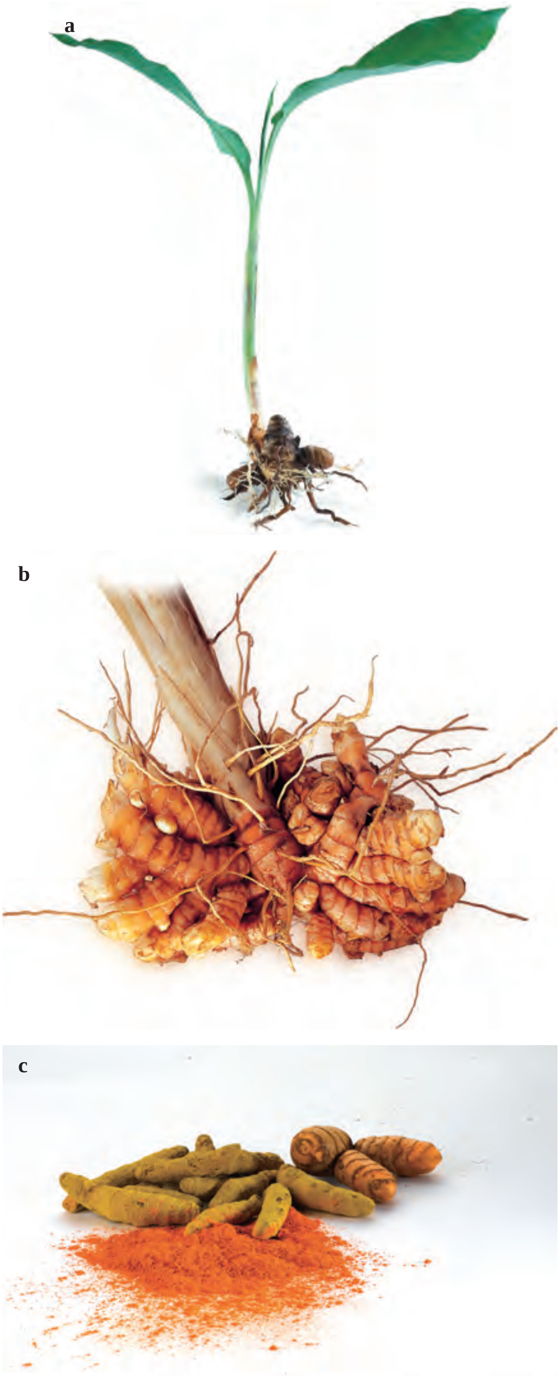

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