

# 3 Natural Raw Materials in the Flavor and Fragrance Industry

## 3.1 Introduction

Although synthetic flavor and fragrance materials are produced on an industrial scale, naturally occurring raw materials continue to be essential, important ingredients in the manufacture of flavor and fragrance compositions for several reasons. First, the composition and sensory nature of natural products are often too complex to be reproduced by a combination of synthetic fragrance substances. Second, the characteristic flavor and fragrance substances of a particular product often cannot be synthesized at a competitive price. Third, the use of natural materials in the production of certain flavor compositions is compulsory. Moreover, an increasing demand for perfumes based on natural materials has been observed recently.

Currently, raw materials for the flavor and fragrance industry are obtained from more than 250 different plant species, but only a handful of products originate from animals.

Raw materials are isolated from various parts of plants, e.g., blossoms, buds, fruit, peel, seeds, leaves, bark, wood, roots, or from resinous exudates. Different parts of the same plant may yield products with different compositions. For instance, steam distillation of the bark of the cinnamon tree gives cinnamon bark oil, which contains mainly cinnamaldehyde, whereas cinnamon leaf oil obtained from the leaves of the tree contains eugenol as its major constituent.

The quality of natural products depends considerably on their geographic origin, even if they are isolated from the same plant species. This may be partly due to variations in cultivation conditions, such as soil structure and climate, but also results from the fact that different varieties of the same plant species are cultivated in different areas. Thus, more than 500 natural raw materials are available for the creation of perfumes and flavors.

The flavor and fragrance industry has expanded so much that the plants required to supply the raw materials are now grown on a very large scale. Examples are the peppermint and spearmint plantations in the United States, the lavandin plantations in southern France and the cornmint plantations in China and India.

The economic importance of the cultivation of aromatic plants has led to the systematic breeding of new varieties, which are obtained either by alternation of

generations or by vegetative means in an attempt to improve yield, oil quality, and resistance to disease and insects.

The production of some essential oils has decreased to low levels or even been discontinued due to competition from synthetic products. Nevertheless, the worldwide production of flavor and fragrance materials of natural origin has increased recently due to breeding successes, but their total market share has decreased. Annual worldwide sales currently amount to 700–880 million US\$ [219–221]. The total amount of annually produced essential oils is estimated at 45.000 t [221]. More details of the economic importance of the individual essential oils are given in references [219–222c].

Raw materials derived from intensive agricultural cultivation are usually relatively inexpensive. However, the prices of some natural materials may exceed \$ 1000 per kilogram because cultivation and harvesting of these plants are tedious and product yields are very low. Examples of extremely valuable ingredients of fragrance and flavor creations include rose oil, jasmine absolute, tuberose absolute, orris root oil, ambrette seed oil, angelica root oil, and orange flower oil [220].

## **3.2 Isolation of Natural Fragrance and Flavor Concentrates**

Three main methods are used to concentrate plant flavor and fragrance substances:

1. distillation
2. mechanical separation ('pressing')
3. solvent extraction

The qualitative and quantitative composition and, thus, the sensory properties of the product depend on the isolation procedure. For example, an extract contains large amounts of nonvolatile components that are not found in essential oils obtained by distillation. Since these components markedly influence odor development (complexing and fixing), the two products may have completely different sensory properties, even though the compositions of their odorous volatile constituents are comparable.

In addition, the distillation of essential oils at elevated temperature results in the transformation of thermolabile substances, and some typical components are only released from their precursors in the plants under distillation conditions.

Solvent extraction is generally applied in the separation of heat-labile plant materials or if an essential oil can be obtained only in very low yield (e.g., from

blossoms). It is also used if the nonvolatile components are desired for their fixative properties (e.g., in the preparation of resinoids from exudates).

### 3.2.1 Essential Oils

*Production.* Essential oils are obtained from plant materials by distillation with water or steam. After condensation of the vapor phase, the oil separates from the aqueous phase and is removed. The yield of essential oil, based on the starting plant material, generally ranges from a few tenths of 1% to a few percent. The apparatus used in the production of natural fragrance concentrates is described in [223].

Essential oils consist of volatile, lipophilic substances that are mainly hydrocarbons or monofunctional compounds derived from the metabolism of mono- and sesquiterpenes, phenylpropanoids, amino acids (lower mass aliphatic compounds), and fatty acids (long-chain aliphatic compounds). Unlike fatty oils, essential oils do not leave a grease stain when dabbed on filter paper.

Essential oils are to be distinguished from the so-called distillates which are ethanol-containing products that are obtained from plant materials by distillation with ethanol or with ethanol–water mixtures. *Essence oils* are defined as essential oils that separate from the aqueous phase in the distillation receiver during the distillative concentration of fruit juices (usually citrus juices).

*Citrus peel oils* are a special type of essential oil. They are isolated by pressing the peel to release the volatile substances stored in the pericarp in small oil glands. The resulting products are termed essential oils because they consist largely of highly volatile terpene hydrocarbons. However, they also contain small amounts of nonvolatile compounds, such as dyes, waxes, and furocoumarines.

*Uses.* Most essential oils are used directly as starting materials in the production of flavor and fragrance compositions. However, some essential oils are fractionated or concentrated by distillation, partitioning, or adsorption. Substances that are important for the desired characteristic odor and taste are thus concentrated, and other components, which possess either an unpleasant or very faint odor or are unsuitable for the application in question, are removed.

Individual compounds can be isolated from essential oils containing one or only a few major components by distillation or crystallization. Examples are eugenol from clove oil, menthol from cornmint oil, citronellal from *Eucalyptus citriodora* oil and citral from *Litsea cubeba* oil. These compounds are used as such or serve as starting materials for the synthesis of derivatives, which are also used as flavor and fragrance substances. However, the importance of some of these oils has decreased substantially because of the development of selective synthetic processes for their components.

Although essential oils or their fractions are mixtures of many substances, these oils are occasionally converted as a whole into derivatives. Examples of such

derivatives are vetiveryl acetate from vetiver oil, guaiyl acetate from guaiac wood oil, and acetyl cedrene from cedarwood terpenes. These products are also employed as fragrance substances.

### 3.2.2 Extracts

Extracts of fragrance and flavor substances obtained from plants are termed pomades, concretes, absolutes, resinoids, or tinctures according to their method of preparation.

*Pomades* consist of fats that contain fragrance substances and are produced by the hot or cold enfleurage of flowers. Hot enfleurage is the oldest known procedure for preserving plant fragrance substances. In this method, flowers (or other parts of a plant) are directly immersed in liquid or molten wax.

In cold enfleurage, the volatile components released by flowers into their surroundings are absorbed with fats over a longer period of time. This industrial procedure was developed in southern France in the 19th century for the production of high-grade flower concentrates. It involves the application of fresh flowers to a fat layer, consisting of a mixture of specially refined lard and beef tallow, which is spread on a glass plate in a closed container. This method, however, has been almost totally replaced by the less tedious technique of solvent extraction.

*Concretes* are prepared by extracting fresh plant material with nonpolar solvents (e.g., toluene, hexane, petroleum ether). On evaporation, the resulting residue contains not only volatile fragrance materials, but also a large proportion of non-volatile substances including waxy compounds. For this reason, concretes (like pomades) are not completely soluble in alcohol and, thus, find limited use as perfume ingredients. However, they can be employed in the scenting of soaps.

Concretes, which are actually intermediate products (see below), are prepared mainly from flowers (rose, jasmine, tuberose, jonquil, ylang-ylang, mimosa, boronia, etc.), but also from other plant materials (lavender, lavandin, geranium, clary sage, violet leaves, oak moss, etc.). A yield of ca. 0.3% based on the starting flower material, is obtained in the production of jasmine concrete.

*Absolutes* are prepared by taking up concretes in ethanol. Compounds that precipitate on cooling are then removed by filtration. After evaporation of the ethanol, a wax-free residue called an absolute is left behind. Absolutes are completely soluble in ethanol and, therefore, can be freely used as perfume ingredients. They are usually formed in a yield of ca. 50%, based on the concrete as starting material.

In rare cases, absolutes can be obtained directly by extracting the plant material with alcohol (e.g., tonka absolute).

*Resinoids* are prepared by extracting plant exudates (balsams, oleo gum resins, natural oleo resins, and resinous products) with solvents such as methanol, ethanol, or toluene. Yields range from 50 to 95%. The products are usually highly viscous and are sometimes diluted (e.g., with phthalates or benzyl benzoate) to improve their flow and processing properties.

Resinoids mainly consist of nonvolatile, resinous compounds and are primarily used for their excellent fixative properties.

The resinoids described above should be distinguished from prepared oleoresins (e.g., pepper, ginger, and vanilla oleoresins), which are concentrates prepared from spices by solvent extraction. The solvent that is used depends on the spice; currently, these products are often obtained by extraction with supercritical carbon dioxide [223a]. Pepper and ginger oleoresins contain not only volatile aroma compounds, but also substances responsible for pungency.

*Tinctures* are alcoholic solutions that are prepared by treating natural raw materials with ethanol or ethanol–water mixtures. They can also be obtained by dissolving other extracts in these solvents. Tinctures are sometimes called *infusions*.

### 3.3 Survey of Natural Raw Materials

The following survey of the most important, well-known raw materials used in the flavor and fragrance industry is by no means complete; the materials are listed in alphabetical order. Physical standards for essential oils are described as specified by the International Organization for Standardization (ISO), the Association Française de Normalisation (AFNOR), or the Essential Oil Association of the United States (EOA). Gas chromatograms are widely used for analysis and quality control, but have not been included due to lack of space. Further details are given in the literature, e.g., [224, 224a], and in ISO and AFNOR [224b] specifications, which now include gas chromatograms.

The enumeration of the components of the individual products has been limited to the main constituents and the odor determining compounds; further information is available in the literature, e.g., [214, 225–230a]. Physical data for extracts or concentrates consisting largely of nonvolatile material are not given because the composition of these products varies widely according to the isolation and manufacturing procedure used.

The botanical names of plants are cited in accordance with the International Code of Botanical Nomenclature (ICBN) as described, for example, [231].

**Allium oils** are obtained from garlic and onion (Liliaceae). Their quality is assessed on the basis of their odor and aroma rather than their physical and chemical properties. The EOA specifications given below are, therefore, of limited value only.

1. *Garlic oil* is obtained by steam distillation of crushed bulbs of the common garlic, *Allium sativum* L.; it is a clear, reddish-orange liquid, with a strong, pungent, characteristic garlic odor.

$d_{25}^{25}$  1.040–1.090;  $n_D^{20}$  1.5590–1.5790 [232].

Diallyl disulfide [2179-57-9] is an essential odor component of garlic oil [233].



2. *Onion oil* is obtained by steam distillation of the crushed bulbs of the common onion, *Allium cepa* L. It is an amber-yellow to amber liquid with a strongly pungent, lasting, characteristic onion odor.

$d_{25}^{25}$  1.050–1.135;  $n_D^{20}$  1.5495–1.5695 [234].

Aliphatic sulfur compounds, in particular disulfides such as methyl propyl disulfide, dipropyl disulfide, and especially *cis*- and *trans*-propenyl propenyl disulfide are mainly responsible for the typical odor of onion oil [235]. The presence of 2-hexyl-5-methyl-3(2H)-furanone [33922-66-6] is a characteristic of authenticity [235a].

Garlic and onion oil are used in seasoning mixtures for the food industry [8000-78-0], [8002-72-0], [8008-99-9], [8054-39-5].

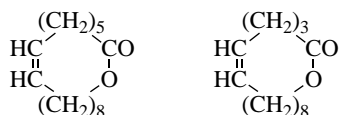
**Allspice oil**, see Pimento oils.

**Ambergris** (ambra), see Animal secretions.

**Ambrette seed oil** is obtained by steam distillation of the dried, crushed seeds of *Ambelmoschus moschatus* Medik. (*Hibiscus abelmoschus* L., Malvaceae), a flowering shrub growing in tropical areas. Due to its content of long-chain fatty acids, the crude product is a waxy mass and, therefore, also called 'Ambrette beurre.' Removal of the fatty acids with alkali gives a clear yellow to amber liquid with the strong, musky odor of ambrettolide.

$d_{25}^{25}$  0.898–0.920;  $n_D^{20}$  1.4680–1.4850;  $\alpha_D^{20}$  –2°30' to +3'; acid number: max. 3; saponification number: 140–200 [236].

The constituents responsible for the musk odor of the oil are (*Z*)-7-hexadecen-16-olide [123-69-3] (ambrettolide) and (*Z*)-5-tetradecen-14-olide [63958-52-1]:



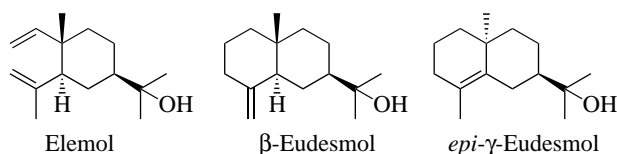
Ambrettolide    5-Tetradecen-14-olide

Other components are acyclic aliphatic esters and terpenes, such as farnesol and farnesyl acetate [237–239a]. Ambrette seed oil is one of the most expensive essential oils and, thus, is used mainly in fine fragrances and in alcoholic beverages. FCT 1975 (13) p. 705; [8015-62-1], [84455-19-6].

**Amyris oil** is obtained by steam distillation of the wood from the tree *Amyris balsamifera* L. (Rutaceae), which grows in the Caribbean area and around the Gulf of Mexico. It is a pale yellow to amber, slightly viscous liquid with a mild wood odor.

$d_{20}^{20}$  0.946–0.978;  $n_D^{20}$  1.505–1.510;  $\alpha_D^{20}$  +10° to +60°; solubility: 1 vol in 1 vol of 90% ethanol at 20 °C; solutions sometimes become opalescent on dilution; acid number: max. 3.0; ester number (after acetylation): 180–198 [240].

The oil is sometimes incorrectly called West Indian sandalwood oil. However, its composition and odor are different from those of the oils obtained from sandalwood species. The major components of amyris oil are sesquiterpenoids such as elemol [639-99-6],  $\beta$ -eudesmol [473-15-4], and *epi*- $\gamma$ -eudesmol [15051-81-7] [241–244].



Amyris oil is used in perfume compositions, mainly as a fixative [8015-65-4], [90320-49-3].

**Angelica oil** is prepared from *Angelica* roots or seeds.

1. *Angelica root oil* is obtained by steam distillation of the dried roots of *Angelica archangelica* L. [*Archangelica officinalis* (Moench) Hoffm.], a plant occurring predominantly in Europe (Apiaceae). The oil is a pale yellow to deep amber liquid with a green, herbaceous, peppery, musk-like odor and a bittersweet taste.

$d_{25}^{25}$  0.850–0.880, occasionally up to 0.930 for oils from stored roots;  $n_D^{20}$  1.4735–1.4870;  $\alpha_D^{20}$  0° to +46°; acid number: max. 7; ester number: 10–65; solubility: 1 vol in at least 1 vol of 90% ethanol, often with turbidity [245].

2. *Angelica seed oil* is similarly obtained from fresh seeds of the plant. It is a light yellow liquid with an odor that is sweeter and more delicate than that of the root oil.

$d_{25}^{25}$  0.853–0.876;  $n_D^{20}$  1.4800–1.4880;  $\alpha_D^{20}$  +4° to +16°; acid number: max. 3; ester number: 14–32; solubility: 1 vol in at least 4 vol 90% ethanol, often with considerable turbidity [246].

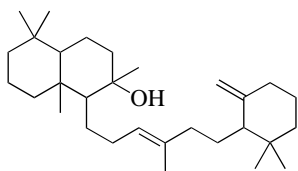
Angelica root oil contains ca. 90% terpenoids and sesquiterpenoids.  $\alpha$ -Pinene, 3-carene, limonene, and  $\beta$ -phellandrene are the major components (together ca. 60%). In addition, the oil contains a large number of oxygen-containing compounds, of which the macrolides 15-pentadecanolide and 13-tridecanolide are essential odor components [247–253]. The two angelica oils are used mainly in the alcoholic beverage industry, and in very low dosages also in fine fragrances. FCT 1974 (12) p. 821; [8015-64-3], [84775-41-7].

**Animal secretions** are of minor commercial importance because some of the animal species from which they are obtained are virtually extinct, and the killing quota for others has been sharply reduced. Few odoriferous secretions of

mammals have actually been shown to possess pheromone-like properties linked with reproduction. However, the odor of animal secretions is known to be important for communication and behavior of a particular species. Most of the products described below contain strong-smelling compounds with relatively high molecular masses. Therefore, they are used as long-lasting fragrance complexes. Most of their odoriferous constituents are now produced synthetically and are used for the same purposes. Therefore, these fragrance materials are mentioned only for reasons of history.

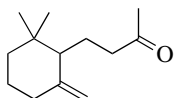
1. *Ambergris (ambra)* is a secretion of the sperm whale *Physeter catodon* (*P. macrocephalus* L.), that possibly results from a pathological condition. Ambergris has a lower density than water and washes ashore along the ocean coasts. The major quantity is obtained from killed animals, but only a low percentage contain ambergris in their intestines.

Fresh ambergris is almost black, but it turns light gray and develops a pleasant odor when exposed to light and seawater over a period of time. The major components of ambergris are epicoprosterol and the odorless triterpene alcohol, ambrein [473-03-0].

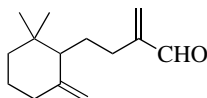


Ambrein

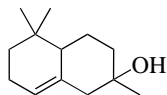
Ambrein is the likely precursor of a number of strongly odoriferous mono-, bi-, and tricyclic compounds that are formed by autoxidation or photooxidation [254, 255]. Examples are as follows:



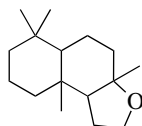
$\gamma$ -Dihydroionone  
[13720-12-2]  
(odor: tobacco)



2-Methylene-4-(2,2-dimethyl-6-methylenecyclohexyl)butanal  
[72892-63-8]  
(odor: seawater)



$\alpha$ -Ambrinol  
[41199-19-3]  
(odor: moldy, animal, fecal)



3a,6,6,9a-Tetramethyldodecahydronaphtho[2,1-b]furan  
[6790-58-5]  
(odor: ambergris)



Together, these compounds largely represent the odor of ambergris. Ambergris is applied as a 3% tincture in 90% ethanol, which is matured by standing over a period of time with occasional shaking. It was used in fine fragrances. FCT 1976 (14) p. 675.

2. *Beeswax absolute* is obtained by alcohol extraction of beeswax. The yield is generally less than 1%. The yellowish-brown viscous product has a mild, honey-like odor and high tenacity; it is used almost exclusively in fine fragrances. FCT 1976 (14) p. 691.

3. *Castoreum* is an unpleasantly sharp-smelling, oily substance secreted by special glands of beavers, *Castor fiber* L. (Castoridae), living in Canada, Alaska, and Siberia. Both sexes secrete the substance, which accumulates in an abdominal pouch, also called castoreum. Dilute castoreum (e.g., as a tincture in ethanol) smells pleasantly of birch tar and musk and is slightly fruity.

Castoreum is a byproduct of the fur industry. The beaver pouches are dried in the air or over a wood fire, the color of their contents then changes from yellow to dark brown, and the consistency from a butter-like to resinous character.

In addition to alcoholic tinctures, castoreum is available in the form of resinoids, which are prepared by extracting dried, comminuted pouches with suitable solvents.

The intense, for the Siberian beaver leathery, odor of castoreum is caused largely by phenolic compounds (e.g., 4-alkylphenols and catechol derivatives [256]), which beavers take in with their food and excrete into their abdominal pouch. Castoreum was used mainly in fine fragrances for its characteristic, long-lasting odor, particularly for delicate leather nuances. FCT 1973 (11) p. 1061; [8023-83-4], [92704-04-6], [92704-05-7].

4. *Civet* is a glandular secretion produced by both sexes of the civet cat (Viverridae). Two species are known: *Civettictis civetta* that inhabits Ethiopia, and *Viverra zibetha* that is found in India and southeast Asia.

The animals are kept in cages, and the fresh secretion is taken from the pouches at regular (about one-week) intervals. Civet is almost liquid with a light yellow color. It darkens when exposed to light and takes on a consistency like salve. In dilutions (e.g., as an alcoholic tincture), civet has a pleasant, sweetish odor. A resinoid prepared by extraction with acetone is a dark brown-red mass [257]. Civetone (see p. 88) is the main odoriferous constituent of civet (2.5–3.4%). Civet contains other macrocyclic ketones such as cyclohexa- and cycloheptadecanone and 6-*cis*-cycloheptadecanone. Traces of indole and skatole contribute to the animal note [258].

Civet has a distinctly different odor from musk and was formerly a versatile ingredient of fine fragrances. FCT 1974 (12) p. 863; [68991-27-5].

5. *Musk* is secreted exclusively by the male animals of *Moschus moschiferus*, a wild deer living in the mountains of Nepal, Tibet, and Mongolia. The light yellow

secretion with a salve consistency accumulates in an abdominal pouch and probably serves to attract females. When the pouch is dried, the secretion solidifies to form a brittle, brown mass with a characteristic odor. Since several *Moschus* species occur, large variations exist in the quality and specifications of musk. Hunting of the animals has been prohibited; therefore, only small quantities of musk are occasionally offered at extremely high prices [259]. In the USA and Europe, natural musk is no longer used as a fragrance ingredient.

(-)-Muscone and related macrocyclic ketones are responsible for the odor of musk [260, 261]. Like other animal secretions, musk was preferentially used as an alcoholic tincture in fine fragrances. FCT 1983 (21) p. 865; [68991-41-3], [90064-09-8].

**Anise oil, Aniseed oil** is obtained by steam distillation of the fruits of *Pimpinella anisum* L. (Apiaceae). It is a colorless to pale yellow liquid or crystalline mass with a powerful, sweet odor, characteristic of anethole.

$d_{20}^{20}$  0.980–0.990;  $n_D^{20}$  1.552–1.561;  $\alpha_D^{20}$   $-2^\circ$  to  $+2^\circ$ ; solubility: 1 vol in 3 vol of 90% ethanol at  $20^\circ\text{C}$ ;  $fp$   $15\text{--}19.5^\circ\text{C}$  [262].

The main component of anise oil is *trans*-anethole, which is present at a concentration of 87–94% and which determines the melting point of the oil [263–266b].

The oil was formerly produced in many countries, mainly in eastern Europe, but has now been replaced, to a large extent, by the less expensive star anise and fennel oils which also contain a high percentage of anethole.

Anise oil is used for flavoring foods, beverages, and oral care products. FCT 1973 (11) p. 865; [8007-70-3], [84775-42-8].

**Artemisia oil (Armoise oil)** is obtained by steam distillation of the herb *Artemisia herba-alba* Asso (Asteraceae) that grows in Morocco. It is a light yellow to yellow liquid with a light herbaceous odor characteristic of thujone.

$d_{25}^{25}$  0.917–0.935;  $n_D^{20}$  1.4600–1.4720;  $\alpha_D^{20}$   $-25^\circ$  to  $-8^\circ$ .

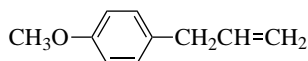
The major components of artemisia oil are the ketones camphor (15–40%) and  $\alpha$ - and  $\beta$ -thujone (see p. 217) (together 70–25%) [267–270]. Since *Artemisia herba-alba* exists as various chemotypes, the composition of the oil may vary widely.

Artemisia oil is used in fairly large amounts in fine fragrances (e.g., for chypre notes). The annual production is about 50 tons. FCT 1975 (13) p. 719; [8022-37-5], [84775-75-7].

**Basil oil** is available in several types that differ in their major components; the most important are described.

1. *Basil oil, methylchavicol-type (Réunion type, exotic type)* is obtained by steam distillation of the flowering tops or whole plants of *Ocimum basilicum* L. (Lamiaceae). This oil is produced mainly in Réunion, the Comores, Madagascar, and the Seychelles. It is a light yellow liquid with a fresh, green, spicy odor characteristic of methylchavicol (estragole) [140-67-0].

$d_{20}^{20}$  0.948–0.970;  $n_D^{20}$  1.5100–1.5200;  $\alpha_D^{20}$   $-1^\circ$  to  $+2^\circ$ ; solubility: 1 vol in max. 7 vol. 80% ethanol; content by GC: methylchavicol 75–87%; linalool 0.5–3% [271].



Methylchavicol (estragole)

This basil oil variety is used predominantly for seasoning foods.

2. *Basil oil, linalool-type (European type; mediterranean type)* is produced mainly in the mediterranean area (France, Egypt). It is light yellow to amber-colored oil with typical fresh-spicy odor.

$d_{20}^{20}$  0.895–0.920;  $n_D^{20}$  1.4750–1.4950;  $\alpha_D^{20}$   $-2^\circ$  to  $-14^\circ$ ; content by GC: linalool 45–62%; methylchavicol trace to 30%; eugenol 2–15% [272].

It is used for food flavoring and in perfumery. For further constituents of these two basil oil types see [273–279a].

3. *Indian Basil oil* is produced exclusively in India. It contains ca. 70% methylchavicol and 25% linalool. It is used mainly for the isolation of the pure compounds. Methylchavicol is used as starting material for the production of anethole.

FCT 1973 (11) p. 867; [8015-73-4], [84775-71-3].

**Bay oil** is obtained by steam distillation of the leaves of *Pimenta racemosa* (Miller) Moore (Myrtaceae). It is a dark brown liquid with a strong, spicy, clovelike odor.

$d_{20}^{20}$  0.943–0.984;  $n_D^{20}$  1.505–1.517; phenols content: min. 50% [280].

Evergreen bay trees or bay-rum trees, which are up to 12 m high, grow wild and are also cultivated in northern South America and in the West Indies. The main cultivation area is the island of Dominica.

The major components of the oil are myrcene (20–30%), eugenol (44–56%), and chavicol (8–11%) [281–283b]. The phenol content is determined largely by the last two compounds.

Total production of bay oil is ca. 50 t/yr. It has antiseptic properties because of its high phenol content and is, therefore, a classical ingredient for perfuming after-shave lotions. FCT 1973 (11) p. 869; [8006-78-8], [85085-61-6].

### Benzoe resinoids

1. *Benzoe Siam resinoid* is obtained by solvent extraction of the resin from *Styrax tonkinensis* (Pierre) Craib ex Hartwich trees (Styracaceae). The wild growing *Styrax* tree is widespread in Thailand, Laos, Cambodia, and Vietnam.

Benzoe Siam resinoid is a reddish to light brown, viscous liquid with a long-lasting, chocolate-like, sweet, balsamic odor. It is used in perfumery for balsamic nuances and as a fixative [9000-72-0], [84012-39-5].

2. *Benzoe Sumatra resinoid* is obtained by solvent extraction of the resin from *Styrax benzoin* Dryand, a tree growing predominantly on the island of Sumatra.

Benzoe Sumatra resinoid is a dark brown viscous liquid with a warm, powdery, sweet-balsamic odor. Its main volatile, odor-determining components are derivatives of benzoic and cinnamic acids and vanillin [284, 284a].

Benzoe Sumatra resinoid is used in perfumery, mainly as a fixative with a warm, balsamic note [9000-73-1], [84929-79-3]. FCT 1973 (11) p. 871.

**Bergamot oil** see Citrus oils.

**Bitter almond oil** (free from hydrogen cyanide) contains benzaldehyde as its main component. Benzaldehyde does not occur as such in the plant, but is formed, together with hydrogen cyanide, by the hydrolytic cleavage of the glycoside amygdalin.

Amygdalin is present in bitter almonds, the seeds of *Prunus amygdalus* Batsch var. *amara* (DC.) Focke, and ripe apricot kernels, *Prunus armeniaca* L. (Rosaceae). The press cake, which remains after removal of the fatty oils, is macerated with water and left to stand for several hours, after which the 'essential oil' is separated by steam distillation. The crude oil contains 2–4% hydrogen cyanide, which is removed by washing with alkaline solutions of iron(II) salts. Subsequent redistillation yields an oil free from hydrogen cyanide. It is a colorless to slightly yellow liquid with an intense, almond-like, cherry aroma and a slightly astringent, mild taste.

$d_{25}^{25}$  1.025–1.065;  $n_D^{20}$  1.5350–1.5550; acid value: max. 8; solubility: 1 vol in max. 6 vol 50% ethanol. HCN content: <0.01%; benzaldehyde content by GC: min. 98% [285].

Bitter almond oil is used almost exclusively in natural aroma compositions.

**Blackcurrant absolute** (Bourgeons de cassis absolute, cassis absolute) is obtained by solvent extraction via the concrete obtained from the dormant buds of the blackcurrant bush *Ribes nigrum* L. (Saxifragaceae). The yield is ca. 3%. Blackcurrant absolute is a dark green paste with the characteristic, powerful, penetrating odor of blackcurrants. The typical 'catty' note is caused by a sulfurous trace constituent, 4-methoxy-2-methyl-2-butenethiol [80324-91-0] [286–288].

Blackcurrant absolute is used in fine fragrances and in fruity food flavors.

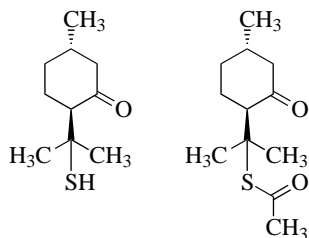
**Bois de rose oil**, see Rosewood oil.

**Buchu leaf oils** are obtained by steam distillation of *Barosma betulina* (Bergius) Bartl. and Wendl. and *B. crenulata* (L.) Hook. (Rutaceae) leaves. The oils are dark yellow to brown liquids with a characteristic minty-fruity odor, reminiscent of blackcurrant.

$d_{25}^{25}$  0.912–0.956;  $n_D^{20}$  1.474–1.488;  $\alpha_D^{20}$   $-36^\circ$  to  $-8^\circ$ ; acid number: 1–5; ester number: 20–85.

The bushes grow wild and are cultivated in South Africa. The major components of the oils are (+)-limonene (ca. 10%) and other cyclic terpenoids that are structurally related to menthone. However, the constituents responsible for the

characteristic blackcurrant odor are *trans-p*-menthane-8-thiol-3-one [34352-05-1] and its *S*-acetate derivative [57074-34-7] which are two of the small number of naturally occurring sulfur-containing terpenoids known to date [289, 290].

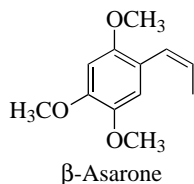


Buchu oil is used as a flavor ingredient (e.g., in fruit aromas) and in perfumery in chypre bases and in certain types of eau de cologne; only very small amounts are employed because of its intensity [68650-46-4], [84649-93-4].

**Calamus oil (sweet flag oil)** is obtained by steam distillation of fresh or unpeeled, dried roots of *Acorus calamus* L. (Araceae). It is a yellow to medium brown, moderately viscous liquid with a pleasant, spicy, aromatic odor.

The plant occurs in polyploid varieties and the corresponding essential oils differ predominantly in their content of  $\beta$ -asarone (*cis*-isoasarone) [5273-86-9]:

diploid (American)	0%
triploid (European)	0–10%
tetraploid (East Asian)	up to 96%



The following data are typical for European and Indian oils, respectively:  $d_{25}^{25}$  0.940–0.980 and 1.060–1.080;  $n_D^{20}$  1.5010–1.5160 and 1.5500–1.5525;  $\alpha_D^{20}$  +5° to +35° and –2° to +6.5°; acid number: max. 4; ester number: 3–20; solubility: 1 vol in 5 vol of 90% ethanol; solutions may be turbid [291]. Main constituents of European oil are sesquiterpene ketones (shyobunone, preisocalamenediol and acorenone), but its characteristic odor is formed by a number of trace constituents, especially unsaturated aldehydes like *Z,Z*-4,7-decadienal [22644-09-3] [292–294a].

Calamus oil is used in perfumery for spicy-herbaceous notes; small quantities are also employed in the alcoholic beverage industry. However, use is legally restricted because of the potential toxicity of  $\beta$ -asarone. For determination of  $\beta$ -asarone content in calamus oil see [295]. FCT 1977 (15) p. 623; [8015-79-0], [84775-39-3].

**Camphor oil** is obtained by steam distillation of the wood of the camphor tree *Cinnamomum camphora* Sieb. (Lauraceae) growing in China, Taiwan, and Japan. The main constituent of the crude oil is camphor (ca. 50%), which can be separated by crystallization on cooling and subsequent centrifugation. Fractionation of the mother liquor gives two oils:

1. *White camphor oil* is the first distillation fraction (ca. 20% of the crude camphor oil). It is a colorless or almost colorless liquid with a cineole-like odor.  $d_{25}^{25}$  0.855–0.875;  $n_D^{20}$  1.4670–1.4720;  $[\alpha]_D +16^\circ$  to  $+28^\circ$ ; solubility: 1 vol in 1 vol of 95% ethanol; solutions usually become cloudy on further dilution [296].

In addition to monoterpene hydrocarbons, this oil contains up to 35% 1,8-cineole.

2. *Brown camphor oil* is a fraction with a boiling point higher than that of camphor (ca. 20%). It is a pale yellow to brown liquid with the characteristic odor of sassafras oil.

$d_{25}^{25}$  1.064–1.075;  $n_D^{20}$  1.5100–1.5500;  $\alpha_D^{20}$   $0^\circ$  to  $+3^\circ$ ;  $fp$   $6^\circ\text{C}$ ; solubility: 1 vol in 2 vol of 90 % ethanol [297].

The oil contains more than 80% safrole and, like Brazilian sassafras oil is therefore used as a raw material for the production of heliotropin (piperonal, see p. 137) via isosafrole.

Camphor oils with a high safrole content can also be obtained by steam distillation from other *Cinnamomum* species (see sassafras oils).

The production of natural camphor and camphor oils was formerly several thousand of tons per year, but has declined as a result of the production of synthetic camphor. The same is true for the distillation of linalool-containing camphor oils (Ho oil, Ho leaf oil), which are derived from other varieties of the camphor tree.

China still produces 500 t per year of camphor oil [298]; [8008-51-3], [92201-50-8].

**Cananga oil**, see Ylang-Ylang and Cananga oils.

**Caraway oil** is obtained by steam distillation of crushed caraway seeds from *Carum carvi* L. (Apiaceae). It is a colorless to yellow liquid with a characteristic caraway odor and a mild-spicy taste.

$d_{20}^{20}$  0.901–0.920;  $n_D^{20}$  1.4840–1.4890;  $\alpha_D^{20}$   $+67^\circ$  to  $+80^\circ$ ; solubility: 1 vol in max. 8 vol. 80% ethanol. Carbonyl value 179–243 corresponding to a carbonyl content calculated as carvone: 48–65% [299–299d].

The major constituents of common caraway oil are (+)-limonene and (+)-carvone, which together may make up more than 95% of the oil. (+)-Carvone is the essential odor component.

Caraway oil is used primarily for flavoring foods and alcoholic beverages, but also for the production of (+)-carvone. FCT 1973 (11) p. 1051; [8000-42-8], [85940-31-4].

**Cardamom oil** is obtained by steam distillation of the seeds of *Elettaria cardamomum* (L.) Maton (Zingiberaceae). It is a colorless or very pale yellow liquid with an

aromatic, penetrating, slightly camphoraceous odor and a persistent, pungent, strongly aromatic taste.

$d_{20}^{20}$  0.919–0.936;  $n_D^{20}$  1.4620–1.4680;  $\alpha_D^{20}$  +22° to +41°; solubility: 1 vol in max. 5 vol. 70% ethanol [300].

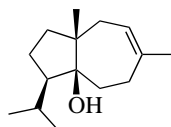
The major components of cardamom oil are 1,8-cineole and  $\alpha$ -terpinyl acetate (ca. 30% each). Trace constituents like unsaturated aliphatic aldehydes may be important for the typical aroma [301–307b]. It is produced from cultivated or wild plants in the mountainous regions of southern India, Sri Lanka, Indonesia, and Guatemala.

Cardamom oil is used primarily for seasoning foods, alcoholic beverages, and in small dosages also occasionally in perfumery. FCT 1974 (12) p. 837; [8000-66-6], [93062-62-5], [93062-63-6].

**Carrot seed oil** is obtained by steam distillation of the crushed seeds of *Daucus carota* L. (Apiaceae). It is a light yellow to amber-yellow liquid with a pleasant, aromatic odor.

$d_{20}^{20}$  0.900–0.945;  $n_D^{20}$  1.4800–1.4930;  $\alpha_D^{20}$  –30° to –4°; solubility: 1 vol in max. 2 vol of 90% ethanol; solutions in up to 10 vol of ethanol are clear to opalescent [308].

The main constituent of carrot seed oil is carotol [465-28-1], which may be present in over 50% concentration [309–313a].



Carotol

Carrot seed oil is used in the alcoholic beverage industry, in food flavors, and in perfume compositions. FCT 1976 (14) p. 705; [8015-88-1], [84929-61-3].

**Castoreum**, see Animal secretions.

**Cedar Oils.** Several different conifer species are called cedars and the corresponding oils vary considerably in composition. The following cedar oils are commercially important:

1. *Cedar leaf oil* (Thuja oil) is produced by steam distillation of fresh leaves and branch ends of the tree *Thuja occidentalis* L. (Cupressaceae). It is a colorless to yellow liquid with a powerful, herbaceous odor, characteristic of thujone, see p. 217, [314–319a].

$d_{25}^{25}$  0.910–0.920;  $n_D^{20}$  1.4560–1.4590;  $\alpha_D^{20}$  –14° to –10°; ketone content (calculated as thujone): min. 60%; solubility: 1 vol in 3 vol of 70% ethanol at 25 °C [320].

The oil is produced in the northern states of the United States and in Canada. It is used in perfumery for dry nuances in citrus and woody compositions. FCT 1974 (12) p. 843; [8007-20-3], [90131-58-1].

2. *Chinese cedarwood oil* is similar in composition to Texas cedarwood oil (see below). Chinese cedarwood oil is obtained by steam distillation of *Chamaecyparis funebris* (Endl.) France (*Cupressus funebris* Endl., Cupressaceae), which is a weeping cypress, indigenous to China. Commercial Chinese cedarwood oil is a colorless to slightly yellow oil with an odor more smoke-like than the American oils.

$d_{20}^{20}$  0.938–0.960;  $n_D^{20}$  1.5000–1.5080;  $\alpha_D^{20}$   $-35^\circ$  to  $-20^\circ$ ; solubility: 1 vol in max. 5 vol. 95% ethanol. Composition by GC:  $\alpha$ -cedrene 13–29%; thujopsene 18–31%; cedrol 10–16% [321], [85085-29-6].

3. *Texas cedarwood oil* is produced by steam distillation of chopped wood of the Texas cedar, *Juniperus mexicana* Schiede (Cupressaceae). It is a brown to reddish-brown, viscous liquid that may partially solidify at room temperature. It has a characteristic cedarwood odor.

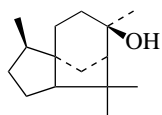
$d_{20}^{20}$  0.950–0.966;  $n_D^{20}$  1.5020–1.5100;  $\alpha_D^{20}$   $-52^\circ$  to  $-30^\circ$ ; total alcohol content (calculated as cedrol): 35–48%; solubility: 1 vol in not more than 5 vol of 90% ethanol at  $20^\circ\text{C}$ . Composition by GC:  $\alpha$ -cedrene 15–25%; thujopsene 25–32%, cedrol 20% minimum [322], [91722-61-1].

For uses, see Virginia cedarwood oil

4. *Virginia cedarwood oil* is produced by steam distillation of sawdust, finely chipped waste wood from the manufacture of cedarwood products, or from stumps and logs of the red cedar; *Juniperus virginiana* L. (Cupressaceae). It is a light yellow to pale brown, viscous liquid with a characteristic cedarwood odor. The oil sometimes solidifies at room temperature.

$d_{20}^{20}$  0.941–0.965;  $n_D^{20}$  1.5010–1.5100;  $\alpha_D^{20}$   $-36^\circ$  to  $-16^\circ$ ; solubility: 1 vol in max. 5 vol of 95% ethanol. Composition by GC:  $\alpha$ -cedrene 22–35%; thujopsene 10–25%, cedrol 15–30% [323].

While the Texas cedar grows in Mexico and other Central American countries, the Virginia cedar grows exclusively in the Southeast of the United States. Both cedar oils are used mainly for perfuming soaps and other products, as well as a starting material for the isolation of cedrol [77-53-2]. Further fragrance substances such as cedryl acetate (see p. 74) and cedryl methyl ether (see p. 59) are produced from cedrol. The other sesquiterpenes, particularly  $\alpha$ -cedrene and thujopsene [324–326a] can be converted to valuable fragrance materials by acetylation (cedryl methyl ketone, see p. 69). The worldwide annual production amounts to 1500–2000 t. FCT 1974 (12) p. 845, 1976 (14) 711; [85085-41-2], [8000-27-9].



(+)-Cedrol

**Celery seed oil** is obtained by steam distillation of the crushed, ripe seeds of field-grown celery, *Apium graveolens* L. (Apiaceae). It is an almost colorless to

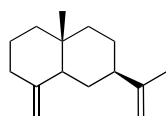


brownish-yellow liquid with a characteristic, pervasive, sweet-spicy, long-lasting odor.

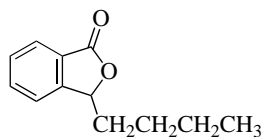
$d_{20}^{20}$  0.867–0.908;  $n_D^{20}$  1.4780–1.4880;  $\alpha_D^{20}$  +65° to +78°; solubility: 1 vol in no more than 6 vol of 90% ethanol at 20 °C; saponification number: 20–70 [327].

Major mono- and sesquiterpene hydrocarbons in the oil are (+)-limonene (58–79%) and  $\beta$ -selinene [17066-67-01], 5–20%. Its typical, long-lasting odor is caused primarily by two lactones, 3-butylphthalide [6066-49-5] and sedanenolide [62006-39-7] (1.5–11%) [328–334].

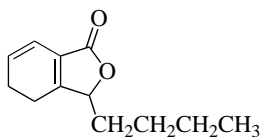
Celery seed oil is used chiefly for flavoring foods, although small quantities are also used in perfumery. FCT 1974 (12) 849; [8015-90-5], [89997-35-3].



(+)- $\beta$ -Selinene



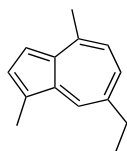
3-Butylphthalide



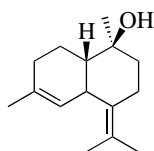
Sedanenolide (3-butyl-4,5-dihydrophthalide)

**Chamomile oils** are available in two types:

1. *Blue chamomile oil* (German chamomile oil) is obtained by steam distillation of the flowers and stalks of *Chamomilla recutita* (L.) Rauschert (*Matricaria recutita*. L., *M. chamomilla* L. p.p.-Asteraceae), which is grown mainly in central and eastern Europe, Egypt, and Argentina. It is a deep blue or bluish-green liquid that turns green and, finally, brown when exposed to light and air. The oil has a strong, characteristic odor and a bitter-aromatic taste. Chamazulene [529-05-5] is responsible for its blue color. Chamazulene and (–)- $\alpha$ -bisabolol [23089-26-1] contribute to the anti-inflammatory properties of blue chamomile oil [335, 336].



Chamazulene



(–)- $\alpha$ -Bisabolol

$d_{25}^{25}$  0.910–0.950; acid number: 5–50; ester number: 0–40; ester number (after acetylation): 65–155; solubility: solutions in 95% ethanol usually remain turbid [337]. Blue chamomile oil is used preferentially in pharmaceutical preparations, but also in small quantities in flavoring of alcoholic beverages. FCT 1974 (12) p. 853, [8002-66-2].

2. *Roman chamomile oil* (English chamomile oil) is produced from the dried flowers of *Chamaemelum nobile* (L.) All. (*Anthemis nobilis* L.), which are cultivated primarily in Belgium, but also in England, France, and Hungary. The oil is distilled in France and England. It is a light blue or light greenish-blue liquid with a strong aromatic odor characteristic of the flowers.

$d_{20}^{20}$  0.900–0.920;  $n_D^{20}$  1.4380–1.4460; acid value: max. 8, ester value. 250–340; solubility: 1 vol in max. 0.6 vol. 90% ethanol [338].

The constituents of Roman chamomile oil include esters of angelic and tiglic acid. Main constituents are isobutyl and isoamyl esters of angelic acid [339–344a]. Roman chamomile oil is used in very low dosages in flavoring of alcoholic beverages and in fine fragrances. FCT 1974 (12) p. 853, [8002-66-2].

### Cinnamon oils

1. *Cassia oil* (Chinese cinnamon oil) is obtained by steam distillation of the leaves, twigs, and bark of *Cinnamomum aromaticum* Nees (*C. cassia* Bl., Lauraceae). It is a reddish-brown liquid with a sweet-spicy, cinnamon-like odor.

$d_{20}^{20}$  1.052–1.070;  $n_D^{20}$  1.6000–1.6140; solubility: 1 vol in 3 vol of 70% ethanol at 20 °C; acid number: max. 15; content of carbonyl compounds (calculated as cinnamaldehyde): min 80% [345].

In contrast to cinnamon bark oil, cassia oil contains a considerable amount of 2-methoxycinnamaldehyde (3–15%) in addition to its main constituent, cinnamaldehyde (70–88%) [346–350a]. Cassia oil is used predominantly in flavoring soft drinks (cola-type). Annually a few hundred tons are produced. FCT 1975 (13) p. 109; [8007-80-5], [91844-89-2].

2. *Cinnamon leaf oil* is produced by steam distillation of the leaves of the cinnamon tree, *Cinnamomum zeylanicum* Bl. (*C. verum* J.S. Presl). The main countries in which the oil is produced are Sri Lanka, the Seychelles, southern India, Madagascar, and the Comoro Islands. It is a reddish-brown to dark brown liquid with a characteristic spicy odor, reminiscent of clove buds.

Specifications of cinnamon leaf oil from Sri Lanka are  $d_{20}^{20}$  1.037–1.053;  $n_D^{20}$  1.5270–1.5400;  $\alpha_D^{20}$   $-2.5^\circ$  to  $+2^\circ$ ; solubility: 1 vol in 2 vol of 70% aqueous ethanol at 20 °C; phenol content: 75–85%; carbonyl value: 21.2 maximum [351].

The main component of cinnamon leaf oil is eugenol (70–83%) [352–354b]. The oil is used as such in spicy oriental perfumes, for flavoring sweets, alcoholic beverages or as a source of high-grade eugenol.

Annually, some hundred tons are produced. FCT 1975 (13) p. 749; [8015-96-1], [84649-98-9].

3. *Sri Lanka cinnamon bark oil* is obtained by steam distillation of the dried bark of the cinnamon tree. It is a yellow liquid with the odor and burned-spicy taste of cinnamon. Main constituent is cinnamaldehyde [350, 350a, 355–356].

$d_{25}^{25}$  1.010–1.030;  $n_D^{20}$  1.5730–1.5910;  $\alpha_D^{20}$   $-2^\circ$  to  $0^\circ$ ; aldehyde content (calculated as cinnamaldehyde): 55–78%; solubility: 1 vol in at least 3 vol of 70% ethanol [357].

The oil is used predominantly in flavor compositions. FCT 1975 (13) p. 111; [8015-91-6], [84649-98-9].

**Cistus oil**, see Labdanum oil.

**Citronella oil**, see Cymbopogon oils.

**Citrus oils** comprise both essential oils obtained from the peels of citrus fruits and essence oils obtained by concentrating citrus juice (see Section 3.2.1).

Oils isolated from other parts of citrus plants (blossoms and leaves) are not classified as citrus oils because the former show marked differences in composition and organoleptic properties, they are described in other sections (see Neroli Oil, and Petitgrain Oils).

*Production of Citrus Peel Oils.* Apart from distilled lime oil, citrus peel oils are produced by pressing. Pressing of the peels for oil is often combined with juice production [357a].

In the first industrial production process, the citrus fruit was cut into halves and the juice was then pressed out. Further pressing of the peel liberated the desired oil. This mechanical procedure, which is still used, is known as cold pressing. Currently, citrus peel oils are also produced by other methods. For instance, the outer peel of the whole fruit (albedo) is rasped or punctured before juice extraction to release the oil. The oil is then rinsed off with water and is subsequently separated from the resulting emulsion by centrifugation. The so-called ‘sfumatrice’ process belongs to the type of first mentioned methods, the so-called ‘pelatrice’ process to the second type. In Italy, both methods are used to produce cold-pressed lemon oil. Occasionally, inferior qualities of some kinds of citrus oils are also obtained by steam distillation of the oil which remains in the sponge-like inner peel (flavedo) after the cold-pressing process (e.g., lemon and bergamot oils).

*Production of Citrus Essence Oils.* Distillative concentration of citrus juices yields essence oils, which separate from the aqueous phase in the receiver when the distillate condenses. The composition of essence oils is similar to that of peel oils, but the essence oils usually contain larger quantities of aliphatic ethyl esters (e.g., ethyl butyrate in orange essence oil). Thus, their aroma resembles that of a particular juice more than that of peel oils.

Citrus oils contain up to 95% monoterpene hydrocarbons (usually limonene, but others as well, e.g., lemon oil also contains  $\alpha$ -terpinene and  $\beta$ -pinene). The important aroma-determining components of citrus oils are functionalized terpenes and aliphatic compounds (predominantly carbonyl compounds and esters), present only in relatively low concentrations [358]. Thus, several methods are employed to concentrate citrus oils on an industrial scale. The monoterpene hydrocarbon

content is decreased by distillation, liquid–liquid partitioning between two immiscible solvents, or absorption on a carrier such as silica gel. The deterpenized concentrates are marketed under the name ‘Citrus oil  $x$ -fold,’ depending on the concentration factor.

1. *Bergamot oil, Italian* is obtained by pressing peels from the unripe fruits of *Citrus aurantium* L. subsp. *bergamia* (Risso et Poit.) Engl. (Rutaceae). It is a green to greenish-yellow liquid, which sometimes contains a deposit. The oil has a pleasant, fresh, sweet, fruity odor.

$d_{20}^{20}$  0.876–0.883;  $n_D^{20}$  1.4650–1.4700;  $\alpha_D^{20}$   $+15^\circ$  to  $+32^\circ$ ; evaporation residue: 4.5–6.4%; solubility: 1 vol. in max. 1 vol. 85% ethanol; acid value: max. 2; ester value: 86–129; bergaptene content by HPLC: 0.18–0.38% [359].

Bergamot is grown in the Italian province of Calabria, in Brazil, and in the Ivory Coast. The quality of the oil is determined by its ester content and varies with the species. Annual production is 100–200 t/yr.

Linalyl acetate (22–36%), linalool (3–15%), and geranial (0.25–0.5%) are important components of bergamot oil. Its terpene content (25–50%) is relatively low for a citrus oil [360–370e].

Use of the untreated oil in cosmetics is limited by the photosensitizing properties of bergaptene (a furocoumarin) present in the oil. Bergamot oil is used in flavoring food (‘Earl Grey tea’); furocoumarin-free bergamot oil is used in many perfumes and is an important ingredient in eau de cologne. FCT 1973 (11), p. 1031, p. 1035; [8007-75-8], [93763-04-3], [68648-33-9] (furocoumarin-free).

2. *Grapefruit oil* is obtained by cold pressing of the outer peels of the fruits of *Citrus paradisi* Macfad. (Rutaceae). It is a greenish-yellow liquid, with an odor resembling that of sweet orange oil, but more herbaceous and bitter.

$d_{20}^{20}$  0.852–0.860;  $n_D^{20}$  1.4740–1.4790;  $\alpha_D^{20}$   $+91^\circ$  to  $+96^\circ$ ; carbonyl value 0.9–3.25, corresponding to a carbonyl content calculated as decanal of 0.28–1%; evaporation residue: min. 5.0%, max. 10.0% [371].

Grapefruit oil is produced mainly in the United States and its composition varies with the species. White grapefruit oil obtained from the varieties Marsh seedless and Duncan that are grown in Florida, contains more than 90% terpene hydrocarbons ((+)-limonene, 93.5–95%), 0.5% alcohols (mainly linalool), 1% aldehydes (mainly octanal and decanal), 0.05–0.8% nootkatone [371]. Worldwide production is ca. 200 t/yr.

The sesquiterpene ketone nootkatone is primarily responsible for the characteristic aroma of grapefruit oil [370a], [370d], [372–379a].

Grapefruit oil is used mainly for flavoring fruit beverages. FCT 1974 (12) p. 723; [8016-20-4], [90045-43-5].

3. *Lemon oil* is obtained by pressing peel from the fruits of *Citrus limon* (L.) Burm. (Rutaceae). It is a pale yellow or pale greenish-yellow to dark green liquid with a characteristic lemon peel odor.

The composition of lemon oils depends on the variety of lemon and the country of origin. Specifications for the qualities of different origins are given in Table 3 [380].

**Table 3.** Specifications for qualities of lemon oils of different origins

Parameter	Type				
	American		Mediterranean		Equatorial
	Origin				
	Coast	Desert	Italy	Spain	Ivory coast
	0.851–0.857	0.849–0.854	0.850–0.858	0.849–0.858	0.845–0.854
	1.4370–1.4760	1.4370–1.4760	1.4370–1.4760	1.4370–1.4760	1.4370–1.4790
	+57° to +65°6'	+67° to +78°	+57° to +66°	+57° to +66°	+57° to +70°
Composition by GC [area %]					
$\beta$ -Pinene	9–14	10–13	10–16.5	10–16.5	7–16
Limonene	63–70	70–80	60–68	60–69	59–75
$\gamma$ -Terpinene	8.3–9.5	6.5–8	8–12	8–12	6–12
Neral	0.6–0.9	0.3–0.6	0.6–1.2	0.4–1	0.2–1.2
Geranial	1.0–2	0.5–0.9	0.8–2	0.6–2	0.5–2
Evaporation residue [weight %]					
	1.75–3.9		1.5–3.9	1.5–3.9	1.5–4
Carbonyl value					
	8–14	6.25–12	11–17	11–17	6–17
CD value	min. 0.2	min. 0.2	0.45–0.9	0.4–0.9	0.2–0.96

The characteristic odor of lemon oil differs from that of other citrus oils and is largely due to neral and geranial. The content of these compounds in Italian lemon oil generally exceeds 3% [369, 370a, 370d, 370e, 381–394e].

Annual worldwide production is nearly 6000 t, most of which originates from the United States, Italy, Argentina, Spain and Brazil [394f].

Lemon oil is used in many food flavors. Because of its fresh odor, relatively large quantities are also employed in eau de cologne and other perfumery products. FCT 1974 (12) 725; [8008-56-8], [84929-31-7].

4. *Lime oil* may be either pressed or distilled, but the distilled oil is produced on a much larger scale.

Two varieties of limes are of importance in the commercial production of lime oils: the West Indian (Mexican or Key) lime, *Citrus aurantifolia* (Christm.) Swingle and the Persian (Tahiti) lime, *C. latifolia* Tanaka. The former has small fruits with many seeds, and the latter bears larger, seedless fruits. West Indian limes are grown primarily in Mexico, the West Indies, and Peru; Persian limes are cultivated in Florida and Brazil.

Persian lime oils contain lower concentrations of the typical sensorially important components than the West Indian lime oils and are thus comparatively mild and flat [395]. Consequently, West Indian lime oils are more popular.

*Pressed lime oils* are obtained by rasping and puncturing as described on p. 185, so-called type B. Other methods are also employed for West Indian limes: the whole fruits may be chopped and the separated oil–juice emulsion subsequently centrifuged, so-called type A [396], [397].

Pressed lime oil is a yellow to greenish-yellow liquid with a strong, characteristic odor, reminiscent of lemon.

$d_{20}^{20}$  0.875–0.884/0.880–0.888,  $n_D^{20}$  1.482–1.486/1.484–1.488,  $\alpha_D^{20}$  +35° to +41°; carbonyl value 16–31/18–35, corresponding to a calculated content of citral of 4.5–8.5%/5–9.5%; evaporation residue: 10–14.5%/13–19% (data for Mexican oils of type A/type B) [398].

The composition [399–406c] and uses of pressed lime oil are similar to those of pressed lemon oil. FCT 1974 (12) p. 731, 1993 (31), p. 331; [90063-52-08].

*Distilled lime oils* are produced by steam distillation of an oil–juice emulsion that is obtained by chopping the whole fruit. The acid present in the juice acts on the oil released from the peel and changes its characteristics. The original components are modified to form a series of new compounds. The main constituent is still limonene.

Distilled (Mexican) lime oil is a colorless to pale yellow liquid, with a characteristic odor, which differs from that of the fresh fruit and the cold-pressed oil.

$d_{20}^{20}$  0.856–0.865;  $n_D^{20}$  1.474–1.478;  $\alpha_D^{20}$  +34° to +45°; evaporation residue: max. 2.5%; content of carbonyl compounds (calculated as citral): max. 1.5% [407].

Acid-catalyzed cyclization and dehydration of citral and linalool give rise to several compounds that occur at comparatively high concentrations and contribute to the typical aroma of distilled lime oil (e.g., 1,4-cineole [470-67-0], 1,8-cineole [470-82-6], 2,2,6-trimethyl-6-vinyltetrahydropyran [7392-19-0], and 2-(2-buten-2-yl)-5,5-dimethyltetrahydrofuran [7416-35-5]) [406–406b, 408–412a].

Annual worldwide production of distilled West Indian lime oil is nearly 1000 t. The oil is used primarily in soft drinks of cola-type. FCT 1974 (12) p. 729; [8008-26-2].

5. *Mandarin oil* is obtained by cold pressing the peel of mandarin oranges, the fruits of *Citrus reticulata* Blanco (Rutaceae). The oil is a greenish-yellow to reddish-orange liquid, depending on the degree of ripeness of the fruit, with a pale blue fluorescence and a characteristic odor, reminiscent of mandarin peel.

$d_{20}^{20}$  0.848–0.855;  $n_D^{20}$  1.474–1.478;  $\alpha_D^{20}$  +64° to +75°; evaporation residue: 1.6–4.0%; content of carbonyl compounds (calculated as decanal): 0.4–1.2%; solubility: 1 vol. in not more than 10 vol. 90% ethanol [413].

The main components are limonene (65–75%) and  $\gamma$ -terpinene (16–22%). The characteristic feature of mandarin oil is its content of  $\alpha$ -sinensal (0.2–0.5%), methyl *N*-methylantranilate (0.3–0.6%, which is responsible for fluorescence), and long-chain unsaturated aliphatic aldehydes [369, 370a, 370d, 370e, 381, 394c, 414–421b].

Annual production of mandarin oil in Italy is ca. 100 t; smaller quantities are produced in Spain, Brazil, and Argentina.

Mandarin oil is used to enrich the bouquet of flavor compositions containing sweet orange oils as the main component. It is also used in liqueurs and perfumery. FCT 1992 (30 suppl.) p. 69 S; [8008-31-9], [84929-38-4].

6. *Bitter orange oil* is obtained by pressing fresh peel from the fruits of *Citrus aurantium* L. subsp. *aurantium* (Rutaceae). It is produced mainly in Mediterranean countries and is a pale yellow to yellowish-brown liquid with a slightly mandarin-like odor and a somewhat bitter aroma.

$d_{20}^{20}$  0.840–0.861;  $n_D^{20}$  1.4720–1.4760;  $\alpha_D^{20}$  +88° to +98°; evaporation residue: 2.2–5%; aldehyde content, calculated as decanal: 0.5–2.9% solubility: 1 vol in max. 8 vol. 90% ethanol [422].

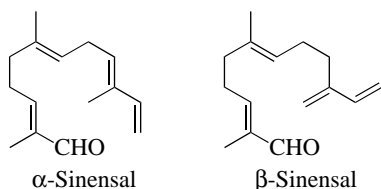
The composition of bitter orange oil differs from that of sweet orange oil; i.e., its aldehyde content is lower and its ester content is higher [369–370a, 370d, 370e, 394, 423–428].

Worldwide production of bitter orange oil is much lower than that of other pressed peel oils. Bitter orange oil is predominantly used for flavoring alcoholic beverages (liquers). FCT 1974 (12) 735; [68916-04-1], [72968-50-4].

7. *Sweet orange oil* is obtained from the peel of the fruits of *Citrus sinensis* (L.) Osbeck. It is a yellow to reddish-yellow liquid with the characteristic odor of orange peel and may become cloudy when chilled. Sweet orange oil is often produced in combination with orange juice (e.g., in the United States, Brazil, Israel, and Italy).

$d_{20}^{20}$  0.842–0.850;  $n_D^{20}$  1.4700–1.4760;  $\alpha_D^{20}$  +94° to +99°; evaporation residue: 1–5%; aldehyde content, calculated as decanal: 0.9–3.1% solubility: 1 vol in max. 8 vol. 90% ethanol [429].

The oils have a high terpene hydrocarbon content (>90%, mainly (+)-limonene), but their content of oxygen-containing compounds differs and affects their quality. Important for aroma are aldehydes, mainly decanal and citral, and aliphatic and terpenoid esters. The sesquiterpene aldehydes  $\alpha$ -sinensal [17909-77-2] and  $\beta$ -sinensal [6066-88-8], which contribute particularly to the special sweet orange aroma, also occur in other citrus oils, although in lower concentration [369–370a, 370d, 394, 421, 430–438].



Worldwide production of cold-pressed orange oil is nearly 20 000 t/yr. Its main uses are the flavoring of beverages and confectioneries and perfuming eau de cologne, soaps and household products. FCT 1974 (12) 733; [8008-57-9], [8028-48-6].

**Civet**, see Animal secretions.

**Clary sage oil**, see Sage oils.

**Clove oils** are produced from the 15–20 m high clove tree *Syzygium aromaticum* (L.) Merr. et Perry [*Eugenia caryophyllus* (Spreng.) Bullock and Harrison].

1. *Clove bud oil* is obtained in 15–20% yield by steam distillation of the dried flower buds. Clove bud oil, like the leaf oil, is a yellow to brown, sometimes slightly viscous liquid. It turns dark purple-brown on contact with iron. The oil has the spicy odor characteristic of eugenol.

$d_{20}^{20}$  1.042–1.063;  $n_D^{20}$  1.5280–1.5380;  $\alpha_D^{20}$   $-1.5^\circ$  to  $0^\circ$ ; phenol content: 85% to 93%; content by GC: eugenol 75–85%, caryophyllene 2–7%, eugenyl acetate 8–15% [439]. FCT 1975 (13) p. 761; [8000-34-8], [84961-50-2].

2. *Clove leaf oil* is obtained in 2–3% yield by steam distillation of the leaves of the above-mentioned.

$d_{20}^{20}$  1.039–1.049;  $n_D^{20}$  1.5280–1.5350; phenol content: min. 80%, for Indonesian origin 78%; content by GC: eugenol 80–92%, caryophyllene 4–17%, eugenyl acetate 0.2–1% [440]. FCT 1975 (13) p. 765; [8015-97-2].

3. *Clove stem oil* is obtained in ca. 5% yield by steam distillation of the dried flower stems. It is a yellow to light brown oil with a sweet-spicy, slightly woody odor similar to that of bud oil but without the fresh-fruity top note.

$d_{20}^{20}$  1.041–1.059;  $n_D^{20}$  1.5310–1.5360;  $\alpha_D^{20}$   $-1^\circ$  to  $+1^\circ$ ; phenol content: 85–95% (v/v); content by GC: eugenol 83–92%, caryophyllene 4–12%, eugenyl acetate 0.5–4% [441]. FCT 1978 (16) p. 695; [8015-98-3].

The main component of all clove oils is eugenol (up to 80%, sometimes more), which is responsible for their odor and antiseptic properties. Other major constituents are eugenyl acetate and caryophyllene [442–449]. Clove bud oil has a higher acetate content and a more delicate odor than the other oils, therefore it is much more expensive. Leaf oil is produced and used in the largest quantities. The composition of clove stem oil resembles that of bud oil but with a lower content of eugenyl acetate.

The most important countries that produce clove oils are Madagascar, Tanzania, and Indonesia. Smaller quantities are produced in other tropical areas (e.g., Malaysia and Sri Lanka). Worldwide production of clove oils is more than 2000 t/yr, of which Indonesia produces about half.

The oils are used in many perfume and aroma compositions, because of their spicy clove odor. A small amount is used as an antiseptic, mainly in dentistry. The leaf oil, in particular, is also used as a raw material for the production of eugenol, which is the starting material for further commercially important fragrance compounds, such as isoeugenol and eugenyl esters.

**Copaiba (balsam) oils** are obtained by steam distillation of the exudate (balsam) from the trunk of several species of *Copaifera* L. (Fabaceae), a genus of trees growing in the Amazon basin. They are colorless to light yellow liquids with the characteristic odor of the corresponding balsams and an aromatic, slightly bitter, pungent taste.



$d_{25}^{25}$  0.880–0.907;  $n_D^{20}$  1.4930–1.5000;  $\alpha_D^{20}$   $-33^\circ$  to  $-7^\circ$ ; solubility: 1 vol in 5–10 vol of 95% ethanol [450].

The oils consist primarily of sesquiterpene hydrocarbons; their main component is caryophyllene (>50%) [284a, 450a, 450b].

Copaiba balsam oils and balsams are used mainly as fixatives in soap perfumes. FCT 1973 (11) p. 1075, 1976 (14) p. 687; [8013-97-6].

**Coriander oil** is obtained by steam distillation of ripe fruits of *Coriandrum sativum* L. (Apiaceae). It is an almost colorless to pale yellow liquid with a characteristic odor, reminiscent of linalool.

$d_{20}^{20}$  0.862–0.878;  $n_D^{20}$  1.4620–1.4700;  $\alpha_D^{20}$   $+7^\circ$  to  $+13^\circ$ ; acid number: max. 3.0; content of linalool by GC: 65–78% [451].

The main component of coriander oil is (+)-linalool (60–80%) [452–460c]. Mono- and polyunsaturated fatty aldehydes, although minor components, contribute to the characteristic aroma of the oil because of their powerful odor. In contrast to the seed oil, coriander leaf oil contains these aldehydes as main constituents, e.g. 2-decenal and 2-dodecenal.

Coriander is mainly cultivated in Eastern Europe. World-wide oil production is 50–100 t/yr. Coriander oil is no longer important as a raw material for the production of linalool and its derivatives. However, it is still used extensively in seasoning mixtures and in perfume compositions. FCT 1973 (11) 1077; [8008-52-4], [84775-50-8].

**Cornmint oil**, see Mint oils.

**Cymbopogon oils** are produced from several aromatic grasses that belong to the genus *Cymbopogon* Spreng. (Poaceae). The oils are obtained by steam distillation of the aerial parts of the plants. The following oils are of commercial interest:

1. *Citronella oil* is available in two types:

(a) *Sri Lanka (Ceylon) citronella oil* is produced by steam distillation of fresh or partly dried leaves and stems of the grass species *Cymbopogon nardus* (L.) W. Wats. – ‘lenabatu’ – cultivated in Sri Lanka. It is a pale yellow to brownish liquid with a fresh, grassy, camphoraceous odor.

$d_{20}^{20}$  0.891–0.910;  $n_D^{20}$  1.479–1.490;  $\alpha_D^{20}$   $-25^\circ$  to  $-12^\circ$ ; solubility: 1 vol in not more than 2 vol of 80% ethanol at  $20^\circ\text{C}$ ; ester number (after acetylation): 157–200; carbonyl number: 18–55, corresponding to 5–15% carbonyl compounds (calculated as citronellal). The content of citronellal by GC varies from 3 to 6%. Other typical constituents are borneol (4–7%), citronellol (3–8.5%), geraniol (15–23%) and methyl isoeugenol (7–11%) [461].

Sri Lanka (Ceylon) oil is less valuable than Java oil and is used almost exclusively for perfuming toilet soaps, washing powders, and household products [91844-97-7].

(b) *Java citronella oil* is obtained by steam distillation of fresh or partially dried stems and leaves of *Cymbopogon winterianus* Jowitt – ‘mahapengiri’ –

which is grown in Southeast Asia, India, China and Indonesia, as well as in Central and South America. It is a pale yellow to pale brown liquid with a slight, sweet, flowery, roselike odor with the strong citrus note of citronellal.

$d_{20}^{20}$  0.880–0.893;  $n_D^{20}$  1.467–1.473;  $\alpha_D^{20}$   $-5^\circ$  to  $0^\circ$ ; solubility: 1 vol in not more than 2 vol of 80% ethanol at  $20^\circ\text{C}$ , opalescence is sometimes observed when ethanol is continuously added; ester number (after acetylation): min. 250, corresponding to 85% acetylizable compounds (calculated as geraniol, this percentage includes citronellal, since it is converted quantitatively into isopulegyl acetate under the acetylation conditions); carbonyl number: min. 127, corresponding to 35% carbonyl compounds (calculated as citronellal) [462].

Java citronella oil may contain up to 97% acetylizable compounds and up to 45% carbonyl compounds, depending on the time of harvesting. It is used extensively not only in perfumery, but also as one of the most important raw materials for the production of citronellal. In addition, a fraction with a high geraniol content is obtained from the oil. Both citronellal and the geraniol fraction are starting materials for the synthesis of a large number of other fragrance compounds. The oil produced in Taiwan and in Java contains, in addition to the major components citronellal (31–40%) and geraniol (20–25%), citronellol (8.5–14%), geranyl acetate (2.5–5.5%), citronellyl acetate (2–4%), and many other minor components [463–464a].

Annual worldwide production was reported to be >5000 t in 1971 and is now ca. 2000 t. Main producers are Taiwan, China, and Java. FCT 1973 (11) p. 1067; [8000-29-1], [91771-61-8].

2. *Lemongrass oil* is available in two types, which are produced by steam distillation.

(a) *West Indian or Guatemala lemongrass oil* is obtained from *Cymbopogon citratus* (DC.) Stapf in Central and South America, as well as in a number of African and East Asian countries. It is a pale yellow to orange-yellow liquid with a lemon-like odor, characteristic of citral.

$d_{20}^{20}$  0.872–0.900;  $n_D^{20}$  1.483–1.489;  $\alpha_D^{20}$   $-6^\circ$  to  $0^\circ$ ; content of carbonyl compounds (calculated as citral): min. 75%; citral content by GC: 31–40% neral and 40–50% geraniol; solubility: freshly distilled oil is soluble in 70% ethanol at  $20^\circ\text{C}$ , but solubility diminishes on storage and the oil may become insoluble in 90% ethanol [465], [89998-14-1].

(b) *Indian lemongrass oil* is obtained from the so-called Indian variety of lemongrass, *Cymbopogon flexuosus* (Nees ex Steud.) W. Wats. The oil is produced mainly in India. It is a pale yellow to brownish-yellow oil.

$d_{20}^{20}$  0.855–0.905;  $n_D^{20}$  1.4830–1.4890;  $\alpha_D^{20}$   $-4^\circ$  to  $+1^\circ$ ; solubility: 1 vol in max. 3 vol 70% ethanol; content of carbonyl compounds (calculated as citral): min. 73% citral; content by GC: 25–35% neral and 35–47% geraniol [466].

The two oils were formerly the main source of natural citral, obtained as a ca. 4:1 mixture of geraniol and neral by distillation [463, 466a]. However, lemongrass oil has declined in commercial importance due to the competitive synthesis of citral and isolation of natural citral from *Litsea cubeba* oil. Today, some 100 t/yr are still

produced. In addition to being processed into citral, it is used to some extent for perfuming soap and household products. FCT 1976 (14) p.455; [8007-02-1], [91844-92-7].

3. *Palmarosa oil* is obtained by steam distillation of wild or cultivated *Cymbopogon martinii* (Rox.) W. Wats. var. *motia*, collected when in blossom. It is a pale yellow liquid with a characteristic rose-like odor and a grassy note.

$d_{20}^{20}$  0.880–0.894;  $n_D^{20}$  1.4710–1.4780;  $\alpha_D^{20}$  +1.4° to +3°; solubility: 1 vol in 2 vol of 70% ethanol at 20 °C; ester number (after acetylation): 255–280, corresponding to a total alcohol content of 80–95%, free alcohol content (calculated as geraniol): 72–94% [467]. High-grade palmarosa oil may contain up to 95% geraniol and its esters [463, 467a]; it is produced in smaller quantities than other oils obtained from aromatic grasses. Annual worldwide production (India, Guatemala, Indonesia) exceeds 100 t [468]. Palmarosa oil the starting material for geraniol and geranyl esters of high odor quality, but it is so used for perfuming soaps and cosmetics. FCT 1974 (12) 947; [8014-19-5], [91722-54-2].

4. *Gingergrass oil* is produced in India from the *sofia* variety of *Cymbogon martinii* and is less important than palmarosa oil.

**Cypress oil** is produced by steam distillation of terminal branches of *Cupressus sempervirens* L. (Cupressaceae). It is a liquid with a wood-like odor that has an ambergris note.

$d_{20}^{20}$  0.863–0.885;  $n_D^{20}$  1.4680–1.4780;  $\alpha_D^{20}$  +15° to +30°; solubility: 1 vol in 8 vol of 90% ethanol [469].

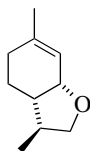
This oil is produced exclusively in southern France and Algeria; its major components are  $\alpha$ -pinene and 3-carene. Degradation products of higher terpenoids are responsible for the typical ambergris note [470–473]. FCT 1978 (16) 699; [8013-86-3], [84696-07-1].

**Davana oil** is obtained by steam distillation of the herb *Artemisia pallens* Wall. (Asteraceae), grown in south India. It is an orange-brown liquid with a sweet tea-like odor reminiscent of dried fruits. The composition of the oil is very complex; its main components are furanoid sesquiterpenes [474–476a]. It is used predominantly for aroma compositions. FCT 1976 (14) p.737; [8016-03-3], [91844-86-9].

**Dill oil** is obtained from the dill plant, *Anethum graveolens* L. (Apiaceae), in two different forms:

1. *Dill weed oil*, which is the most important, is obtained by steam distillation from dill weed (herb) before the fruits become mature. Its main constituents are  $\alpha$ -phellandrene (10–20%), limonene (30–40%), carvone (30–40%) and the so-called (+)-dill ether [74410-10-9] (up to 10%) [477–485]. The

latter is responsible for the typical organoleptic properties of the dill plant and, thus, of dill weed oil.



(+)-Dill ether

2. *Dill seed oil* is prepared by steam distillation of the crushed ripe fruits of the dill plant. Its main components are limonene (up to 40%) and (+)-carvone (up to 60%) [486]. In contrast to the weed oil, this oil has a typical caraway odor and taste which is characteristic of (+)-carvone.

*Indian dill oil* is obtained by steam distillation of the seeds of a closely related plant, *Anethum sowa* Roxb. It contains also larger quantities of limonene and carvone [486].

Dill oils are used primarily for seasonings in the pickling and canning industries. FCT 1976 (14) p. 747; [8006-75-5], [90028-03-8].

**Elemi oil, Elemi resinoid** are obtained from exuded gum resin of *Canarium luzonicum* (Miqu.) A. Gray (Burseraceae), a tree growing in the Phillipines. The resin is extracted with a solvent to form the resinoid, which is a yellow to orange mass of high viscosity. The oil is produced by steam distillation of the gum resin and is a colorless to light yellow liquid.

$d_{20}^{20}$  0.850–0.910;  $n_D^{20}$  1.4720–1.4900;  $\alpha_D^{20}$  +44° to +85° [487].

The major components of elemi oil are limonene (40–72%),  $\alpha$ -phellandrene (10–24%), and the sesquiterpene alcohol elemol (1–25%) [488–491]. Both the resinoid and the oil have a fresh, citrus-like, peppery odor and are used predominantly in soap perfumes. (FCT 1976 (14) p. 755; [8023-89-0] (oil), [9000-74-2] (resin).

**Estragon oil**, see Tarragon oil.

**Eucalyptus oils** are produced from plants belonging to the genus *Eucalyptus* (Myrtaceae), which includes ca. 500 species in Australia, the country of origin, alone. Correct botanical classification was possible only by determining the chemical composition of the essential oils obtained from the leaves. At present, few of these oils are commercially important.

#### 1. Cineole-rich *Eucalyptus* oils

(a) *Australian eucalyptus oil* is obtained by steam distillation of the foliage of certain *Eucalyptus* species indigenous to Australia, mainly from *Eucalyptus fruticetorum* F.v. Muell. (*E. polybractea* R. T. Bak.)

$d_{20}^{20}$  0.918–0.928;  $n_D^{20}$  1.458–1.465;  $\alpha_D^{20}$  –2° to +2°; solubility: 1 vol in 3 vol of 70% ethanol at 20 °C; 1,8-cineole content: 80–85% [492].

The minor components of this oil differ from those of *E. globulus* oil. Despite its high cineole content, annual production of Australian eucalyptus oil is only 50 t.

(b) *Eucalyptus globulus* oil is produced by steam distillation of the leaves of *Eucalyptus globulus* Labill. It is an almost colorless to pale yellow liquid with a fresh odor, characteristic of cineole. The crude oil contains more than 65% 1,8-cineole and between 10 and 22%  $\alpha$ -pinene [493–499]. Rectified qualities have a cineole content of 70–75% or 80–85%. The respective specifications of these three types are as follows:

$d_{20}^{20}$  0.905–0.925/0.904–0.920/0.906–0.920;  $n_D^{20}$  1.457–1.470/1.460–1.468/1.458–1.465;  $\alpha_D^{20}$   $+2^\circ$  to  $+8^\circ$ / $+2^\circ$  to  $+10^\circ$ / $0^\circ$  to  $+10^\circ$ ; solubility: 1 vol in max. 7/5/5 vol 70% ethanol. 1,8-cineole content 60/70/80% minimum [500].

The oil is produced mainly in Spain and Portugal, where the wood is used in the cellulose industry, and in China. Worldwide production exceeds 1500 t/yr.

Eucalyptus oils with a high cineole content are used for cineole production. The oils and cineole itself are used primarily in pharmaceutical preparations. Fairly large quantities are also used in perfumery, e.g., to imitate the odor of cineole-containing essential oils and flavoring of food (sweets) and oral care products. FCT 1975 (13) p. 107; [8000-48-4], [84625-32-1].

2. *Eucalyptus citriodora* oil is obtained by steam distillation of leaves and terminal branches of *Eucalyptus citriodora* Hook. It is an almost colorless, pale yellow, or greenish-yellow liquid with a citronellal-like odor.

$d_{20}^{20}$  0.860–0.870;  $n_D^{20}$  1.4500–1.4560;  $\alpha_D^{20}$   $-1^\circ$  to  $+3^\circ$ ; content of carbonyl compounds calculated as citronellal: min. 70%; content of citronellal by GC: min. 75% [501].

In addition to the main component, citronellal, the oil contains citronellol and isopulegol (5–10% each) [502–504a].

Young *E. citriodora* trees that are grown exclusively for essential oil production are cut back to a height of 1–1.50 m and develop into shrubs. The leaves can be harvested throughout the year; more than 200 kg of oil can be obtained per hectare.

The major producer is Brazil with over 500 t/yr, but considerable quantities are also produced in other countries (e.g., South Africa and India). *Eucalyptus citriodora* oil is a starting material for the manufacture of citronellal and products derived from it. It is also used in perfumery for the same purposes as citronellal. FCT 1988 (26) p. 323; [85203-56-1].

3. *Eucalyptus dives* oil is obtained by steam distillation of fresh leaves of *Eucalyptus dives*, Schau, piperitone-type, grown in Australia and South Africa.

In addition to (–)-piperitone the oil contains 15–25%  $\alpha$ -phellandrene [505]. The oil was previously used as a starting material in the manufacture of (–)-menthol, but has lost much of its significance. Annual worldwide production has dropped to 50 t [85203-58-3], [90028-48-1].

**Fennel oil** is obtained by steam distillation of the the aerial parts of *Foeniculum vulgare* Mill. ssp. *vulgare* var. *vulgare* (bitter fennel). It is a colorless to pale yellow liquid with a camphoraceous sweet-spicy odor and a slightly bitter sweet

camphoraceous taste.  $d_{20}^{20}$  0.889–0.921;  $n_D^{20}$  1.4840–1.5680;  $\alpha_D^{20}$  +20° to +68°. Main constituents are monoterpene hydrocarbons like  $\alpha$ -phellandrene (1–6 %) and limonene (8–30%), fenchone (4–25%), estragole (1–7 %) and anethole (30–85 %). With increasing maturity of the fruits, the content of monoterpenes decreases. The ripe fruits yield an oil with 50–70 % anethole and 5–25 % fenchone. In contrast, the oil of the ripe fruits of sweet fennel (*Foeniculum vulgare* Mill. ssp. *vulgare* var. *dulce*) contains less than 5% fenchone and more than 75% anethole [506–513c].

Fennel oil is mainly used in flavoring oral care products and in pharmaceutical preparations. A reasonable quantity of fennel oil is used for the production of pure anethole for flavouring alcoholic beverages (anise liqueurs) [513d]. FCT 1976 (17) p. 529; [8006-84-6], [84625-39-8].

**Fir needle oils**, see Pinaceae Oils.

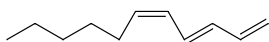
**Galbanum oil** and **galbanum resinoid** are produced from the gumlike exudate of *Ferula galbaniflua* Boissier and Buhse (Apiaceae) growing in northern Iran and *F. rubricaulis* Boissier growing in southern Iran.

The gum is collected from a cut in the upper part of the uncovered roots. The annual yield of gum is ca. 100 t.

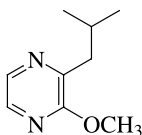
The oil is produced by steam distillation and is a yellow liquid with a green, slightly spicy odor.

$d_{20}^{20}$  0.867–0.890;  $n_D^{20}$  1.4780–1.4850;  $\alpha_D^{20}$  +7° to +17°; acid value: max. 2 [514].

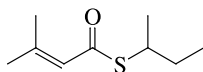
In addition to 75% monoterpene hydrocarbons (9 $\alpha$ -pinene 5–21%;  $\beta$ -pinene 40–70%; 3-carene 2–16%) and ca. 10% sesquiterpene hydrocarbons, galbanum oil contains a fairly large number of terpene and sesquiterpene alcohols and their acetates. Minor components, with entirely different structures and low odor threshold values, contribute strongly to the characteristic odor [284a, 515–519]. Examples are as follows:



(*E,Z*)-1,3,5-Undecatriene (0.4–2%)  
[51447-08-6]



2-Methoxy-3-isobutylpyrazine  
[24683-00-9]



*S*-*sec*-Butyl 3-methyl-2-butenethioate  
[34322-09-3]

Galbanum oil is used for creating green top notes in perfume compositions.

Galbanum resinoid is produced by extraction of the gum with a nonpolar solvent. It is used for the same purposes as the oil and has excellent fixative properties. FCT 1978 (16) p. 765 (oil), 1992 (30) p. 395 (resin); [8023-91-4], [93165-40-3].

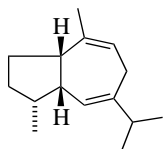
**Table 4.** Specifications of geranium oils

Parameter	Origin of geranium oil		
	Bourbon	North Africa	China
$d_{20}^{20}$	0.884–0.892	0.883–0.905	0.882–0.892
$n_D^{20}$	1.4610–1.4700	1.4610–1.4770	1.4600–1.4720
$\alpha_D^{20}$	–148 to –108	–148 to –88	–148 to –88
Solubility in 70% ethanol, vol:vol	1:3	1:3	1:5
Acid value	max. 10	max. 10	max. 10
Ester value	53–76	31–80	55–75
Ester value (acetylated)	205–239	192–240	215–232
Content of carbonyl compounds, calc. as isomenthone [%]	16	16	10

**Geranium oil** is obtained by steam distillation of the flowering herb *Pelargonium graveolens* l'Heritier ex Aiton, *P. roseum* Willdenow, and other nondefined hybrids that have developed into different ecotypes in different geographical regions. The oil is an amber to greenish-yellow liquid with the characteristic roselike odor of the plant.

The main cultivation areas are Réunion and Madagascar (Bourbon type), Egypt (North African type), and China. The Bourbon quality is more valuable and thus more expensive. Annual worldwide production is some hundred tons. Specifications of geranium oils [520] are given in Table 4.

The composition of the Bourbon oil differs quantitatively as well as qualitatively from that of North African oil. However, they both contain an unusually high percentage of (–)-citronellol, isomenthone, formates, and tiglates, which are rarely found in essential oils. The two types of oil can be differentiated by two characteristic minor constituents: the Bourbon type contains (–)-6,9-guaiadiene [36577-33-0] and the African type contains 10-*epi*- $\gamma$ -eudesmol [15051-81-7] see p. 167 [521–531b].



(–)-6,9-Guaiadiene

The qualitative composition of Chinese oil is very similar to that of Bourbon oil, but it contains more citronellol (ca. 40%) and lower amounts of linalool (ca. 4%) and geraniol (ca. 8%).

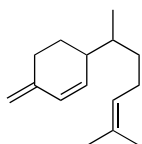
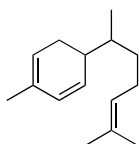
Geranium oil is one of the most important natural raw materials in the fragrance industry. It shows a broad variety of application possibilities. FCT 1974 (12) p. 883, 1975 (13), p. 451; [90082-51-2].

**Ginger oil** and **ginger oleoresin** are produced from the ginger plant *Zingiber officinale* (L.) Rosc. (Zingiberaceae).

*Ginger oil* is produced by steam distillation of dried, ground rhizomes. It is a light yellow to yellow liquid with the aromatic, persistent odor of ginger, but lacking the pungency usually associated with ginger. The citrus note of ginger oil is produced by citral.

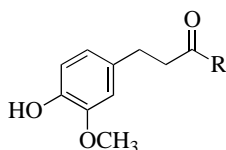
$d_{25}^{25}$  0.871–0.882;  $n_D^{20}$  1.4880–1.4940;  $\alpha_D^{20}$   $-45^\circ$  to  $-28^\circ$ ; saponification number: max. 20; soluble in ethanol, solutions are usually turbid [532].

The major components of the oil are  $\beta$ -sesquiphellandrene [20307-83-9] and zingiberene [495-60-3] [533–540a].

 $\beta$ -Sesquiphellandrene

Zingiberene

*Ginger oleoresin* is prepared by extracting ginger rhizomes with acetone or alcohol. The product contains the essential oil along with the substances responsible for the pungency of ginger. These compounds are substituted phenols of the following structure:



Gingerols:  $R = \text{CH}_2\underset{\text{OH}}{\text{C}}\text{H}(\text{CH}_2)_n\text{CH}_3$ ;  $n = 1-4, 8, 10$

Shogaols:  $R = \text{CH}=\text{CH}(\text{CH}_2)_n\text{CH}_3$ ;  $n = 2, 4, 6, 8$

Main cultivation areas for ginger are India, Malaysia, Taiwan, Australia and the Fiji Islands. Ginger concentrates are used in large amounts in beverages (e.g., ginger ale), as well as in baked goods and confectioneries. FCT 1974 (12) p. 901; [8007-08-7], [84696-15-1].

**Grapefruit oil**, see Citrus oils.

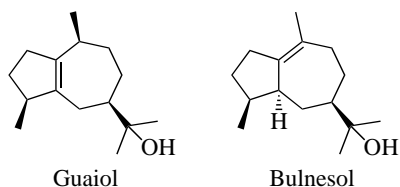
**Green cognac oil**, see Lie de vin oil.



**Guaiac wood oil** is obtained by steam distillation of ground wood and sawdust from the tree *Bulnesia sarmienti* Lorentz (Zygophyllaceae), which is up to 20 m high and grows wild in the Gran Chaco region of Paraguay and in Argentina. The oil is a dark yellowish, viscous liquid with a mild, pleasant odor reminiscent of that of tea roses and faintly of violets. The oil solidifies at room temperature to a yellow-white to light amber colored mass (*mp* 40–50 °C).

$d_{25}^{25}$  0.9600–0.975;  $n_D^{20}$  1.5020–1.5070;  $\alpha_D^{20}$  –12° to –3°; solubility: 1 vol in at least 7 vol of 70% ethanol; solutions are sometimes slightly turbid or opalescent; total alcohol content (calculated as guaiol): min. 85% [541].

The main constituents of the oil are the sesquiterpene alcohols guaiol [489-86-1] and bulnesol [22451-73-6] [542]. The oil may be used as a starting material for the synthesis of guaiazulene, which has anti-inflammatory properties.

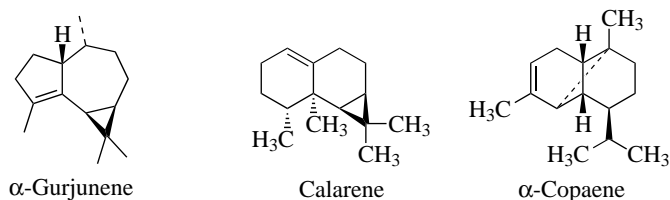


Guaiac wood oil is used extensively in perfume compositions for its excellent fixative properties (see also guajyl acetate, p. 71). FCT 1974 (12) p. 905; [89958-10-1].

**Gurjun balsam oil** is produced by steam distillation of balsams obtained from several *Dipterocarpus* species (Dipterocarpaceae); the trees grow in South and East Asia. The oil is a yellow, slightly viscous liquid with a weak, woodlike odor.

$d_{15}^{20}$  0.918–0.930;  $n_D^{20}$  1.5010–1.5050;  $\alpha_D^{20}$  –130° to –35°; solubility: 1 vol in 10 vol of ethanol.

It consists almost entirely of sesquiterpene hydrocarbons, and its main component (>60%) is  $\alpha$ -gurjunene [489-40-7] [543]. Other qualities of gurjun balsam oil containing Calarene [17334-55-3] and  $\alpha$ -Copaene [38565-25-5] as main constituents are also found on the market.



Gurjun balsam oil and gurjun balsams are used for their good fixative properties, e.g., in soap perfumes and serve also as a starting material for the production of guaiazulene. FCT 1976 (14) p. 789, p. 791; [8030-55-5].

**Japanese mint oil**, see mint oils.

**Jasmin absolute** is obtained by solvent extraction, via the concrete, from the flowers of *Jasminum grandiflorum* L. (Oleaceae), cultivated in Egypt, Italy, Morocco, and India, and of *J. sambac* (L.) Ait. from China and India. The concrete is usually a brown to dark brown waxy mass, with a characteristic jasmin odor.

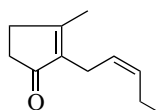
*mp* 48–51 °C; ester number: 70–125.

The absolute is generally a reddish-brown liquid with a delicate jasmin odor; the color deepens on storage.

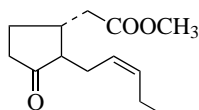
$n_D^{20}$  1.4780–1.4920; acid number: 8–14; ester number: 120–220.

When extracted two or three times with hexane one ton of jasmin blossoms yields ca. 2.5–3 kg of concrete. Extraction of the concrete with ethanol gives a ca. 60% yield of the absolute.

The main volatile component of jasmin oil is benzyl acetate. However, minor components such as indole [120-72-9], *cis*-jasnone [488-10-8], and methyl jasmonate [1211-29-6] contribute strongly to the typical jasmin fragrance [544–549].



*cis*-Jasnone



Methyl jasmonate

Annual worldwide production of jasmin concrete is ca. 10 t. The absolute is one of the most valuable blossom fragrances used in fine fragrances. FCT 1976 (14) p. 331; [8022-96-6], [84776-64-7].

**Juniper berry oil** is obtained by steam distillation of ripe fruits of *Juniperus communis* L. var. *erecta* Pursh. (Cupressaceae). It is a colorless, pale green or yellowish liquid with a characteristic, conifer-like odor, and an aromatic-bitter taste.

$d_{20}^{20}$  0.857–0.872;  $n_D^{20}$  1.4710–1.4830;  $\alpha_D^{20}$   $-15^\circ$  to  $0^\circ$ ; solubility: 1 vol in max. 10 vol of 95% ethanol [550].

The slightly turpentine-like odor and the relatively low solubility of the oil are caused by its high content of  $\alpha$ -pinene and other monoterpene hydrocarbons. The main oxygen-containing component is 1-terpinen-4-ol [551–556].

The oil is used to a limited extent in perfumery for creating fresh, dry effects and as an aroma ingredient in alcoholic beverages of the gin type. FCT 1976 (14) p. 333; [8012-91-7], [84603-69-0].

**Labdanum absolute** and **Labdanum oil** are obtained from labdanum gum, which is exuded when twigs of *Cistus ladaniferus* L. (Cistaceae) are boiled in water.

*Labdanum absolute* is produced by extraction of the gum with alcohol (e.g., methanol or ethanol). So-called colorless absolutes are obtained from absolutes by extraction with, for example, hexane.

Steam distillation of the gum yields *labdanum oil* which is a golden yellow, viscous liquid that quickly turns dark brown on standing:

$d_{25}^{25}$  0.905–0.993;  $n_D^{20}$  1.4920–1.5070;  $\alpha_D^{20}$   $+0^\circ 15'$  to  $+7^\circ$ , often difficult to determine due to its dark color; solubility: 1 vol in 0.5 vol of 90% ethanol,

solutions frequently opalescent to turbid, paraffins may separate upon further dilution; acid number: 18–86; ester number: 31–86 [557].

Other odoriferous materials are derived from the leaves and young twigs of *Cistus ladaniferus*. Cistus oil is obtained by steam distillation; solvent extraction yields cistus concrete. Cistus oil, in contrast to labdanum oil, consists mainly of monoterpene hydrocarbons.

Cistus and labdanum products come from Mediterranean countries, mainly Spain, where the *Cistus* shrub grows abundantly. They are used widely in perfumery, giving perfume compositions a warm, balsamic tonality with a touch of ambergris. The typical odor originates from a number of compounds which are formed by oxidative degradation of diterpenes with labdane skeleton, which are the main constituents of labdanum gum [284a, 558–565a]. The resinoids and absolutes are excellent natural fixatives. FCT 1976 (14) p. 335; [8016-26-0], [89997-74-0].

**Laurel leaf oil** is obtained by steam distillation of leaves from *Laurus nobilis* L. (Lauraceae), an evergreen tree cultivated primarily in Mediterranean countries. The oil is a light yellow to yellow liquid with an aromatic, spicy odor.

$d_{25}^{25}$  0.905–0.929;  $n_D^{20}$  1.4650–1.4700;  $\alpha_D^{20}$   $-19^\circ$  to  $-10^\circ$ ; solubility: 1 vol in at least 1 vol of 80% ethanol; acid number: max. 3; saponification number: 15–45; saponification number (after acetylation): 36–85 [566].

The main component of the oil is 1,8-cineole (30–70%); other important components are linalool (ca. 10%) and eugenol [567–572a].

Laurel leaf oil is used extensively in the food industry, e.g., for seasoning meat products and soups. FCT 1976 (14) p. 337; [8002-41-3], [84603-73-6].

**Lavandula products** comprise the following oils and extracts:

1. *Lavender oil* is produced by steam distillation of freshly cut, flowering tops of *Lavandula angustifolia* Mill. (Lamiaceae). It is a pale yellow, amber-tinged liquid with a fresh, sweet, floral, herbaceous odor on a woody balsamic base.

$d_{20}^{20}$  0.880–0.890;  $n_D^{20}$  1.4580–1.4640;  $\alpha_D^{20}$   $-11.5^\circ$  to  $-7^\circ$ ; solubility: 1 vol in max. 2 vol of 75% ethanol; acid value: max. 1; ester value 102.5–165, corresponding to an ester content calculated as linalyl acetate: 35.8–58%; content of linalyl acetate by GC: 25–45% (specification for French population lavender oil) [573].

True French lavender grows in the Haute Provence at an altitude of 600–1500 m. The plants are grown from seeds of the wild lavender ('population' lavender). Lavender oil is produced in a yield of 10–25 kg/ha. It has the following typical composition (%): *cis*-ocimene (4–10), *trans*-ocimene (1.5–6), 1,8-cineole ( $\leq 1$ ), camphor ( $\leq 0.5$ ), linalool (25–38), linalyl acetate (25–45), 1-terpinen-4-ol (2–6), and lavandulyl acetate ( $\geq 2$ ) [574–583a].

Cloned varieties of lavender (e.g., *mailette*) yield more oil per hectare and can be grown at lower altitudes; however, they produce a poorer quality oil.

Lavender oils with a similar composition are also produced in several other areas throughout the world (e.g., Bulgaria, Tasmania, China and Russia). Worldwide annual production is estimated at 200 t. FCT 1976 (14) p. 451; [8000-28-0], [90063-37-9].

2. *Spanish spike lavender oil* is produced by steam distillation of the flowering tops of spike, *Lavandula latifolia* Medik. It is an almost colorless to pale greenish-yellow liquid with a characteristic, rough odor slightly like cineole and camphor.

$d_{20}^{20}$  0.894–0.907;  $n_D^{20}$  1.4610–1.4680;  $\alpha_D^{20}$   $-7^\circ$  to  $+2^\circ$ ; solubility: 1 vol in not more than 3 vol of 70% ethanol; solutions may become opalescent on dilution; acid number: max. 1; ester number: 3–14; ester number (after acetylation): 130–200 [584].

The main components of Spanish spike lavender oil are linalool (34–50%), 1,8-cineole (16–39%), and camphor (8–16%) [585–591a].

Spike plants grow wild in the entire Mediterranean area and prefer warmer, lower-lying regions than lavender and lavandin. Oil is primarily produced from plants cultivated in Spain; in comparison to lavender and lavandin oils, only small quantities are produced annually. FCT 1976 (14) p. 453; [8016-78-2], [97722-12-8].

3. *Lavandin oil* is obtained by steam distillation of freshly cut flowering tops of lavandin, which is a hybrid of lavender and spike (*Lavandula angustifolia* Mill.  $\times$  *Lavandula latifolia* Medik.). It is a pale yellow to amber liquid with a lavender-like and a slightly camphoraceous note.

$d_{20}^{20}$  0.887–0.897;  $n_D^{20}$  1.460–1.466;  $\alpha_D^{20}$   $-5^\circ$  to  $-2^\circ$ ; solubility: 1 vol in 4 vol of 70% ethanol at 20°C; acid number: max. 1.0; ester number: 77–108, corresponding to an ester content of 27–38%, calculated as linalyl acetate (lavandin oil *abrial*) [592].  $d_{20}^{20}$  0.891–0.899;  $n_D^{20}$  1.4580–1.4620;  $\alpha_D^{20}$   $-7^\circ$  to  $-3.5^\circ$ ; solubility: 1 vol in max. 3 vol of 70% ethanol; acid value: max. 1; ester value 100–137, corresponding to an ester content, calculated as linalyl acetate: 35–48%; (lavandin oil *grosso*) [593].

Lavandin plants are sterile and can be propagated only by using cuttings. The oils from the most important varieties, *abrial* and *grosso*, contain linalool (26–38/24–35%) and linalyl acetate (20–29/28–38%) as major constituents as well as 1,8-cineole (6–11/4–7%) and camphor (7–11/6–8%) [594–601]. A third variety is called *super* because its oil contains a high concentration of linalyl acetate (35–47%), and, thus, resembles lavender oil most closely.

Although lavender oil is more valuable than lavandin oil as a fragrance raw material, lavandin plants are more commonly cultivated because they give a higher yield of oil (ca. 50–100 kg/ha) and are hardier than lavender plants.

Cultivation in southern France is no longer restricted to the traditional lavender regions, but also now includes the Languedoc. Approximately 650–800 t of oil are produced annually in this area.

All three oils are used primarily in soap perfumes; considerable quantities are also employed in eau de cologne and in bath products. FCT 1976 (14) p. 447; [8022-15-9], [91722-69-9], [93455-96-0] *abrial*, [93455-97-1] *grosso*.

4. *Lavender and lavandin extracts* are also commercially important and are produced in southern France by solvent extraction of flowering lavender and lavandin herbs. Production of lavandin concrete is higher than that of lavender. Extraction of the paste-like concretes with ethanol, followed by evaporation, yields absolutes. These extracts differ from the essential oils in being more soluble and in

having a green color and a longer-lasting odor with a hay-like, spicy note. They are also used in eau de cologne and fine fragrances, sometimes after decoloration (removal of chlorophyll with activated charcoal). FCT 1992 (30 suppl.) p. 65.

**Lemon oil**, see Citrus oils.

**Lemongrass oil**, see Cymbopogon oils.

**Lie de vin oil** (green cognac oil or wine lees oil) is obtained by steam distillation of the yeast and other sediments (lees) formed in wine. It is a green to bluish-green liquid with a characteristic cognac aroma.

$d_{25}^{25}$  0.864–0.870;  $n_D^{20}$  1.4275–1.4295;  $\alpha_D$   $-1^\circ$  to  $+2^\circ$ ; acid number: 32–70; ester number: 200–245; solubility: 1 vol in at least 2 vol of 80% ethanol [602].

Lie de vin oil consists mainly of the ethyl and isoamyl esters of fatty acids, formed during fermentation [603]. It is used mostly in aroma compositions; only very small amounts are employed in perfume compositions.

**Lime oil**, see Citrus oils.

**Litsea cubeba oil** is produced by steam distillation of the fruits of *Litsea cubeba* C. H. Persoon (Lauraceae) growing in East Asia. It is a pale yellow liquid with a fresh odor, reminiscent of citral.

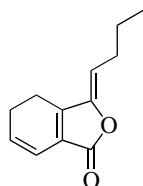
$d_{20}^{20}$  0.880–0.892;  $n_D^{20}$  1.4800–1.4900;  $\alpha_D^{20}$   $+3^\circ$  to  $+12^\circ$ ; carbonyl content (calculated as citral): min. 74%; content by GC: 25–33% neral, 38–45% geranial; solubility: 1 vol in 3 vol of 70% ethanol at 20°C [604].

The oil is used mainly for the production of citral as a starting material for many other fragrance materials [605–607]; smaller quantities are employed for perfuming household products. The main producer is China. Worldwide annual production is ca. 1000 t. FCT 1982 (20) p. 731; [68855-99-5], [90063-59-5].

**Lovage oils** are obtained by steam distillation of either the leaves (leaf oil) or the fresh roots (root oil) of the perennial plant *Levisticum officinale* Koch (Apiaceae). Both oils are yellow-greenish-brown to dark brown liquids with a strong, characteristic, aromatic odor and taste.

$d_{20}^{20}$  1.010–1.090;  $n_D^{20}$  1.5350–1.5580;  $\alpha_D^{20}$   $-1^\circ$  to  $+5^\circ$ ; solubility: 1 vol in max. 1.5 vol of 85% ethanol; acid value: max. 2–16; ester value 170–260 [608].

The main constituent of the leaf oil is  $\alpha$ -terpinyl acetate, while the main constituent and odor-determining component of the root oil is ligustilide [4431-01-0] (3-butylidene-4,5-dihydrophthalide) [609–612a].



Ligustilide

The oils are very expensive. They are mainly used in the alcoholic beverage industry and for flavoring of tobacco; small amounts are also used in perfumery. FCT 1978 (16) p. 813; [8016-31-7], [84837-06-9].

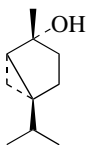
**Mace oil**, see Nutmeg oil.

**Mandarin oil**, see Citrus oils.

**Marjoram oil** (sweet marjoram oil) is obtained by steam distillation of the herb *Origanum majorana* L. (*Majorana hortensis* Moench, Lamiaceae). It is a yellow to greenish- yellow liquid with a characteristic earthy-spicy odor.

$d_{25}^{25}$  0.890–0.906;  $n_D^{20}$  1.4700–1.4750;  $\alpha_D^{20}$  +14° to +24°; acid number: max. 2.5; saponification number: 23–40; saponification number (after acetylation) 68–86; solubility: 1 vol in 2 vol of 80% ethanol [613].

The main constituent of the oil is 1-terpinen-4-ol (>20%), which with (+)-*cis*-sabinene hydrate [15537-55-0] (3–18%) is responsible for the characteristic flavor and fragrance of marjoram oil [614–620b].



(+)-*cis*-Sabinene hydrate

Sweet marjoram oil is used mainly for flavoring foods, but also in smaller amounts in perfumery for spicy shadings in men's fragrances. FCT 1976 (14) p. 469; [8015-01-8], [84012-24-8].

*Spanish marjoram oil* is distilled from *Thymus mastichina* L., a wild plant growing in Spain. The oil is a slightly yellow liquid with a fresh camphoraceous odor. Its main constituent is 1,8-cineole (up to 65%).

**Mimosa absolute** is obtained from the blossoms of the mimosa trees *Acacia dealbata* Link and *A. decurrens* Willd. var. *mollis* (Fabaceae), which grow in the forests of southern France and in Morocco.

The absolute is a yellowish brown liquid with a slightly green, flowery odor and extremely high tenacity.

Annual production is only some few tons [621]. Mimosa absolute is used mainly in fine fragrances as a flowery fixative. FCT 1975 (13) p. 873; [8031-03-6], [93685-96-2].

**Mint oils** are listed in order of the quantities produced.

1. *Cornmint oil*, *Japanese mint oil* is produced by steam distillation of the flowering herb *Mentha arvensis* var. *piperascens* Malinv. The crude oil contains ca. 70% (–)-menthol, which can be isolated by crystallization at low temperature.

**Table 5.** Specifications of dementholized cornmint oils

Parameter	Origin of cornmint oil	
	China	India
$d_{20}^{20}$	0.890–0.908	0.890–0.910
$n_D^{20}$	1.4570–1.4650	1.4570–1.4650
$\alpha_D^{20}$	–248 to –158	–228 to –138
Acid value	max. 1	max. 1
Ester value	8–25	8–25
Content of ester, calc. as menthyl acetate [%]	3–9	3–9

The residual dementholized oil is a colorless to yellow liquid with a characteristic minty odor; typical specifications are given in Table 5 [622].

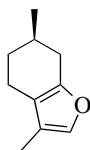
Dementholized oil still contains ca. 33–45% (–)-menthol; (–)-menthone and (+)-isomenthone (25–40% together) are other major components [623–626e]. Dementholized *Mentha arvensis* oil was formerly produced primarily in Brazil; maximum production was 3000 t (together with 3000 t of (–)-menthol) in 1973. Currently, cornmint oil is produced mainly in China (3000–4000 t/yr), and in India which has become a second major cornmint oil producer since ca. 1990 and produced ca. 8000 t in 1996.

Dementholized cornmint oil tastes more bitter and stringent than peppermint oil. Thus, the former is used as a cheaper substitute for the latter and for the production of (–)-menthol. FCT 1975 (13) p. 771; [68917-18-0], [91722-84-8].

2. *Peppermint oil* is produced by steam distillation of the flowering herb *Mentha piperita* L. It is an almost colorless to pale greenish-yellow liquid with a characteristic peppermint odor.

$d_{20}^{20}$  0.898–0.918;  $n_D^{20}$  1.459–1.465;  $\alpha_D^{20}$  –30° to –14°; solubility: 1 vol in 5 vol of 70% ethanol at 20 °C; ester number: 12–30; ester number (after acetylation): 135–200; carbonyl number: 54–115 [627].

As in cornmint oil, the main component of peppermint oil is (–)-menthol (32–49%); it also contains (–)-menthone (13–28%) and (–)-menthyl acetate (2–8%). However, peppermint oil, unlike cornmint oil, has a higher content of (+)-menthofuran [17957-94-7] (1–8%) [628–633h].



(+)-Menthofuran

**Table 6.** Characteristic components of Scotch and native spearmint oils

Compound	Content of compound in spearmint oil, %	
	Scotch	Native
Limonene	18.5–26.5	11.5–16.5
Carvone	60–66	60–67
Menthone	0.5–1.3	0–0.1
Viridiflorol	0–0.1	0.2–0.5

The leading producer of peppermint oil is the United States, where annual production from the variety *M. piperita* L. var. *vulgaris* Sole (Black Mitcham) is more than 4500 t. Cultivation areas are located in the Midwest states, Idaho, Oregon, and Washington. The oils differ in quality and are named according to their geographic origin (e.g., Midwest, Idaho, Madras, Willamette, Yakima). Production of European oil has decreased significantly, despite its high quality. Peppermint oil is used mainly for flavoring toothpaste, other oral hygiene products, and chewing gum. Smaller quantities are used for flavoring confectioneries. Due to its high price, peppermint oil is not used for the production of menthol [8006-90-4], [84082-70-2].

3. *Spearmint oils* are obtained by steam distillation of the flowering herbs of *Mentha spicata* L. (native spearmint) and *Mentha cardiaca* Ger. (Scotch spearmint). They are colorless to yellow-green liquids with a fresh, caraway-minty odor.

$d_{20}^{20}$  0.921–0.938;  $n_D^{20}$  1.484–1.491;  $\alpha_D^{20}$   $-59^\circ$  to  $-48^\circ$ ; solubility: 1 vol in 1 vol of 80% ethanol at 20 °C; carbonyl number: min. 200, corresponding to a carvone content of 55% [634–634d].

The compositions of Scotch and native spearmint oils differ as shown in Table 6 [486, 635–637a]. The main producer of spearmint oil is the United States, primarily the state of Washington. Smaller amounts are also produced in some Midwest states. Total annual production is about 1500 t, 30–50% being of the native type and 50–70% of the Scotch type [637b]. Other minor cultivation areas for spearmint oils exist in China and India where oils with up to 80% carvone are produced [634b–634d].

By far the most spearmint oil is used for flavoring toothpaste and chewing gum. Smaller quantities are used in other oral care products and in pharmaceutical preparations. FCT 1976 (16) p. 871; [8008-79-5], [84696-51-5].

**Musk**, see Animal secretions.

**Myrrh oil** and **myrrh resinoids** are produced from the air-dried gum of *Commiphora myrrha* (Nees) Engl. var. *molmol* Engl., *C. abyssinica* (Berg) Engl. and *C. schimperi* (Berg) Engl. (Burseraceae), shrubs that grow in Northeast Africa and Arabia.



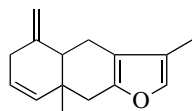
*Myrrh resinoids* are obtained in 20–45% yield by extracting the gum with suitable solvents (e.g., toluene, hexane). They are wax-like, brown-yellow to red-brown masses with a balsamic odor and an aromatic bitter taste. Specifications depend on the solvents used.

Acid number: 20–35; ester number: 165–200; carbonyl number: 20–75 [638].

*Myrrh oil* is obtained from the gum by steam distillation; it is a light brown or green liquid with the characteristic odor of the gum.

$d_{25}^{25}$  0.995–1.014;  $n_D^{20}$  1.5190–1.5275;  $\alpha_D^{20}$   $-83^\circ$  to  $-60^\circ$ ; acid number: 2–13; saponification number: 9–35; solubility: 1 vol in 7–10 vol of 90% ethanol; solutions are occasionally opalescent or turbid [639].

Typical aroma-determining compounds of the myrrh plant are furanosesquiterpenoids such as lindestrene [2221-88-7] [640, 641]. FCT 1976 (14) p. 621, 1992 (30 suppl.) p. 91S; [8016-37-3], [84929-26-0].



Lindestrene

**Neroli oil** and **orange flower absolute** are obtained from the blossoms of the bitter orange tree, *Citrus aurantium* L. subsp. *aurantium*, which is grown in France, Italy, and North Africa. *Neroli oil* is produced by steam distillation and is a pale yellow to amber-colored liquid, with a slight blue fluorescence and a characteristic sweet, spicy-bitter odor of orange blossom.

$d_{20}^{20}$  0.864–0.876;  $n_D^{20}$  1.460–1.474;  $\alpha_D^{20}$   $+2^\circ$  to  $+11^\circ$ ; solubility: 1 vol in not more than 3.5 vol of 85% ethanol at  $20^\circ\text{C}$ ; acid number: max. 2.0; ester number: 26–60 [642].

After separation of neroli oil, the aqueous layer of the steam distillate, known as orange blossom water, is extracted with suitable solvents (e.g., petroleum ether). Evaporation gives *orange flower water absolute* (absolue de l'eau de fleurs d'oranger), which is a dark brown-red liquid. It contains less terpene hydrocarbons and correspondingly more polar compounds than neroli oil.

*Orange flower absolute* is obtained from the blossoms by solvent extraction via the concrete. It is a dark brown liquid with a warm, spicy-bitter odor.

The main volatile constituent of all three products is linalool (in neroli oil 28–44%). Their typical flavor is created by a number of nitrogen-containing trace constituents, such as indole and derivatives of anthranilic acid [428, 643, 644].

Neroli oil and the related products are some of the most expensive natural raw materials and are produced only in small quantities (a few tons per year). They are used in fine fragrances; neroli oil, for example, is one of the classical components of eau de cologne. FCT 1976 (14) p. 813, 1982 (20) p. 785; [8016-38-4], [89957-91-5].

**Nutmeg (mace) oil** is obtained by steam distillation of the seeds (nutmeg) and/or the seed-coverings (mace), which are obtained from the fruits of *Myristica fragrans*

Houtt. (Myristicaceae). The tree grows in Indonesia and in the West Indies and becomes 15–20 m high.

Nutmeg/mace oils are colorless to pale yellow liquids with a pleasant spicy odor. The physical constants and odor vary with the origin. Specifications of Indonesian nutmeg oil are as follows:

$d_{20}^{20}$  0.885–0.907;  $n_D^{20}$  1.4750–1.4850;  $\alpha_D^{20}$  +6° to +18°; solubility: 1 vol in 5 vol of 90% ethanol at 20 °C (solutions sometimes opalescent), for freshly distilled oils, 1 vol in 3–4 vol [645].

Indonesian oils contain a higher percentage of higher boiling components than do West Indian oils.

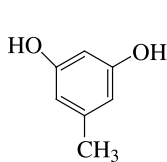
Indonesian oils contain ca. 90% terpene hydrocarbons, mainly sabinene (14–29%) and  $\alpha$ - (15–28%) and  $\beta$ -pinene (13–18%). Major oxygen-containing constituents are 1-terpinen-4-ol (2–6%) and phenol ether derivatives like myristicine (5–12%) [646–650c].

Nutmeg oil is used mainly in food flavorings (soft drinks of the cola-type) and to a lesser extent in perfumery. More than 100 t/a is produced in Indonesia. FCT 1976 (14) p. 631, 1979 (17) p. 851; [8007-12-3], [84082-68-8].

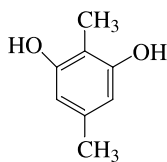
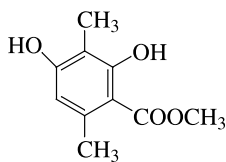
**Oakmoss absolute** and **tree moss absolute** are obtained from tree lichens. *Oakmoss absolute* is derived from *Evernia prunastri* (L.) Arch. (Usnaceae), a lichen growing on oak trees. The lichen is first extracted with nonpolar solvents to give a concrete. The waxes are then removed by precipitation with ethanol, leaving an absolute.

The concretes are green to brown waxy pastes; the absolutes are more or less viscous liquids with an earthy, mossy, woody odor and a slight phenolic, leather note.

Resorcinol derivatives, e.g., orcinol [504-15-4],  $\beta$ -orcinol [488-87-9], their monomethyl ethers, and methyl 3,6-dimethylresorcyate [4707-47-5] (see p. 141) are mainly responsible for the characteristic earthy-moss-like odor of the oakmoss products [651–655b].



Orcinol

 $\beta$ -Orcinol

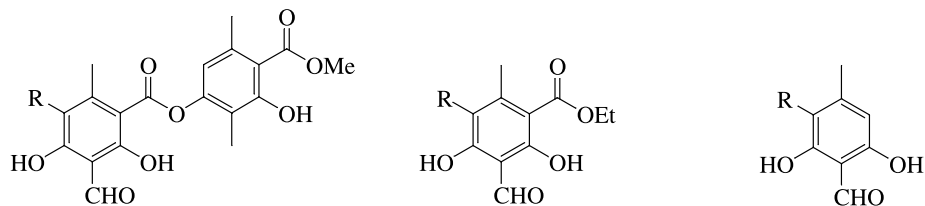
Methyl 3,6-dimethylresorcyate

*Tree moss concretes and absolutes* are prepared from *Evernia furfuracea* Fr., a lichen growing on conifer bark. Their odors are different from those of the corresponding oakmoss products.

The quantities of oakmoss (mousse de chêne) and tree moss (mousse d'arbre) that are collected annually in the Balkan countries, France, and Morocco exceed 4000 t [656].

The extracts and absolutes are used in perfumery for nuances and as a fixative to give compositions a dry, sweet base note, e.g., in fougère and chypre perfumes. Occasionally occurring allergenic responses to oakmoss and treemoss products are

probably caused by aromatic aldehydes like atranorin [479-20-9] and chloroatranorin [479-16-3] and the corresponding products which are formed during the work-up process as a result of transesterification and decarboxylation reactions, e.g., ethyl hemmatomate [39503-14-5], ethyl chlorohemmatomate [57857-81-5], atranol [526-37-4], and chloroatranol [57074-21-2] [655a, 655b].



R = H: atranorin

R = Cl: chloroatranorin

R = H: ethyl hematommate

R = Cl: ethyl chlorohematommate

R = H: atranol

R = Cl: chloroatranol

Methods to obtain oakmoss and treemoss products of low allergenic properties have been reported [656a, 656b]. [9000-50-4], [68606-93-9], [90028-68-5], [68917-10-2], [90028-67-4].

**Olibanum oil** and **olibanum resinoid** are obtained from frankincense, which is a gum resin collected from the bark of the tree *Boswellia carterii* Birdw. or *B. frereana* Birdw. (Burseraceae) growing in Arabia and Somalia. The resinoid is produced by solvent extraction, and steam distillation gives the oil, which is a pale yellow, slightly viscous liquid with a balsamic odor and a faint lemon note.

$d_{25}^{25}$  0.862–0.889;  $n_D^{20}$  1.4650–1.4820;  $\alpha_D^{20}$   $-15^\circ$  to  $+35^\circ$ ; solubility: 1 vol in 6 vol of 90% ethanol, solutions occasionally opalescent; acid number: max. 4.0; ester number: 4–40 [657].

Various qualities are commercially available. Their compositions may vary considerably because they are prepared from the resins of different *Boswellia* species. Main constituents of the oil are monoterpene hydrocarbons [284a, 658–661a].

Olibanum oil and resinoid are used in oriental type perfumes, the resinoid especially for its good fixative properties. FCT 1978 (16) p. 835, p. 837; [8016-36-2], [89957-98-2].

**Opopanax oil** and **opopanax resinoid** are obtained from the resin of *Commiphora erythraea* Engl. var. *glabrescens* Engl., a tree growing in Somalia (Burseraceae). The resinoid is prepared by solvent extraction, and steam distillation of the resin gives the essential oil, which is a yellow to greenish-yellow liquid with a warm, sweet, balsamic odor.

$d_{25}^{25}$  0.865–0.932;  $n_D^{20}$  1.488–1.504;  $\alpha_D^{20}$   $-32^\circ$  to  $-9^\circ$ ; acid number: max. 4; saponification number: 4–20; solubility: 1 vol in 10 vol of 90% ethanol; solutions are occasionally turbid [662]. Sesquiterpene hydrocarbons like  $\alpha$ -santalene, (*E*)- $\alpha$ -bergamotene and (*Z*)- $\alpha$ -bisabolene make up the main constituents of opopanax oil [663].

Opopanax oil and resinoid are used in perfume compositions with oriental characteristics, the resinoid also for its fixative properties, [8021-36-1], [100084-96-6].

**Orange flower absolute**, see Neroli oil.

**Orange oils**, see Citrus oils.

**Origanum oils** are produced from several species of the flowering herb of mediterranean *Origanum* (Lamiaceae) mainly *O. vulgare* L. ssp. *hirtum* [664]. Spanish origanum oil is derived from *Coridothymus capitatus* Rchb., syn. *Thymbra capitata* (L.) Cav. The oils differ mainly in their content of carvacrol and thymol, which are major constituents [665–672a]. Oil with a high carvacrol content [499-75-2] is a yellowish-red to dark brown liquid with a spicy, herbaceous odor, reminiscent of thyme. The color quickly turns to black when in contact with iron.

$d_{20}^{20}$  0.930–0.955;  $n_D^{20}$  1.5000–1.5130;  $\alpha_D^{20}$   $-5^\circ$  to  $+2^\circ$ ; phenol content: 60–75%; solubility: 1 vol in not more than 4 vol of 70% ethanol; solutions may become opalescent when further diluted. Composition:  $\gamma$ -terpinene 3.5–8.5%; p-cymene 5.5–9%, thymol 0–5%, carvacrol 60–75% (Spanish type) [673].

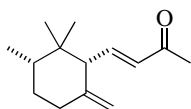
Origanum oils are used in perfume compositions for herbal-spicy, leathery notes and in seasoning mixtures. FCT 1974 (12) p. 945; [8007-11-2], [90131-59-2].

**Orris root oil** is obtained by steam distillation of the rhizomes of the sweet iris, *Iris pallida* Lam. (Iridaceae) cultivated in the Italian province of Tuscany or *Iris germanica* L. cultivated in Morocco. Prior to distillation the rhizomes are stored for several years and are then ground. The steam distillate is a light yellow to brown-yellow solid mass with a violet-like odor. The solid liquefies to a yellow to yellow-brown liquid at 38–50 °C.

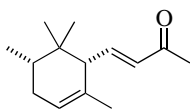
Acid number: 175–235, corresponding to an acid content of 71–95% (calculated as myristic acid); ester number: 4–35; ketone content (calculated as irone): 9–20%; soluble with ethanol in all proportions at 50 °C [674].

Because of its high content of myristic and other fatty acids, the steam distillate is a waxy mass that resembles a concrete and is sold under this name or as *Beurre d'Iris* (Orris butter). In addition, a neutral product, obtained after removal of the acids with alkali, is marketed under the name *orris oil absolute* or as *orris oil 10-fold*.

Main constituents of the oils are *cis*- $\gamma$ -irone (usually 30–40%) and *cis*- $\alpha$ -irone (usually 20–30%) which are also responsible for the typical odor. *I. pallida* oil contains the dextrorotatory enantiomers while *I. germanica* oil contains the laevorotatory enantiomers [675, 676].



(-)-*cis*- $\gamma$ -Irone  
[89888-04-0]



(-)-*cis*- $\alpha$ -Irone  
[89888-03-9]

Fresh orris roots do not contain any irones. These compounds are formed by an oxidative degradation process from higher molecular precursors, the so-called iridales, only when the dried orris roots are stored for a longer period. To avoid such a time-consuming procedure, microbiological processes for the oxidative degradation have been developed [677].

The oil is very expensive and is used in perfumery and in flavor compositions. FCT 1975 (13) p. 895; [8002-73-1], [90045-90-2], [85085-39-8].

**Palmarosa oil**, see Cymbopogon oils.

**Parsley oils** are produced from the plant *Petroselinum crispum* (Mill.) Nym. ex A. W. Hill (*P. sativum* Hoffm.), (Apiaceae):

1. *Parsley leaf oil* is produced by steam distillation of the aerial parts of the plant, including the immature seeds. It is a yellow to light-brown liquid with the typical odor of the herb.

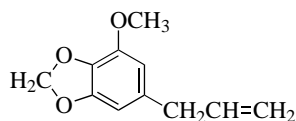
$d_{25}^{25}$  0.908–0.940;  $n_D^{20}$  1.5030–1.5300;  $\alpha_D^{20}$   $-9^\circ$  to  $+1^\circ$ ; acid number: max. 2; soluble in 95% ethanol; solutions may be opalescent [678].

The oil consists mainly of monoterpene hydrocarbons. Its main constituent is 1,3,8-menthatriene [18368-95-1], which is important for the aroma of parsley leaves [679–688].

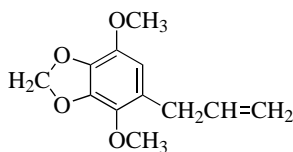
2. *Parsley seed oil* is obtained by steam distillation of ripe fruits of parsley. It is an almost colorless to amber-yellow liquid whose dry odor is characteristic of the crushed fruit, but different from that of the green parts of the plant.

$d_{20}^{20}$  1.043–1.083;  $n_D^{20}$  1.5130–1.5220;  $\alpha_D^{20}$   $-10^\circ$  to  $-4^\circ$ ; acid number: max. 4; ester number: max. 10; solubility: 1 vol in at least 6 vol of 85% ethanol, solutions are sometimes slightly turbid [689].

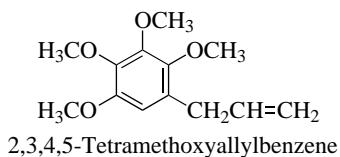
Characteristic components of parsley seed oil are myristicin [607-91-0] (25–50%), apiol [523-80-8] (5–35%), and 2,3,4,5-tetramethoxyallylbenzene [15361-99-6] (1–12%) [679–688a].



Myristicin



Apiol



2,3,4,5-Tetramethoxyallylbenzene

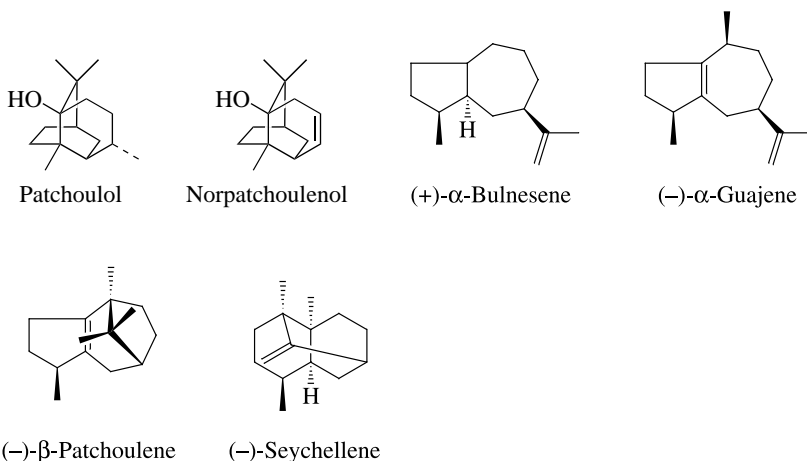
Parsley oils are used in the food industry in seasonings, for example, for meat and sauces. FCT 1983 (21) p. 871, 1975 (13) p. 897; [8000-68-8], [84012-33-9].

**Patchouli oil** is produced by steam distillation of the dried leaves of *Pogostemon cablin* (Blanco) Benth. (Lamiaceae). It is a reddish-brown to greenish-brown, more or less viscous liquid with a characteristic, slightly camphoraceous, woody balsamic odor.

$d_{20}^{20}$  0.952–0.975;  $n_D^{20}$  1.5050–1.5150;  $\alpha_D^{20}$   $-60^\circ$  to  $-40^\circ$ ; solubility: 1 vol in not more than 10 vol of 90% ethanol at  $20^\circ\text{C}$ ; acid number: max. 4; ester number: max. 10 [690].

The patchouli shrub is cultivated primarily in Indonesia. It grows to 1 m, but during harvesting is cut back to 10–15 cm. The oil yield from preferably sun-dried leaves is ca. 2%.

Although the sesquiterpene alcohol (–)-patchoulol [5986-55-0] is the main component of patchouli oil (27–35%), this compound contributes less to the characteristic odor of the oil than norpatchoulol [41429-52-1] present only at a concentration of 0.35–1% [261, 691–695a]. Other typical constituents are (+)- $\alpha$ -Bulnesene [3691-11-0] (13–21%), (–)- $\alpha$ -Guajene [3691-12-1] (11–16%), (–)- $\beta$ -Patchoulene [514-51-2] (1.8–3.5%), and (–)-Seychellene [20085-93-2] (1–3%).

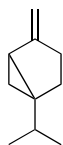


Worldwide production amounts to some 100 t/yr. Patchouli oil is very tenacious and is used in perfumery for oriental and masculine notes. It is used to a large extent in fabric conditioner perfumes due to its high substantivity. FCT 1982 (20) p. 291; [8014-09-3], [84238-39-1].

**Pepper oil** and **pepper oleoresin** are obtained from the black pepper *Piper nigrum* L. (Piperaceae). Pepper oil is produced by steam distillation of whole or crushed fruits. The oil is an almost colorless to bluish-green liquid with a characteristic odor, reminiscent of pepper, but without the pungency of the spice.

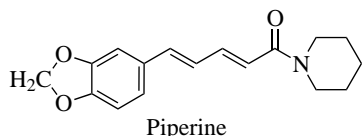
$d_{20}^{20}$  0.870–0.890;  $\alpha_D^{20}$   $-16^\circ$  to  $+4^\circ$ ; solubility: 1 vol in 3 vol of 95% ethanol; ester number: max. 11 [696].

The oil contains mainly monoterpene hydrocarbons (ca. 80%), its main constituent being sabinene [3387-41-5] (20–25%) [697–700c].



Sabinene

Pepper oleoresin is produced by solvent extraction and, unlike the oil, contains the principal pungent compound, piperine [94-62-2], along with some essential oil.



Piperine

Pepper products are used for flavoring foods; pepper oil is also employed to a small extent in perfume compositions. FCT 1978 (16) p. 651; [8006-82-4], [84929-41-9].

**Peppermint oil**, see Mint oils.

**Peru balsam oil** is obtained by distillation of the balsam of the tree *Myroxylon pereira* (Royle) Klotzsch (Fabaceae), called *peru balsam*. It is a yellow to pale brown, slightly viscous liquid, which may form crystals. The oil has a rather sweet, balsamic odor.

$d_{25}^{25}$  1.095–1.110;  $n_D^{20}$  1.5670–1.5790;  $\alpha_D^{20}$   $-1^\circ$  to  $+2^\circ$ ; acid number: 30–60; ester number: 200–225; solubility: 1 vol in at least 0.5 vol of 90% ethanol [701].

Peru balsam is produced almost exclusively in El Salvador. The oil yield from the balsam is ca. 50%. Major components are benzyl benzoate and benzyl cinnamate. Nerolidol and vanillin contribute to the odor [284a].

The oil is used for its excellent fixative properties in perfumes for soap and cosmetics. Use of Peru balsam itself is banned because it is allergenic. FCT 1974 (12) p. 951, p. 953; [8007-00-9], [92704-46-6].

**Petitgrain oils** are obtained by steam distillation of the leaves of citrus trees. The oils derived from the bitter orange tree are the most important. Other petitgrain oils (mandarinier, citronnier, and bergamottier) are less important. Petitgrain oil mandarinier is a source of natural methyl *N*-methylantranilate, which is present at a concentration of nearly 50%. Petitgrain oils are essential constituents of eau de cologne.

*Petitgrain oil Paraguay* is obtained from an acclimatized variety of the bitter orange tree, *Citrus aurantium* L. subsp. *aurantium*, which is grown in Paraguay. It is pale yellow liquid with a characteristic, strong, pleasant odor, reminiscent of linalool and linalyl acetate.

$d_{20}^{20}$  0.882–0.893;  $n_D^{20}$  1.455–1.463;  $\alpha_D^{20}$   $-6^\circ$  to  $-1^\circ$ ; solubility: 1 vol in 4 vol of 70% ethanol at 20 °C; acid number: max. 1; ester number: 127–184, corresponding to an ester content of 45–65% (calculated as linalyl acetate) [702]. Main constituents are linalool (15–30%) and linalyl acetate (40–60%). A number of trace constituents contribute essentially to the odor [370a, 428, 703–706d].

Annual production is ca. 200 t.

*Petitgrain oil bigarade* is derived from the bitter orange tree *Citrus aurantium* L. subsp. *aurantium*, grown in France, Italy, Spain, and North Africa. FCT 1992 (30 suppl.) p. 101S; [8014-17-3].

**Pimento oils** (allspice oil) are derived from pimento fruits and leaves. Pimento berry oil is obtained by steam distillation of the dried, fully grown, unripe, berry-like fruits of the pimento shrub, *Pimenta dioica* (L.) Merrill. (Myrtaceae), growing in the islands of the West Indies and Central America. It is a pale yellow to brown liquid with a spicy odor, reminiscent of eugenol.

$d_{20}^{20}$  1.027–1.048;  $n_D^{20}$  1.5250–1.5400;  $\alpha_D^{20}$   $-5^\circ$  to  $0^\circ$ ; solubility: 1 vol in 2 vol of 70% ethanol at 20 °C; phenol content: min. 65% [707]

The major components of pimento berry oil are eugenol (up to 75%), 1,8-cineole, and caryophyllene [708–712]. Distillation of the leaves gives an oil that has an even higher content of eugenol (80–90%). Annual production of leaf oil is ca. 50 t, which exceeds that of the berry oil.

Pimento oils, like the spice itself, are used mainly in the food industry, as well as in perfume compositions for creating spicy, clovelike notes. FCT 1974 (12) p. 971, 1979 (17) p. 381; [8006-77-7].

**Pinaceae needle oils from Pinaceae species** contain (–)-bornyl acetate as their main odoriferous component. Other main constituents are monoterpene hydrocarbons such as  $\alpha$ - and  $\beta$ -pinene, limonene, 3-carene, and  $\alpha$ - and  $\beta$ -phellandrene [713–718b]. The oils are used in perfumes for soap, bath products, and air fresheners and in pharmaceutical preparations.

1. *European silver fir oil* is produced in central Europe by steam distillation of needle-bearing twigs of *Abies alba* Mill. It is a colorless to pale yellow liquid with a pleasant odor of freshly cut fir needles.

$d_{25}^{25}$  0.867–0.878;  $n_D^{20}$  1.4700–1.4750;  $\alpha_D^{20}$   $-67^\circ$  to  $-34^\circ$ ; solubility: 1 vol in 7 vol of 90% ethanol; ester content (calculated as bornyl acetate): 4–10% [719]; [90028-76-5].

Silver fir cone oil (templin oil) obtained from the cones of *Abies alba* Mill. has similar properties.

2. *Siberian fir needle oil* is obtained by steam distillation of needles and twigs of *Abies sibirica* Ledeb., the Siberian silver fir. It is an almost colorless or pale yellow liquid with a characteristic fir odor.

$d_{25}^{25}$  0.898–0.912;  $n_D^{20}$  1.4685–1.4730;  $\alpha_D^{20}$   $-45^\circ$  to  $-33^\circ$ ; solubility: 1 vol in 1 vol of 90% ethanol, solutions may become hazy when further diluted; ester content (calculated as bornyl acetate): 32–44% [720]. FCT 1975 (13) p. 450; [8021-29-22], [91697-89-1].



3. *Canadian fir needle oil* (balsam fir oil) is produced in Canada and in several northern states of the United States from needles and twigs of *Abies balsamea* (L.) Mill. It is an almost colorless to pale yellow liquid with a pleasant balsamic odor.

$d_{25}^{25}$  0.872–0.878;  $n_D^{20}$  1.4730–1.4760;  $\alpha_D^{20}$   $-24^\circ$  to  $-19^\circ$ ; solubility: 1 vol in 4 vol of 90% ethanol (turbidity may occur), ester content (calculated as bornyl acetate): 8–16% [721].

4. *Pine-needle oil* is produced primarily in Austria (Tyrol), and Eastern and Southeastern Europe by steam distillation of the needles of the Norwegian or Scotch pine, *Pinus sylvestris* L. or *Pinus nigra* Arnold. It is a colorless or yellowish liquid with an aromatic, turpentine-like odor.

$d_{25}^{25}$  0.857–0.885;  $n_D^{20}$  1.4730–1.4785;  $\alpha_D^{20}$   $-4^\circ$  to  $+10^\circ$ ; solubility: 1 vol in 6 vol of 90% ethanol, sometimes slightly opalescent; ester content (calculated as bornyl acetate): 1.5–5% [722]. FCT 1976 (14) p. 845, 2000 (38, suppl. 3) p. S177; [8023-99-2], [84012-35-1].

5. *Dwarf pine-needle oil* is obtained in Austria (Tyrol) and other mountainous areas of central and southeast Europe by steam distillation of fresh needles and twig tips of *Pinus mugo* Turra subsp. *mugo* Zenan and subsp. *pumilio* (Haenke) Franco. It is a colorless liquid with a pleasant, balsamic odor.

$d_{25}^{25}$  0.853–0.871;  $n_D^{20}$  1.475–1.480;  $\alpha_D^{25}$   $-16^\circ$  to  $-3^\circ$ ; solubility: 1 vol in 10 vol of 90% ethanol; bornyl acetate content is similar to that of pine needle oil. FCT 1976 (14) p. 843; [8000-26-8], [90082-72-7].

6. *Spruce and hemlock oils* are produced in Canada and the Northeast of the United States by steam distillation of needles and twigs from *Picea mariana* (Mill.) B.S.P. (black spruce), *Picea glauca* (Moench) Voss (white spruce), *Tsuga canadensis* (L.) Carr. (Hemlock spruce), and related species. They are very pale to light yellow liquids with a pleasant odor reminiscent of pine needles.

$d_{25}^{25}$  0.900–0.915;  $n_D^{20}$  1.4670–1.4720;  $\alpha_D^{20}$   $-25^\circ$  to  $-10^\circ$ ; solubility: 1 vol in at least 1 vol of 90% ethanol; solutions may become hazy when  $>2$  vol of 90% ethanol are added; ester content (calculated as bornyl acetate): 37–45% [723].

**Pine oil**, see Turpentine oil.

**Rose oil** and **rose absolute** are used mainly in fine fragrances. Rose oil is also used in small amounts for flavoring purposes.

1. *Rose oil* is obtained by steam distillation of blossoms of *Rosa*  $\times$  *damascena* Mill. that is mainly cultivated in Turkey, Morocco, and Bulgaria (Kazanlik rose). Since a reasonable amount of rose oil is still dissolved in the aqueous phase after steam distillation, the distillation water (*rose water*) is redistilled or extracted.

Rose oil is a yellow partly crystallized liquid with the characteristic odor of rose blossoms and distinct tea and honey notes.

$d_{20}^{20}$  0.848–0.880;  $n_D^{20}$  1.4520–1.4700;  $\alpha_D^{20}$   $-5^\circ$  to  $-1.8^\circ$ ;  $fp$   $+16$ – $23.5^\circ\text{C}$ ; ester value: 7–24; content by GC (Bulgaria/Turkey/Morocco): citronellol: 20–34/34–49/30–47%; geraniol 15–22/8–20/6–23%; nerol 5–12/3–11/3–11%; phenylethyl alcohol  $<3/ <2/ <3\%$  [724].

The major constituents of rose oil are (–)-citronellol, geraniol, and nerol. In contrast to the absolute (see below), the oil contains only a minor amount of phenethyl alcohol, which is extremely soluble in water.

In addition to the major components mentioned above, rose oil also contains a number of components which, although present in low concentrations, contribute to the characteristic fragrance [725–731b]. Among these are  $\beta$ -damascenone (see p. 68) and rose oxide (see p. 143).

Since ca. 3 t of blossoms are required to prepare ca. 1 kg of oil, rose oil is one of the most expensive essential oils. Production is just a few tons per year.

2. *Rose absolute* is prepared from the concrete extracted from *Rosa  $\times$  damascena* in the countries mentioned above, as well as from *Rosa centifolia* L. types in Morocco and the south of France (rose de mai).

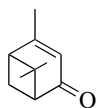
The absolute is a reddish liquid with a typical rose odor. The phenethyl alcohol content of its volatile fraction is 60–75%.

FCT 1974 (12) p. 979, p. 981, 1975 (13), p. 911, p. 913; [8007-01-0], [90106-38-0] *R. damascena*, [84604-12-6] *R. centifolia*.

**Rosemary oil** is obtained by steam distillation of the twigs and flowering tops of *Rosmarinus officinalis* L. (Lamiaceae). It is an almost colorless to pale yellow liquid with a characteristic, refreshing, pleasant odor.

$d_{20}^{20}$  0.892–0.910/0.907–0.920;  $n_D^{20}$  1.4640–1.4720 (both);  $\alpha_D^{20}$   $-5^\circ$  to  $+8^\circ/ -2^\circ$  to  $+5^\circ$ ; ester value: 2–15 (both); ester value after acetylation: 35–55/30–72 (Spanish/North African type) [732].

Major constituents are 1,8-cineole (17–25%/38–55%),  $\alpha$ -pinene (18–26%/9–14%) and camphor (12.5–22%/5–15%) (Spanish/North African oils). Verbenone [18309-32-5] is usually a trace constituent in North African oils (0–0.4%), but occurs in Spanish oils in quantities between 0.7 and 2.5% [733–742].



Verbenone

The main producers of rosemary oil are Tunisia, Morocco and Spain with ca. 150 t annually. Rosemary oil is used widely in perfumery and in large amounts for perfuming bath foams, shampoos, and hair tonics. FCT 1974 (12), p. 977; [8000-25-7], [84604-14-8].

**Rosewood oil, Brazilian** (Bois de rose oil) is obtained by steam distillation of wood from *Aniba rosaeodora* A. Ducke var. *amazonica* A. Ducke and/or *A. parviflora*

Meissner Mez. (Lauraceae). It is an almost colorless to pale yellow liquid with a characteristic, sweet odor, reminiscent of linalool, its main constituent [743, 743a].

$d_{20}^{20}$  0.870–0.887;  $n_D^{20}$  1.4620–1.4690;  $\alpha_D^{20}$   $-2^\circ 50'$  to  $+4^\circ$ ; solubility: 1 vol in 9 vol of 60% ethanol at 20 °C; ester number (after acetylation): 247–280, corresponding to an alcohol content of 82–96% (calculated as linalool); linalool content by GC: 75–95% [744].

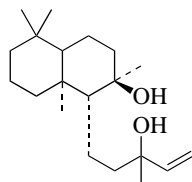
Brazilian rosewood oil is no longer competitive as a raw material for linalool. Increasing production costs, as well as the development of large-scale processes for fully synthetic linalool (for production of vitamin A), have led to a sharp decline in production. Currently, rosewood oil is, if ever, only produced in very small quantities. FCT 1978 (16) p. 653; [8015-77-8], [83863-32-5].

**Sage oils** are of three main types:

1. *Clary sage oil* is obtained by steam distillation of flowering tops and foliage of cultivated *Salvia sclarea* L. (Lamiaceae). It is a pale yellow to yellow liquid with a fresh herbaceous odor and a wine-like bouquet.

$d_{20}^{20}$  0.890–0.908;  $n_D^{20}$  1.4560–1.4660;  $\alpha_D^{20}$   $-10^\circ$  to  $-26^\circ$ ; ester value: 180–235 corresponding to an ester content of 63–82% calculated as linalyl acetate; solubility: 1 vol in max 3 vol 80% ethanol; content by GC: 56–78% linalyl acetate and 6.5–24% linalool [745].

In addition to linalyl acetate, the oil contains linalool and other terpene alcohols, as well as their acetates. When the volatile components are evaporated, a distinct ambergris note develops that is attributed to oxidative degradation products of sclareol [515-03-7] [746–750a]. Sclareol is the main component in the concrete, obtained by solvent extraction of *S. sclarea* L. leaves [750b].



Sclareol

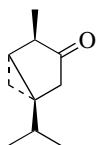
Sclareol is used as a starting material for a number of ambergris fragrances. Major cultivation areas for *S. sclarea* L. are Russia, the Mediterranean countries, and the United States.

Clary sage oil is used extensively in fine fragrances. FCT 1974 (12) p. 865; 1982 (20) p. 823; [8016-63-5], [84775-83-7].

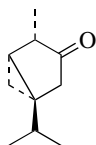
2. *Dalmatian sage oil* is obtained by steam distillation of the partially dried leaves of *Salvia officinalis* L. (Lamiaceae). It is a yellowish to greenish-yellow liquid with a warm camphoraceous, thujone-like odor and taste.

$d_{20}^{20}$  0.910–0.930;  $n_D^{20}$  1.4580–1.4740;  $\alpha_D^{20}$   $+2^\circ$  to  $+30^\circ$ ; solubility 1 vol in max. 2 vol 80% ethanol; carbonyl value: 103–288, corresponding to carbonyl compound

content of 28–78%, calculated as thujone; content by GC: 18–43%  $\alpha$ -thujone, 3–8.5%  $\beta$ -thujone, 5.5–13% 1,8-cineole, 3–8.5% camphor [751]. For further constituents see [752–758b].



$\alpha$ -Thujone  
[546-80-5]  
[(-)-thujone]



$\beta$ -Thujone  
[471-15-8]  
[(+)-isothujone]

The oil is used in pharmaceutical preparations and in perfumery to create dry, spicy-herbaceous notes. FCT 1974 (12) p. 987; [8022-56-8], [84082-79-1].

3. *Spanish sage oil* is produced by steam distillation of leaves and twigs of *Salvia lavandulifolia* Vahl growing in Spain in the provinces Granada, Murcia, Almaria, and Jaén. The oil is an almost colorless to pale yellow liquid with the characteristic camphoraceous odor of the leaves.

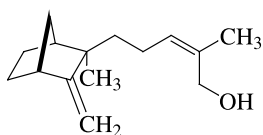
$d_{20}^{20}$  0.913–0.933;  $n_D^{20}$  1.467–1.473;  $\alpha_D^{20}$   $-12^\circ$  to  $0^\circ$  for Jaén oils,  $+16^\circ$  to  $+24^\circ$  for other oils; solubility: 1 vol in 2 vol of 80% ethanol at  $20^\circ\text{C}$ ; ester number: min. 14, max. 57 [759].

Unlike Dalmatian sage oil, Spanish sage oil does not contain  $\alpha$ - or  $\beta$ -thujone; camphor and 1,8-cineole are the major components [760–762a] and are responsible for the odor of the oil, which is used primarily in pharmaceutical preparations and in technical perfumery. FCT 1976 (14) p. 857; [8022-56-8], [95371-15-6].

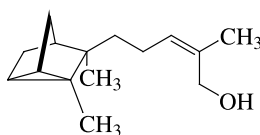
**Sandalwood oil, East Indian** is obtained by steam distillation of the heartwood of *Santalum album* L. (Santalaceae). It is a slightly viscous, almost colorless to yellow liquid with a characteristic, sweet, woody, long-lasting odor.

$d_{20}^{20}$  0.968–0.983;  $n_D^{20}$  1.5030–1.5080;  $\alpha_D^{20}$   $-21^\circ$  to  $-12^\circ$ ; solubility: 1 vol in not more than 5 vol of 70% ethanol at  $20^\circ\text{C}$ ; ester number: max. 10; free alcohol content (calculated as santalol): min. 90% [763].

East Indian sandalwood oil consists almost exclusively of closely related sesquiterpenoids; by far the main constituents are the alcohols  $\alpha$ -santalol [115-71-9], 45–55%, and  $\beta$ -santalol [77-42-9], 18–24%. Mainly responsible for the odor is  $\beta$ -santalol. [261, 764–769].



(-)- $\beta$ -Santalol



(+)- $\alpha$ -Santalol

The trees cultivated for oil production must be at least 30 years old to make oil production profitable. The oil yield, calculated on the amount of wood used for steam distillation, is 4–6.5%. The production in India and Indonesia amounts to ca. 100 t/yr.

East Indian sandalwood oils are used extensively in perfumery as very valuable, stable fixatives. FCT 1974 (12) p. 989; [8006-87-9], [84787-70-2].

### Sassafras oil

Sassafras oil is used as a generic term for commercial essential oils containing high quantities of safrole. They originate from different botanical species. The main use of these oils is the isolation of safrole as the starting material for the production of heliotropin (see p. 136)

1. *Brazilian sassafras oil* is obtained by steam distillation of the roots, trunks, and branches of *Ocotea pretiosa* (Nees) Mez. (Lauraceae) a tree growing wild in South America (Brazil). The oil was formerly called *Ocotea cymbarum* oil due to incorrect botanical naming. It is a yellow to brownish liquid with the characteristic odor of safrole.

$d_{20}^{20}$  1.079–1.098;  $n_D^{20}$  1.5330–1.5370;  $\alpha_D^{20}$   $-2.2^\circ$  to  $-0.8^\circ$ ; solubility: 1 vol in 2 vol of 90% ethanol;  $fp$   $+7.5$  to  $+9.3^\circ\text{C}$  [770].

The main component of the oil is safrole [771], which may make up more than 90% of the oil and determines its freezing point [91770-39-7].

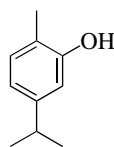
2. *Chinese sassafras oils* are oils or fractions of oils, rich in safrole, that are obtained from different species of the camphor tree (see Camphor Oils) [772].

Worldwide production of sassafras oils exceeds 1500 t/a. FCT 1978 (16) p. 831; [68917-09-9].

**Savory oil** is obtained by steam distillation of the whole dried herb *Satureja hortensis* L. or *S. montana* L. (Lamiaceae). It is a light yellow to dark brown liquid with a spicy odor, reminiscent of thyme or origanum.

$d_{25}^{25}$  0.875–0.954;  $n_D^{20}$  1.4860–1.5050;  $\alpha_D^{20}$   $-5^\circ$  to  $+4^\circ$ ; phenol content: 20–59%; saponification number: max. 6; solubility: 1 vol in 2 vol of 80% ethanol at  $25^\circ\text{C}$ ; solutions in 10 vol of ethanol may be slightly hazy [773].

Several qualities of savory oil exist, depending on the *Satureja* species used. The main cultivation areas are France, Spain, some of the Balkan countries, and some midwestern states of the United States. Characteristic of savory oil is its high content of carvacrol [499-75-2] [774–777a].



Carvacrol

Savory oil is used mainly in the food industry, e.g., for flavoring sauces and soups. FCT 1976 (14) p. 859; [8016-68-0], [84775-98-4], [90106-57-3].

**Spearmint oil**, see Mint oils.

**Spike oil**, see Lavandula products.

**Star anise oil** is obtained by steam distillation of the star-shaped fruits of *Illicium verum* Hook. f. (Illiciaceae), an evergreen tree growing in Vietnam and China. It is a colorless to pale yellow liquid, which solidifies on cooling.

$d_{20}^{20}$  0.979–0.985;  $n_D^{20}$  1.5530–1.5560;  $\alpha_D^{20}$   $-2^\circ$  to  $+2^\circ$ ; solubility: 1 vol in max. 3 vol 90% alcohol;  $fp >15^\circ\text{C}$ ; [778].

The main component of star anise oil, as in anise oil, is *trans*-anethole (86–93%) [779–782b]. Pure anethole can be obtained by rectification (see p. 127). Star anise oil has replaced true anise oil derived from *Pimpinella anisum* in the production of natural anethole.

Star anise oil and its product, anethole, are used primarily in the alcoholic beverage industry (anise liquors), but also for flavoring food and oral care products. FCT 1975 (13) p. 715; [68952-43-2], [84650-59-9].

**Styrax oil** and **styrax resinoid** are obtained from styrax balsam, which is collected from the artificially injured trees, *Liquidamber orientalis* Mill. (Asia Minor) and *L. styraciflua* L. (Central America) (Hamamelidaceae).

*Styrax resinoid* is a light grey to dark grey-brown viscous liquid that is prepared by solvent extraction. It has a sweet balsamic, slightly grass-like odor and is used in perfumery as a fixative.

Steam distillation of the balsam gives *styrax oil*, a light yellow liquid that contains a relatively large amount of cinnamic acid, which partially crystallizes [783]. Styrax oil has a sweet-balsamic odor with a styrene-like top note. It is used in perfumery in flowery compositions, [8024-01-9], [94891-27-7], [94891-28-8].

**Tagetes oil** is produced by steam distillation of the flowering plants *Tagetes minuta* L. (*T. glandulifera* Schrank., Asteraceae). The main producers are in Zimbabwe, South Africa, and India. The oil is a yellow to dark orange liquid with a strong, aromatic-fruity odor. Its main components are *cis*-ocimene, dihydrotagetone, tagetone, and *cis*- and *trans*-ocimenone [784–784b].

It is used in accentuated flowery fragrances and in aroma compositions to achieve fruity effects. FCT 1982 (20) 829; [8016-84-0], [91770-75-1].

**Tarragon oil** (estragon oil) is produced by steam distillation of leaves, stems, and flowers of *Artemisia dracunculus* L. (Asteraceae). It is a pale yellow to amber liquid with a characteristic, spicy, delicate estragon odor reminiscent of liquorice and sweet basil. The following specifications refer to tarragon oil obtained from plants cultivated in southern France and in Piedmont (Italy).

$d_{20}^{20}$  0.918–0.943;  $n_D^{20}$  1.5080–1.5180;  $\alpha_D^{20}$   $+2^\circ$  to  $+6^\circ$ ; acid number: max. 1; saponification number: max. 18; solubility: 1 vol in max. 4 vol of 90% ethanol [785].

Estragole is the main constituent of tarragon oil (68–80%) and primarily determines the sensory properties [786–788].

Worldwide production of tarragon oil only amounts to a few tons per year. It is used mainly in aroma compositions, smaller quantities are employed in perfumery. FCT 1974 (12) p. 706; [8016-88-4], [90131-45-6].

**Tea tree oil** is obtained by steam distillation of leaves and twig tips of *Melaleuca alternifolia* L., and other *Melaleuca* species, which are trees growing in Australia (Myrtaceae). It is a pale to light yellow liquid with an earthy, spicy odor.

$d_{20}^{20}$  0.885–0.906;  $n_D^{20}$  1.4750–1.4820;  $\alpha_D^{20}$  +5° to +15°; solubility: 1 vol in max. 2 vol of 85% ethanol; GC content: cineole max. 15%, 1-terpinen-4-ol min. 30% [789].

The main component of the oil is 1-terpinen-4-ol (up to 40%, or occasionally more) [790–792a].

Tea tree oil is used in perfumery for creating certain nuances and for earthy notes. FCT 1988 (26) 407; [68647-73-4], [85085-48-9].

**Thuja oil**, see Cedar leaf oil.

**Thyme oil** (*Spanish red thyme oil*) is obtained by steam distillation of flowering plants of *T. zygis* L. var. *gracilis* Boissier (Lamiaceae). Thyme oil is a red or reddish liquid with a strong, characteristic, spicy-phenolic odor and a sharp, lasting taste.

$d_{20}^{20}$  0.910–0.937;  $n_D^{20}$  1.4940–1.5040;  $\alpha_D^{20}$  –6° to –1° solubility: 1 vol in max. 3 vol of 80% ethanol; total phenol content: 38–56% [793].

The main constituent of thyme oil is thymol (37–55%) which also determines predominantly the sensory properties of the oil [794–799a].

Thyme shrubs grow in France, Spain, Algeria, and Morocco. Spain is the main producer of the oil. Thyme oil is used mainly for flavoring foods and oral hygiene products, but is also used in perfumery to create spicy, leathery notes. Because of its high phenol content, thyme oil has germicidal and antiseptic properties. FCT 1976 (12) p.1003; [8007-46-3], [85085-75-2].

**Tolu balsam resinoid** is produced by extraction of the balsam of *Myroxylon balsamum* (L.) Harms (Fabaceae). It is a dark orange brown mass with a sweet, resinous, long-lasting odor, reminiscent of hyacinth. An essential oil is also distilled from the balsam.

Tolu balsam resinoid contains a fairly large amount of benzyl and cinnamyl esters of benzoic and cinnamic acid [284a, 800–800b].

Both the resinoid and the balsam are used in perfumery, mainly for their fixative properties. FCT 1976 (14) p. 689; [9000-64-0], [8013-12-5].

**Tonka bean absolute** is prepared by solvent extraction either directly from so-called Tonka beans or via the concrete. Tonka beans are the seeds of fruits from *Dipteryx odorata* (Aubl.) Willd. (Fabaceae).

Tonka bean absolute is a solid or crystalline mass with a sweet, caramel-like odor, reminiscent of coumarin, which is the main constituent of the volatile part of

the absolute [800c]. In perfumery tonka bean absolute is used as a fixative and produces a dry sweetness in men's fragrances. FCT 1974 (12) p. 1005; [8046-22-8], [90028-06-1].

**Tree moss absolute**, see Oakmoss absolute.

**Tuberose absolute** is obtained by solvent extraction, via the concrete, from the blossoms of *Polianthes tuberosa* L. (Agavaceae). The plants are cultivated in Egypt and India. Tuberose absolute was formerly produced in southern France by enfleurage. It is an orange to brown liquid with a sweet-narcotic blossom odor and is used in modern, flowery perfume compositions. Its main constituents are esters of benzoic acid [801, 802], FCT 2000 (38, suppl. 3) p. S231, [8024-05-3], [94334-35-7].

**Turpentine oils** [803, 803a] are used in large quantities by the fragrance industry as starting materials for the manufacture of single fragrance and flavor materials. Turpentine oils are obtained either from balsams or from the wood of various Pinaceae species. They are less valuable as odor materials than the oils obtained from needles, young twigs, and cones (see Pinaceae Needle Oils). Nevertheless, they are used either as such or indirectly as fragrant solvents for perfuming household products.

*Balsam turpentine oil* is obtained from the resins of living trees of suitable *Pinus* species by distillation at atmospheric pressure and temperatures up to 180 °C, or by other fractionation methods, which do not change the terpene composition of the resins. *Wood turpentine oils*, on the other hand, are generally obtained by steam distillation of chopped tree trunks, dead wood, or of resin extracted from this wood. *Sulfate turpentine oil* is produced as waste in the manufacture of cellulose by the sulfate process and is also a wood turpentine. *Pine oil* is another wood turpentine oil that is obtained by dry distillation of suitable pine and fir trees, followed by fractionation. However, the term *pine oil* is nowadays used for a product which is manufactured by hydration of turpentine oil ( $\alpha$ -pinene). The resulting product is a mixture of monoterpenes containing  $\alpha$ -terpineol as the main component. In addition to many other technical purposes, it is used to a large extent in cheap perfumes for technical applications.

**Table 7.** Specifications of turpentine oils

Parameter	Type of turpentine oil			
	Balsam	Wood, steam distilled	Sulfate	Wood, dry distilled
$d_4^{20}$	0.855–0.870	0.855–0.870	0.860–0.870	0.850–0.865
$n_D^{20}$	1.465–1.478	1.465–1.478	1.465–1.478	1.463–1.483
Distillate up to <i>bp</i> 170 °C, %	90	90	90	60
Evaporation residue, %	2.5	2.5	2.5	2.5
Acid number	1	1	1	1



Balsam and wood turpentine oils are colorless liquids with a mild, characteristic odor. Oils obtained by dry distillation often also have a phenolic note. The specifications of turpentine oils are listed in Table 7 [804].

Worldwide production of turpentine oils was ca. 280 000 t in 1990, of which approximately one third was produced in the United States and Canada as sulfate turpentine oil. Other major producers are Russia, China, and Scandinavia.

The main components of all turpentine oils are terpene hydrocarbons. The balsam and sulfate turpentine oils produced in the Southeast of the United States contain mainly  $\alpha$ - and  $\beta$ -pinene (60–70% and 20–25%, respectively); *P. palustris* Mill. (long leaf pine) gives the (+)-enantiomers and *P. caribea* Morelet (slash pine) gives the (–)-enantiomers. The remaining constituents are *p*-menthadienes, oxygen-containing terpenoids, and anethole. In contrast with the Scandinavian and Russian turpentine oils, the American oils contain very little 3-carene or camphene. Large amounts of the American oils are separated by fractional distillation into their components, which are used as starting materials in the manufacture of fragrance and flavor materials. European turpentine oils originate mainly from Portugal, where distillation of *P. pinaster* Soland resin or wood gives a turpentine oil that consists of 71–85% (–)- $\alpha$ -pinene and 11–20% (–)- $\beta$ -pinene:  $d_{20}^{20}$  0.860–0.872;  $n_D^{20}$  1.4650–1.4750;  $\alpha_D^{20}$   $-28^\circ$  to  $-40^\circ$ ; acid value: max. 1 [805].

**Valerian oil** is obtained by steam distillation of well-dried ground roots of *Valeriana officinalis* L. (Valerianaceae). It is a yellow-green to yellow-brown liquid with an extremely strong, characteristic, penetrating odor. The oil becomes dark and viscous on aging or on exposure to air.

$d_{25}^{25}$  0.942–0.984;  $n_D^{20}$  1.4860–1.5025;  $\alpha_D^{20}$   $-28^\circ$  to  $-2^\circ$ ; acid number: 5–50; saponification number: 30–107; solubility: 1 vol in 0.5–2.5 vol of 90% ethanol at 25 °C, solutions are clear to opalescent when up to 10 vol of ethanol is added [806].

The main component of the oil is (–)-bornyl acetate, but it also contains other bornyl esters (e.g., bornyl isovalerate), terpene and sesquiterpene hydrocarbons, as well as free isovaleric acid, which contributes strongly to the odor of the oil [807–807b].

Valerian oil is produced in limited quantities and is used in flavor and fragrance compositions only in very low dosages to create certain effects, [8008-88-6].

**Vanilla extract** (vanilla oleoresin) is produced by extraction of the pods of *Vanilla planifolia* G. Jacks. or *V. tahitensis* Moore (Orchidaceae) with a polar solvent (e.g., methanol, ethanol, or acetone, which may also contain water). The composition of the extract depends on the type and amount of solvent used. Generally, the percentage of vanillin in the extract (yield 25–30%) is 3–4 times higher than that in the pods [807c, 807d].

Vanillin and phenol derivatives are primarily responsible for its aroma [808–811d]. The main producers of *V. planifolia* pods are Madagascar, the Comoro Islands, Réunion (Bourbon), Mexico, and some Pacific Islands; *V. tahitensis* pods are grown mainly in Tahiti.

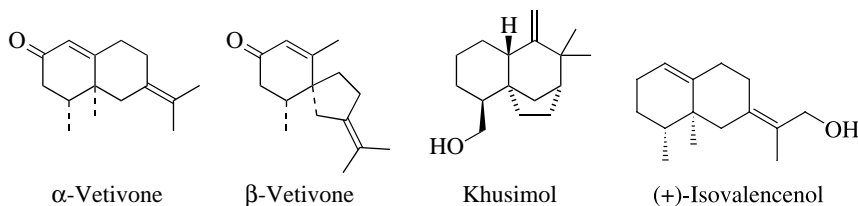
Vanilla extracts are used extensively in chocolate and baked products, but even more so in ice cream. FCT 1982 (20) p. 849; [8023-78-7].

**Vetiver oil** is produced by steam distillation of the roots of the grass *Vetiveria zizanioides* (L.) Nash (Poaceae), which grows wild or is cultivated in many tropical and subtropical countries. The oil is a brown to reddish-brown, viscous liquid with a characteristic precious-wood and rootlike, long-lasting odor. The specifications given in Table 8 refer to oil qualities produced in Réunion, Haiti, Indonesia (Java), and China.

**Table 8.** Specifications of Vetiver oil [812]

Parameter	Origin			
	Réunion	Haiti	Indonesia	China
$d_{20}^{20}$	0.990–1.015	0.980–1.001	0.980–1.018	0.985–1.020
$n_D^{20}$	1.522–1.530	1.516–1.527	1.520–1.530	1.520–1.528
$\alpha_D^{20}$	+19°–+30°	+22°–+46°	+17°–+32°	+17°–+46°
Acid value	4.5–35	1–14	10–35	10–70
Ester value	5–30	5–35	5–26	10–60
Carbonyl contents, calculated as $\alpha$ -vetivone	17–26%	9–23%	–	–

The tenacity of the highly complex vetiver oil is attributed to its high sesquiterpene content. The ketones  $\alpha$ -vetivone [15764-04-2] and  $\beta$ -vetivone [18444-79-6], which usually form more than 10% of the oil, as well as khusimol [16223-63-5] (ca. 15%) and isovalencenol [22387-74-2] are the main constituents.



The oil contains a considerable number of bi- and tricyclic primary, secondary, and tertiary sesquiterpene alcohols called vetiverols or vetivenols [261, 813–817f]. These alcohols, as well as their acetates, are valuable fragrance materials. Since several varieties of vetiver grass exist and since fresh as well as air-dried roots are distilled under conditions that vary with the producer, the quality of the commercial oils differs considerably. Oil yields are up to 3%. The main producer is Indonesia (ca. 100 t/yr), followed by Haiti and Réunion.

Vetiver oil is used in fine fragrances for long-lasting precious-wood notes. It is also used as starting material for vetiveryl acetate (see p. 74). FCT 1974 (12) p. 1013; [8016-94-4], [84238-29-9].

**Violet leaf absolute** is obtained by solvent extraction, via the concrete, from the leaves of *Viola odorata* L. (Violaceae), which is grown predominantly in southern France.

The absolute is a dark green to brown liquid with a strong, green odor. The main constituent of the volatile fraction is 2-*trans*-6-*cis*-nonadienal [557-48-2] (violet leaf aldehyde) [818, 819].

Violet leaf absolute is used frequently in perfume compositions, but only in very low concentration because of its intense odor. FCT 1976 (14) p. 893; [8024-08-6], [90147-36-7].

**Ylang-ylang and cananga oils** are essential oils that are obtained from two subspecies of the cananga tree.

1. *Ylang-ylang oils* are obtained by steam distillation of freshly picked blossoms of *Cananga odorata* (DC.) Hook. f. et Thoms. subsp. *genuina* (Annonaceae). These cananga trees normally grow to a height of 20 m but are pruned to a height of 1.60–1.80 m and flower throughout the year. The oil is produced mainly in Madagascar and the Comoro Islands. Four fractions are collected at progressively longer distillation times and are known as ‘Extra,’ ‘I,’ ‘II,’ and ‘III.’ Occasionally, a first fraction called ‘Extra superior’ is collected. They are all pale to dark yellow liquids with a characteristic floral, spicy, balsamic odor. The first fractions are the most valuable; they have a higher density and a higher saponification number. Specifications of fractions obtained from Comoro Islands and Madagascar oils are given in Table 9 [820].

The compositions of the various oil fractions depend on the duration of distillation. The first fraction, ylang-ylang oil Extra, has the highest content of strongly

**Table 9.** Specifications of ylang-ylang oils from the Comoro Islands (C) and Madagascar (M)

Parameter		Extra superior	Ylang-ylang fractions			
			Extra	I	II	III
$d_{20}^{20}$	(C)	0.970–0.990	0.955–0.976	0.938–0.960	0.925–0.945	0.906–0.925
	(M)		0.950–0.965	0.933–0.949	0.922–0.942	0.906–0.925
$n_D^{20}$	(C)	1.497–1.505	1.4980–1.5060	1.5010–1.5090	1.5020–1.5110	1.5030–1.5130
	(M)		1.4930–1.5090	1.4950–1.5100	1.4960–1.5110	1.5020–1.5130
$\alpha_D^{20}$	(C)	–33° to –40°	–40° to –20°	–46° to –25°	–35° to –72°	–72° to –45°
	(M)		–42° to –20°	–46° to –24°	–58° to –30°	–70° to –45°
Ester value	(C)	160–200	140–185	140–160	75–115	45–75
	(M)		125–160	90–125	65–95	40–70
Acid value	(C/M)	max. 2	max. 2	max. 2	max. 2	max. 2

odoriferous constituents such as *p*-cresyl methyl ether (15–16%), methyl benzoate (4–9%), (–)-linalool (7–24%), benzyl acetate (5.5–17.5%), and geranyl acetate (2.5–14%). The other fractions contain increasing amounts of sesquiterpenes (>70% in ylang-ylang III). Components such as *p*-cresol, eugenol, and isoeugenol are important for the odor, although they are present only in low concentration [821–824a].

Ylang-ylang Extra and I are used mostly in fine fragrances; ylang-ylang II and III are employed in soap perfumes. FCT 1974 (12) p. 1015; [8006-81-3], [83863-30-3].

2. *Cananga oil* is produced by steam distillation of the flowers of *Cananga odorata* (DC) Hook. f. et Thoms. subsp. *macrophylla*. The yield, based on the weight of the flowers, is ca. 1%: The oil is a light to dark yellow liquid with a characteristic, floral, slightly woody odor.

$d_{20}^{20}$  0.906–0.923;  $n_D^{20}$  1.4950–1.5030;  $\alpha_D^{20}$   $-30^\circ$  to  $-15^\circ$ ; solubility: 1 vol in not more than 1 vol of 95% ethanol at 20 °C; acid number: max. 2; ester number: 13–35 [824b, 825].

The qualitative composition of cananga oil resembles that of ylang-ylang III oil but is distinguished by its higher caryophyllene (30–40%) content.

Cananga oil originates almost exclusively in Java, where the flowers are collected throughout the year; annual production is ca. 50 t. The oil is used mainly in perfuming soaps where it is more stable due to its lower ester content in comparison to ylang-ylang oils. FCT 1973 (11) p. 1049; [68606-83-7], [93686-30-7].