Flavors and Fragrances

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1. Introduction

1.1. The Chemical Senses

The sensations “taste” and “odor” are part of our five senses. Whereas seeing, hearing, and feeling react to a physical input (visible light waves, sound waves, and temperature and pressure, respectively) the two so-called chemical senses are stimulated by direct interactions with defined chemicals. The chemical senses are regarded phylogenetically as the oldest senses, i.e., the earliest living species communicated by emitting and receiving chemical signals in their aqueous environment. This communication system was refined when the first species left water to live on land and had to rely on molecules that were transported in the surrounding atmosphere. These molecules had to be volatile and were detected by the odor receptors which consequently developed to a much higher sophistication than the taste receptors. The currently accepted doctrine is that only four basic taste impressions (salty, sweet, sour, and bitter [1]) exist, whereas the types of odor impressions are unlimited. Newer results, however, indicate that the limitation to only four taste impressions is too narrow and that more complex stimulations to the sense of taste do exist [2].

According to E. L. Wick, the term flavor as sensory impression results from the simultaneous stimulation of the two chemical senses, odor and taste [3], so the description of volatile materials will cover both flavor and fragrance materials. As mentioned above, the sense of odor developed to a much higher degree than the sense of taste and in some highly developed mammals (e.g., all canine species) became the most important sense of all. Even in humans, where the sense of sight has become predominant, odor influences considerably the behavior, consciously and subconsciously, it controls for example intake of food and emotions and according to Proust helps in the “search for the past”.

1.2. Definition

Flavor and fragrance compounds are molecules that stimulate the human chemical senses. The physiological importance of compounds that elicit a sensory reaction in other living beings apart from humans will not be treated in the context of this paper.

In the following only compounds that stimulate the sense of smell for flavors and fragrances are discussed. These compounds, that are detected in the upper end of the nose have to have a certain volatility to be transported with the aspired air stream to the receptors. It is generally assumed that compounds with a molecular mass > 300 are not volatile enough to fulfill these conditions. Even if many compounds are used both as flavor and fragrance ingredients, some distinctions exist: in general, flavor compounds consist of molecules that occur naturally in edible materials whereas many fragrance compounds are not produced in nature (see Section 1.5).

1.3. History

The history of odor is as old as the history of mankind. Incense was already offered to the God of the Sea in Ninive, in 5000 B.C. The Gilgamesch Epos, which is considered to be the oldest written document about the genesis of mankind, mentions the use of cedarwood as source of odorants already in 3200 B.C. Sandalwood is described as part of the gifts that the Queen of Sheba gave to Salomon. Greeks and Romans used oil extracts of herbs and flowers as therapeutic agents and for their sensory pleasures. During the middle ages, no real progress in preparing and using odorant materials was reported, apart from the discovery of making concentrated alcohol by the Arabs [4]. Real progress in preparation of odorant compounds and mixtures started nearly simultaneously with the beginning of organic chemistry which is marked by WÖHLER's synthesis of urea [5].

Already in 1830, WÖHLER and LIEBIG synthesized benzaldehyde, which was subsequently identified as the main aroma compound in bitter almonds by ROBIQUET and BOUTRON-CHARLARD in 1932. Worthy of mention is the synthesis of vanillin by REIMER and THIEMANN in 1876, which led to the foundation of the German flavor and fragrance industry.

Analysis of food flavors proved to be cumbersome due to the very low natural abundance of these molecules and the analytical methods available at that time. By 1960, about 450 molecules had been identified to occur in the volatile part of edible materials.

The real breakthrough in knowledge about the chemical nature of odorants started with the invention and application of gas chromatography by JAMES and MARTIN [6]. This analytical and also preparative separation method is the technique of choice for volatile materials such as odorants. The value of gas chromatography was quickly recognized and this technique has undergone enormous progress, e.g., through the introduction of capillary columns [7] and coupling of this separation tool to identification systems such as mass spectrometry and infrared spectroscopy. Extensive use of these and other analytical procedures have since allowed the identification of about 8000 volatile compounds in food materials [8]. Parallel to investigations into foods this method was also used to analyze many odorant extracts from materials such as flowers, leaves, and other natural sources used historically as fragrance materials. Development in synthetic procedures allowed economical syntheses of these identified compounds which can be used as such or as molecular models (lead compounds) for the synthesis of other not naturally occurring odorants.

1.4. Odor Descriptors, Odor Thresholds, Odor Value

Odors can be measured and described qualitatively and quantitatively, but contrary to the stimuli that elicit our other senses (i.e., sight, hearing, touch, temperature) no physical analytical method exist for odor measurement.

1.4.1. Qualitative Measurements

Qualitative measurements are restricted to verbal descriptions of the odor impression. First approaches to classify odors by their descriptors were initiated by HARPER, BATE SMITH, and LAND [9]. Their general conclusion is that the more complex the odor perception the more impossible becomes an exact odor description. A more detailed analysis into description of odors and thus their qualitative measurement has been initiated by KASTNER [10], who distinguishes three main descriptor categories, i.e., general descriptive terms, special descriptive terms, and precise descriptive terms, in which the first one refers to adjectives like attractive, good, bad, stinky, rough, etc.; the second category comprises explications like green, herbaceous, flowery, earthy; and the third one uses terms like sulfury, ambery, sweaty, etc.

1.4.2. Quantitative Measurements

1.4.2.1. Odor Threshold

Odor strength can be described by its odor threshold. Generally, two different thresholds are used: (1) the *detection threshold*, which is defined as the lowest detectable concentration of a compound versus the pure solvent and (2) the *recognition threshold*, which is the lowest concentration that allows an identification of the odor impression of a compound. Both values are strongly dependent on the solvent system [11].

Thresholds measured in air are generally much lower than those measured in water. A compilation of about 2000 thresholds in water and in air document the enormous differences that can occur [12].

Thresholds in air can be measured with commercial olfactometers or by standardized smelling from a gas chromatograph as described in [13], whereas thresholds in water and other liquid solvents are determined by the so-called multiple pair test [14], in which the panel members have to decide which of the bottles contain the compound in question. The concentrations are generally presented in a geometrical line. The threshold is defined as the concentration that is correctly identified by 50 % of a panel consisting of a statistically relevant number of testers [15].

1.4.2.2. Odor Value

The quantitative contribution of a compound to the total odor impression can be described by its odor value. This term has been introduced by ROTHE et al. [16] and is defined as the concentration of a compound in a given mixture divided by the odor threshold of this compound, i.e., the higher the concentration and the lower the threshold the more the compound contributes to the overall odor impression.

1.5. Regulations and Labeling Requirements

1.5.1. Flavors

Different legislative situations for definition and labeling of flavor active materials exist: The Americas base their systems on the United States Code of Federal Regulations, specifically CFR 101.22, which describes as *artificial flavor* or *artificial flavoring* any substance that imparts flavor, which is not derived from a spice, fruit or fruit juice, vegetable or vegetable juice, edible yeast, herb, bark, bud, root, leaf or similar plant material, meat, fish, poultry, eggs, dairy products, or fermentation products thereof [16]. *Natural flavor* or *natural flavoring* means the essential oil, oleoresin, essence or extractive, protein hydrolysate, distillate, or any product of roasting, heating or enzymolysis, which contains the flavoring constituents derived from a spice, fruit or fruit juice, vegetable or vegetable juice, edible yeast, herb, bark, bud, root, leaf or similar plant material, meat, seafood, poultry, eggs, dairy products, or fermentation products thereof, whose significant function in food is flavoring rather than nutritional [17]. In Europe, these regulations are defined in the "EU Flavouring Directive 88/388 EEC". The term flavoring is restricted to flavoring substances, flavoring preparations, process flavorings, smoke flavorings, or mixtures thereof. A flavoring substance is a defined chemical substance with flavoring properties which is obtained: (i) by appropriate physical processes (including distillation and solvent extraction) or enzymatic or microbiological processes from material of vegetable or animal origin either in the raw state or after processing for human consumption by traditional food-preparation processes (including drying, torrefaction, and fermentation), (ii) by chemical synthesis or isolated by chemical processes and which is chemically identical to a substance naturally present in material of vegetable or animal origin as described in (i), (iii) by chemical synthesis but which is not chemically identical to a substance naturally present in material of vegetable or animal origin. "Process flavoring" means a product which is obtained according to good manufacturing practices by heating to a temperature not exceeding 180 °C for a period not exceeding 15 min from a mixture of ingredients not necessarily themselves having flavoring properties in which at least one contains nitrogen (amino) and another is a reducing sugar. "Smoke flavoring" means a smoke extract used in traditional foodstuffs smoking processes [18].

1.5.2. Fragrances

For fragrances no differentiation is made between natural, nature-identical, and artificial substances. Many compounds used in fragrances are components of natural origin, e.g., constituents of essential oils, resins, and, to a much lesser extent, of animal secretions. In addition many chemicals are used in fragrances, whose molecular structures are not found to occur in nature but their fragrance characteristics mimic those of natural products. For use in fragrance components, these chemicals have to comply with the national legal requirements. In addition they have to pass the so-called IFRA tests for (see Chap. 6):

Acute toxicity
Skin irritation
Skin sensitization
Phototoxicity and photosensitization

For those products (e.g., fragrance chemicals, essential oils, resinoids) for which IFRA has edited use recommendations this is mentioned by 'IFRA recommendation'. If IFRA suggests a maximum use level then one will find the remark 'limiting IFRA recommendation'. In those cases one may refer to the IFRA publications for further information.

2. Single Fragrance and Flavor Compounds

Fragrance and flavor compounds of commercial interest are arranged according to the Beilstein system of functional groups, not according to their organoleptic properties, since relationships between odor and structure are difficult to establish. However, the Beilstein system has been abandoned in a few cases for practical reasons.

In each class of parent compounds, hydrocarbons and oxygen-containing compounds are described first. Nitrogen- and sulfur-containing compounds are treated at the end of each of these sections under the heading Miscellaneous Compounds. Aliphatic compounds are discussed in Section 2.1, followed by the terpenes. The terpenes constitute a very important group of compounds and are subdivided into acyclic terpenes (Section 2.2) and cyclic terpenes (Section 2.3). Nonterpenoid cycloaliphatics are described in Section 2.4. Aromatic compounds are discussed in Section 2.5. Phenols and phenol derivatives are described under a separate heading (Section 2.6) on account of their biogenetic and odor relationships. Methylenedioxyphenyl derivatives are also described under this heading for the same reason even though, systematically, they belong to the oxygen-containing heterocycles (Section 2.7). Compounds that are only produced in small quantities, but which are important due to their high odor intensity, are mentioned but not described in detail.

2.1. Aliphatic Compounds

The acyclic terpenes are discussed separately in Section 2.2. Some of the cycloaliphatic fragrance and flavor compounds are structurally related to the cyclic terpenes and are, therefore, discussed in Section 2.4 after the cyclic terpenes.

2.1.1. Hydrocarbons

Saturated and unsaturated aliphatic hydrocarbons with straight as well as branched chains occur abundantly in natural foodstuffs, but they contribute to the odor and taste only to a limited extent. The highly unsaturated hydrocarbons 1,3-*trans*-5-*cis*-undecatriene [*51447-08-6*] and 1,3-*trans*-5-*trans*-undecatriene [*19883-29-5*], however, contribute to the odor of galbanum oil [19].

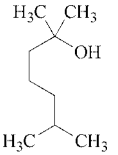
2.1.2. Alcohols (→ Alcohols, Aliphatic; → Fatty Alcohols)

Free and esterified saturated primary alcohols occur widely in nature, e.g., in fruit. Since their odor is relatively weak, their use as components in fragrance compositions is limited. Their use in aroma compositions, especially for fruit flavors, is by far more important (e.g., straight-chain $C_4 - C_{10}$ alcohols, isoamyl alcohol). Unsaturated alcohols are most important (e.g., leaf alcohol with its intensely green odor) and may impart characteristic notes to compositions.

Naturally occurring fatty alcohols used in the fragrance industry are produced principally by reduction of the methyl esters of the corresponding carboxylic acids, which are obtained by transesterification of natural fats and oils with methanol. Industrial reduction processes include catalytic hydrogenation in the presence of copper–chromium oxide catalysts (Adkins catalysts) and reduction with sodium (Bouveault–Blanc reduction); for details, see → Alcohols, Aliphatic, Chap. 2.3.3., → Fatty Alcohols, Chap. 2.3., → Fatty Alcohols, Chap. 2.4. Unsaturated alcohols can also be prepared by the latter method. Alcohols are starting materials for aldehydes and esters.

3-Octanol [*589-98-0*], $CH_3(CH_2)_4CH(OH)CH_2CH_3$, $C_8H_{18}O$, M_r 130.23, *bp* (97.6 kPa) 176 – 176.5 °C, d_4^{20} 0.8264, n_D^{20} 1.4252, may occur in its optically active form. It is a colorless liquid that has a mushroomy-earthy odor and occurs in mushrooms. 3-Octanol can be obtained by hydrogenation of 3-octanone; it is used in lavender compositions and for imparting mushroom-like odors.

2,6-Dimethyl-2-heptanol [*13254-34-7*], $C_9H_{20}O$, M_r 144.26, *bp* (101.3 kPa) 170 – 172 °C, d_4^{20} 0.8085, n_D^{20} 1.4248, which has not yet been found in nature, is a colorless liquid with a delicate, flowery odor reminiscent of fresias. It is synthesized from 2-methyl-2-hepten-6-one and methylmagnesium chloride by a Grignard reaction, followed by hydrogenation, and is used in flowery perfume compositions.



Trade Names. Dimetol (Givaudan Roure), Freesiol (Haarmann & Reimer).

***trans*-2-Hexen-1-ol** [*928-95-0*], $CH_3CH_2CH_2CH{=}CHCH_2OH$, $C_6H_{12}O$, M_r 100.16, *bp* (101.3 kPa) 155 °C, d_4^{20} 0.8459, n_D^{20} 1.4382, occurs in many fruits and has a fruity, green odor, which is sweeter than that of the isomeric *cis*-3-hexen-1-ol and is, therefore, preferred in aroma compositions.

***cis*-3-Hexen-1-ol** [*928-96-1*], leaf alcohol, $CH_3CH_2CH{=}CHCH_2CH_2OH$, $C_6H_{12}O$, M_r 100.16, *bp* (101.3 kPa) 156 – 157 °C, d_4^{20} 0.8495, n_D^{20} 1.4384, is a colorless liquid with the characteristic odor of freshly cut grass. *Robinia pseudacacia* and mulberry leaf oil contain up to 50 % leaf alcohol, and green tea up to 30 %. Small quantities occur in the green parts of nearly all plants.

A stereospecific synthesis for *cis*-3-hexen-1-ol starts with the ethylation of sodium acetylide to 1-butyne, which is reacted with ethylene oxide to give 3-hexyn-1-ol. Selective hydrogenation of the triple bond in the presence of palladium catalysts yields *cis*-3-hexen-1-ol. Leaf alcohol is used to obtain natural green top notes in perfumes and flavors. In addition, it is the starting material for the synthesis of 2-*trans*-6-*cis*-nonadien-1-ol and 2-*trans*-6-*cis*-nonadien-1-al.

1-Octen-3-ol [*3391-86-4*], $CH_3(CH_2)_4CH(OH)CH{=}CH_2$, $C_8H_{16}O$, M_r 128.21, *bp* (94.6 kPa) 175 – 175.2 °C, d_4^{20} 0.8383, n_D^{20} 1.4378, may occur in the optically active form. It is found, for example, in lavender oil and is a steam-volatile component of mushrooms. 1-Octen-3-ol is a liquid with an intense mushroom, forest-earthy odor that can be prepared by a Grignard reaction from vinylmagnesium bromide and hexanal. It is used in lavender compositions and in mushroom aromas.
Trade Name. Matsutake alcohol (Takasago).

9-Decen-1-ol [*13019-22-2*], $CH_2{=}CH(CH_2)_6CH_2OH$, $C_9H_{18}O$, M_r 142.24, *bp* (270 Pa) 85 – 86 °C, n_D^{20} 1.4480, has been identified as a trace constituent of cognac. It is a colorless liquid with a fresh, dewy, rose note that can be prepared by partial dehydration of 1,10-decanediol. It is used in rosy-floral soap perfumes.
Trade Name. Rosalva (IFF).

10-Undecen-1-ol [*112-43-6*], $CH_2{=}CH(CH_2)_8CH_2OH$, $C_{11}H_{22}O$, M_r 170.29, *bp* (2.1 kPa) 133 °C, d_4^{20} 0.8460, n_D^{20} 1.4500, has not yet been found in nature and is a colorless liquid with a fatty-green, slightly citrus-like odor. It can be synthesized from 10-undecylenic acid and is used to give flower perfumes a fresh note.

2-*trans*-6-*cis*-Nonadien-1-ol [*28069-72-9*], $CH_3CH_2CH{=}CHCH_2CH_2CH{=}CHCH_2OH$, $C_9H_{16}O$, violet leaf alcohol, M_r 140.22, *bp* (1.5 kPa) 96 – 100 °C, d_4^{10} 0.8622, n_D^{20} 1.4740, occurs, for example, in cucumber oil, violet leaf oil, and violet blossom oil. It is a colorless liquid with an intense, heavy-fatty, green odor, reminiscent of violet leaves. The starting material for the synthesis of 2-*trans*-6-*cis*-nonadien-1-ol is *cis*-3-hexen-1-ol, which is converted via its halide into the corresponding Grignard reagent. The Grignard reagent is reacted with acrolein to give 1,6-nonadien-3-ol, which is converted into 2-*trans*-6-*cis*-nonadien-1-ol by allylic rearrangement.

Nonadienol is a powerful fragrance substance. It is used in fine fragrances to create refined violet odors and to impart interesting notes to other blossom compositions. In aroma compositions it is used for fresh-green cucumber notes.

2.1.3. Aldehydes and Acetals

(→ Aldehydes, Aliphatic and Araliphatic)

Aliphatic aldehydes are among the most important components used in perfumery. Although the lower fatty aldehydes $C_2 - C_7$ occur widely in nature, they are – with the exception of hexanal – seldom used in fragrance compositions. The lower aldehydes (e.g., acetaldehyde, isobutyraldehyde, isovaleraldehyde, and 2-methylbutyraldehyde) impart fruity and roast characters to flavor compositions. Fatty aldehydes C_8–C_{13}, however, are used, singly or in combination, in nearly all perfume types and also in aromas. Their odor becomes weaker with increasing molecular mass, so that aldehydes $> C_{13}$ are not important as perfume ingredients.

In addition to the straight-chain saturated aldehydes, a number of branched-chain and unsaturated aliphatic aldehydes are important as fragrance and flavoring materials. The double unsaturated 2-*trans*-6-*cis*-nonadienal [*557-48-2*], " violet leaf aldehyde" (the dominant component of cucumber aroma), is one of the most potent fragrance and flavoring substances; it is, therefore, only used in very small amounts.

Acetals derived from aliphatic aldehydes have odor characteristics that resemble those of the aldehydes but are less pronounced. These acetals contribute to the aroma of alcoholic beverages, but can rarely be used in flavoring compositions because they are not sufficiently stable. Since they are resistant to alkali, a number of them (e.g., heptanal dimethyl acetal and octanal dimethyl acetal) are occasionally incorporated into soap perfumes.

Fatty aldehydes are generally produced by dehydrogenation of alcohols in the presence of suitable catalysts (see → Aldehydes, Aliphatic and Araliphatic, Chap. 2.3.). The alcohols are often cheap and available in good purity. Aldehyde synthesis via the oxo process is less suitable since the resultant products are often not pure enough for flavor and perfume purposes. Specific syntheses for the branched-chain and unsaturated aldehydes that are important in perfumery and flavoring techniques are described under the individual compounds.

Hexanal [*66-25-1*], caproaldehyde, $CH_3(CH_2)_4CHO$, $C_6H_{12}O$, M_r 100.16, *bp* (101.3 kPa) 128 °C, d_4^{20} 0.8139, n_D^{20} 1.4039, occurs, for example, in apple and strawberry aromas as well as in orange and lemon oil. It is a colorless liquid with a fatty-green odor and in low concentration is reminiscent of unripe fruit.

Hexanal is used in fruit flavors and, when highly diluted, in perfumery for obtaining fruity notes.

Octanal [*124-13-0*], caprylaldehyde, $CH_3(CH_2)_6CHO$, $C_8H_{16}O$, M_r 128.21, *bp* (101.3 kPa) 171 °C, d_4^{20} 0.8211, n_D^{20} 1.4217, occurs in several citrus oils, e.g., orange oil. It is a colorless liquid with a pungent odor, which becomes citrus-like on dilution. Octanal is used in perfumery in low concentrations, in eaux de cologne, and in artificial citrus oils.

Nonanal [*124-19-6*], pelargonaldehyde, $CH_3(CH_2)_7CHO$, $C_9H_{18}O$, M_r 142.24, *bp* (101.3 kPa) 190 – 192 °C, d_4^{20} 0.8264, n_D^{20} 1.4273, occurs in citrus and rose oils. It is a colorless liquid with a fatty-roselike odor and is used in floral compositions, particularly those with rose characteristics.

Decanal [*112-31-2*], capraldehyde, caprinaldehyde, $CH_3(CH_2)_8CHO$, $C_{10}H_{20}O$, M_r 156.27, *bp* (101.3 kPa) 208 – 209 °C, d_4^{20} 0.8259, n_D^{20} 1.4287, is a component of many essential oils (e.g., neroli oil) and various citrus peel oils. It is a colorless liquid with a strong odor, reminiscent of orange peel, that changes to a fresh citrus odor when diluted. Decanal is used in low concentrations in blossom fragrances (especially to create citrus nuances) and in the production of artificial citrus oils.

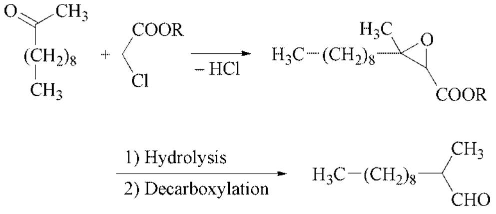
Undecanal [*112-44-7*], $CH_3(CH_2)_9CHO$, $C_{11}H_{22}O$, M_r 170.29, *bp* (2.4 kPa) 117 °C, d_4^{20} 0.8250, n_D^{20} 1.4325, occurs in citrus oils. It is a colorless liquid with a flowery-waxy odor that has aspects of freshness. Undecanal is the prototype of the perfumery aldehydes and is widely used in perfume compositions for imparting an “aldehydic note”.

Dodecanal [*112-54-9*], lauraldehyde, lauric aldehyde, $CH_3(CH_2)_{10}CHO$, $C_{12}H_{24}O$, M_r 184.32, *bp* (13.3 kPa) 185 °C, d_4^{20} 0.8350, n_D^{20} 1.4350, is a colorless liquid with a waxy odor; in high dilution it is reminiscent of violets. Dodecanal occurs in several citrus oils and has been found in small amounts in essential oils obtained from several *Pinus* species. It is used in perfumery in conifer fragrances with fatty-waxy notes, but also in many other odor types. It is added to aroma compositions to obtain citrus notes.

Tridecanal [*10486-19-8*], $CH_3(CH_2)_{11}CHO$, $C_{13}H_{26}O$, M_r 198.34, *bp* (1.3 kPa) 128 °C, d_4^{20} 0.8358, n_D^{18} 1.4384, occurs in lemon oil and has been identified as a volatile constituent of cucumber. It is a colorless liquid having a fatty-waxy, slightly citrus-like odor. Addition of tridecanal to fragrance compositions imparts fresh nuances in the top note as well as in the dry out.

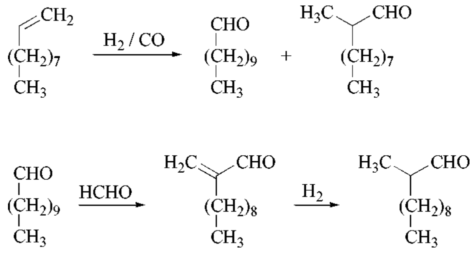
2-Methyldecanal [*19009-56-4*], methyloctylacetaldehyde, $CH_3(CH_2)_7CH(CH_3)CHO$, $C_{11}H_{22}O$, M_r 170.29, *bp* (98.8 kPa) 119 – 120 °C, d_4^{20} 0.8946, n_D^{20} 1.4205, is not reported to have been found in nature. It is a colorless liquid with an aldehydic, citrus-peel-like, waxy-green odor. 2-Methyldecanal is obtained as a byproduct in the manufacture of 2-methylundecanal by hydroformylation of 1-decene. It is used in perfumery to refresh green and citrus nuances.

2-Methylundecanal [*110-41-8*], methylnonylacetaldehyde, $CH_3(CH_2)_8CH(CH_3)CHO$, $C_{12}H_{24}O$, M_r 184.32, *bp* (1.3 kPa) 114 °C, d_4^{20} 0.8303, n_D^{20} 1.4321, has not yet been found in nature. It is a colorless liquid, with an odor markedly different from that of the isomeric dodecanal. It has a fatty odor with incense and ambergris notes.



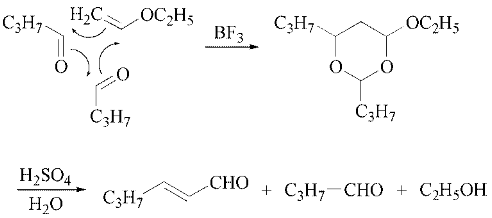
2-Methylundecanal is produced by two routes:

1) Methyl nonyl ketone is converted into its glycidate by reaction with an alkyl chloroacetate. Saponification of the glycidate, followed by decarboxylation, yields 2-methylundecanal.
2) The second synthesis is based on the conversion of undecanal into 2-methyleneundecanal by reaction with formaldehyde in the presence of catalytic amounts of amines [20]. Hydrogenation of 2-methyleneundecanal yields methylnonylacetaldehyde. A convenient process starts from 1-decene: hydroformylation gives a mixture consisting mainly of undecanal and 2-methyldecanal. Reaction of the crude product with formaldehyde in the presence of dibutylamine yields a mixture containing over 50 % 2-methyleneundecanal. After hydrogenation of the double bond, pure 2-methylundecanal is separated from byproducts by fractional distillation [21].



In comparison with other fatty aldehydes, 2-methylundecanal is used in perfumery in rather large amounts to impart conifer notes, particularly fir impressions, but frequently also in phantasy compositions.

***trans*-2-Hexenal** [*6728-26-3*], leaf aldehyde, $CH_3CH_2CH_2CH{=}CHCHO$, $C_6H_{10}O$, M_r 98.14, *bp* (101.3 kPa) 146 – 147 °C, d_4^{20} 0.8491, n_D^{20} 1.4480, is the simplest straight-chain unsaturated aldehyde of interest for perfumes and flavors. It occurs in essential oils obtained from green leaves of many plants. *trans*-2-Hexenal is a colorless, sharp, herbal-green smelling liquid with a slight acrolein-like pungency. Upon dilution, however, it smells pleasantly green and apple-like. The aldehyde can be synthesized by reacting butanal with vinyl ethyl ether in the presence of boron trifluoride, followed by hydrolysis of the reaction product with dilute sulfuric acid [22].



trans-2-Hexenal has an intense odor and is used in perfumes to obtain a green-leaf note, and in fruit flavors for green nuances (limiting IFRA recommendation). (See Sec. 1.5.2 Fragrances).

***cis*-4-Heptenal** [*6728-31-0*], $CH_3CH_2CH{=}CHCH_2CH_2CHO$, $C_7H_{12}O$, M_r 112.17, *bp* (1.33 kPa) 41 °C, n_D^{20} 1.4343, is a widespread volatile trace constituent of food flavors. It is a colorless, oily liquid with a powerful, fatty, somewhat fishy and, in high dilution, creamy odor. It can be prepared from 1-butyne (via lithium 1-butynide) and acrolein (which is converted into 2-bromopropionaldehyde dimethyl acetal). The resulting 4-heptynal dimethyl acetal is cleaved and the triple bond is hydrogenated catalytically to give *cis*-4-heptenal [23].

cis-4-Heptenal is used in cream, butter, and fat flavors.

10-Undecenal [*112-45-8*], $CH_2{=}CH(CH_2)_8CHO$, $C_{11}H_{20}O$, M_r 168.28, *bp* (400 Pa) 103 °C, d_4^{20} 0.8495, n_D^{20} 1.4459, has not yet been found in nature. It is a colorless liquid with a fatty-green, slightly metallic, heavy-flowery odor. The aldehyde can be synthesized from undecylenic acid, for example, by hydrogenation of the acid chloride (Rosenmund reduction) or by reaction with formic acid in the vapor phase in the presence of titanium dioxide. In perfumery, 10-undecenal is one of the aldehydes essential for creating the "aldehydic note".

2.1.4. Ketones (→ Ketones)

Aliphatic monoketones are of minor importance as fragrance and aroma substances. 2-Alkanones (C_3-C_{15}) have been found in the volatile fractions of many fruits and foods, but they do not contribute significantly to their aroma. An exception are the odd-numbered methyl ketones C_7, C_9, C_{11}, which possess a characteristic nutty note; they are used, e.g., in cheese flavor compositions. In perfumery, aliphatic ketones are used for accentuation, e.g., 3-octanone [*106-68-3*] for lavender notes. The hydroxyketone acetoin and the diketone 2,3-butanedione are commercially important aroma substances.

Acetoin [*52217-02-4*], 3-hydroxy-2-butanone, $CH_3COCH(OH)CH_3$, $C_4H_8O_2$, M_r 88.11, *bp* (101.3 kPa) 148 °C, d_4^{20} 1.0058, n_D^{20} 1.4171, has a pleasant buttery odor and both of its optical isomers occur widely in nature. It is synthesized by partial oxidation of 2,3-butanediol and is obtained as a byproduct in the fermentation of molasses. It is used for flavoring margarine.

2,3-Butanedione [*431-03-8*], diacetyl, $CH_3COCOCH_3$, $C_4H_6O_2$, M_r 86.09, *bp* 88 °C (101.3 kPa), d_4^{20} 0.9831, n_D^{20} 1.3950, is a constituent of many fruit and food aromas and well-known as a constituent of butter. Many methods are known for its manufacture, e.g., dehydrogenation of 2,3-butanediol with a copper chromite catalyst [24]. It is used mainly in aromas for butter and roast notes. Large quantities are used for flavoring margarine; small amounts are used in perfumes.

2.1.5. Acids and Esters (→ Carboxylic Acids, Aliphatic; → Esters Organic)

Straight-chain, saturated aliphatic acids are found in many essential oils and foods. These acids contribute to aromas, but are not important as fragrance substances. In flavor compositions, aliphatic acids up to C_{10} are used to accentuate certain aroma characteristics (C_3-C_8 for fruity notes; C_4, C_6-C_{12} for cheese flavors). However, straight-chain and some branched-chain aliphatic acids are of considerable importance as starting materials in the manufacture of esters, many of which are valuable fragrance and flavor materials. Aliphatic esters contribute to the aroma of nearly all fruits and many foods. Some are responsible for a particular fruit aroma, or for the smell of a particular flower; however, many of these esters possess a nonspecific fruity odor.

Most of the esters used are acetates and ethanol is the most common alcohol component. In nature, most esters are derived from alcohols and acids with an even number of carbon atoms. In addition to straight-chain saturated compounds, branched-chain compounds such as isoamyl esters and unsaturated compounds such as hexenyl esters are important.

Although the odor of aliphatic esters with a small number of carbon atoms is strictly fruity, it changes to fatty-soapy and even metallic as the number of carbon atoms increases.

Esters are usually prepared by esterification of carboxylic acids with alcohols. Industrial procedures depend on the physical properties of the esters concerned (see → Esters, Organic).

In perfumery, acetates are the most important aliphatic esters; formates do not keep well. Animal and fatty notes become more pronounced in esters of higher fatty acids. Acetates of alcohols up to C_6 are used principally for fruity notes, whereas the acetates of C_8, C_{10}, and C_{12} alcohols are employed for blossom fragrances and for flower notes in general. Lauryl acetate in particular is also used for conifer notes.

In flavor compositions, aliphatic esters are preferred for artificial fruit aromas; as in nature, acetates and ethyl esters prevail.

Ethyl formate [*109-94-4*], $HCOOCH_2CH_3$, $C_3H_6O_2$, M_r 74.08, *bp* (101.3 kPa) 54.5 °C, d_4^{20} 0.9168, n_D^{20} 1.3598, occurs widely in fruits. It is a liquid with a slightly pungent, fruity, ethereal odor and is used in fruit flavors.

***cis*-3-Hexenyl formate** [*33467-73-1*], $HCOO(CH_2)_2CH{=}CHCH_2CH_3$, $C_7H_{12}O_2$, M_r 128.17, *bp* (101.3 kPa) 155 °C, d_4^{20} 0.9121, n_D^{20} 1.4270, has been identified in tea. It possesses a green-fruity odor and is used in perfumery and flavor compositions to impart fruity green notes.

Ethyl acetate [*141-78-6*], $CH_3COOCH_2CH_3$, $C_4H_8O_2$, M_r 88.11, *bp* (101.3 kPa) 77.1 °C, d_4^{20} 0.9003, n_D^{20} 1.3723, is a fruity smelling liquid with a brandy note and is the most common ester in fruits. It is used in fruit and brandy flavors.

Butyl acetate [*123-86-4*], $CH_3COO(CH_2)_3CH_3$, $C_6H_{12}O_2$, M_r 116.16, *bp* (101.3 kPa) 126.5 °C, d_4^{20} 0.9003, n_D^{20} 1.3942, is a liquid with a strong fruity odor. It occurs in many fruits and is a constituent of apple aromas.

Isoamyl acetate [*123-92-2*], $CH_3COO(CH_2)_2CH(CH_3)_2$, $C_7H_{14}O_2$, M_r 130.19, *bp* (101.3 kPa) 142.5 °C, d_4^{20} 0.8730, n_D^{20} 1.4006, is a strongly fruity smelling liquid and has been identified in many fruit aromas. It is the main component of banana aroma and is, therefore, also used in banana flavors.

Hexyl acetate [*142-92-7*], $CH_3COO(CH_2)_5CH_3$, $C_8H_{16}O_2$, M_r 144.21, *bp* (101.3 kPa) 171.5 °C, d_4^{20} 0.8730, n_D^{20} 1.4092, is a liquid with a sweet-fruity, pearlike odor. It is present in a number of fruits and alcoholic beverages, and is used in fruit aroma compositions.

3,5,5-Trimethylhexyl acetate [*58430-94-7*], $CH_3COO(CH_2)_2CH(CH_3)CH_2C(CH_3)_3$, isononyl acetate, $C_{11}H_{22}O_2$, M_r 186.29, does not occur in nature. Commercial isononyl acetate contains small amounts of byproducts. It is a colorless liquid with a woody-fruity odor and is prepared from diisobutene by the oxo synthesis, followed by hydrogenation to the alcohol and acetylation. It is used in household perfumery.

***trans*-2-Hexenyl acetate** [*2497-18-9*], $CH_3COOCH_2CH{=}CH(CH_2)_2CH_3$, $C_8H_{14}O_2$, M_r 142.20, *bp* (2.1 kPa) 67 – 68 °C, d_4^{20} 0.8975, n_D^{20} 1.4277, occurs in many fruits and in some essential oils, e.g., peppermint. It is a fresh-fruity, slightly green smelling liquid and is used in fruit flavors.

***cis*-3-Hexenyl acetate** [*3681-71-8*], $CH_3COO(CH_2)_2CH{=}CHCH_2CH_3$, $C_8H_{14}O_2$, M_r 142.20, *bp* (1.6 kPa) 66 °C, has been identified in many fruit aromas and green tea. It is a prototype for green odors and is often used in combination with *cis*-3-hexenol.

Ethyl propionate [*105-37-3*], $CH_3CH_2COOCH_2CH_3$, $C_5H_{10}O_2$, M_r 102.13, *bp* (101.3 kPa) 99 °C, d_4^{20} 0.8896, n_D^{20} 1.3839, is found in many fruits and alcoholic beverages. It has a fruity odor reminiscent of rum and is used in flavor compositions for creating both fruity and rum notes.

Ethyl butyrate [*105-54-4*], $CH_3(CH_2)_2COOCH_2CH_3$, $C_6H_{12}O_2$, M_r 116.16, *bp* (101.3 kPa) 121 – 122 °C, d_4^{20} 0.8785, n_D^{20} 1.4000, occurs in fruits and alcoholic beverages, but also in other foods such as cheese. It has a fruity odor, reminiscent of pineapples. Large amounts are used in perfume and in flavor compositions.

Butyl butyrate [*109-21-7*], $CH_3(CH_2)_2COOCH_2(CH_2)_2CH_3$, $C_8H_{16}O_2$, M_r 144.21, *bp* (101.3 kPa) 166 °C, d_4^{20} 0.8709, n_D^{20} 1.4075, is a liquid with a sweet-fruity odor. It is a volatile constituent of many fruits and honey and is used in fruit flavor compositions.

Isoamyl butyrate [*106-27-4*], $CH_3(CH_2)_2COO(CH_2)_2CH(CH_3)_2$, $C_9H_{18}O_2$, M_r 158.23, *bp* (101.3 kPa) 178.5 °C, d_4^{20} 0.8651, n_D^{20} 1.4106, is a liquid with strongly fruity odor that occurs, e.g., in banana. It is used mainly in fruit flavors.

Hexyl butyrate [*2639-63-6*], $CH_3(CH_2)_2COO(CH_2)_5CH_3$, $C_{10}H_{20}O_2$, M_r 172.27, *bp* (101.3 kPa) 208 °C, d_4^{20} 0.8652, n_D^{20} 1.3920, is a liquid with a powerful fruity odor. It has been identified in a number of fruits and berries and is an important constituent of fruit flavor compositions.

***cis*-3-Hexenyl isobutyrate** [*41519-23-7*], $(CH_3)_2CHCOO(CH_2)_2CH{=}CHCH_2CH_3$, $C_{10}H_{18}O_2$, M_r 170.25 is found in spearmint oil. It smells fruity-green and is used in perfumery to create freshness in blossom compositions.

Ethyl isovalerate [*108-64-5*], $(CH_3)_2CHCH_2COOCH_2CH_3$, $C_7H_{14}O_2$, M_r 130.19, *bp* (101.3 kPa) 134.7 °C, d_4^{20} 0.8656, n_D^{20} 1.3962, is a colorless liquid with a fruity odor reminiscent of blueberries. It occurs in fruits, vegetables, and alcoholic beverages. It is used in fruity aroma compositions.

Ethyl 2-methylbutyrate [*7452-79-1*], $CH_3CH_2CH(CH_3)COOCH_2CH_3$, $C_7H_{14}O_2$, M_r 130.19, *bp* (101.3 kPa) 131 – 132 °C, d_4^{25} 0.8689, n_D^{20} 1.3964, is a liquid with a green-fruity odor reminiscent of apples. It is found, for example, in citrus fruits and wild berries and is used in fruit flavor compositions.

Ethyl hexanoate [*123-66-0*], ethyl caproate, $CH_3(CH_2)_4COOCH_2CH_3$, $C_8H_{16}O_2$, M_r 144.21, *bp* (101.3 kPa) 168 °C, d_4^{20} 0.8710, n_D^{20} 1.4073, is a colorless liquid with a strong fruity odor, reminiscent of pineapples. It occurs in many fruits and is used in small amounts for flowery-fruity notes in perfume compositions and in larger quantities in fruit flavors.

2-Propenyl hexanoate [*123-68-2*], allyl caproate, $CH_3(CH_2)_4COOCH_2CH{=}CH_2$, $C_9H_{16}O_2$, M_r 156.22, *bp* (2 kPa) 75 – 76 °C, d_4^{20} 0.8869, n_D^{20} 1.4243, and also to occurs in nature. It has a typical pineapple odor and is used in, for example, artificial pineapple flavors. (Limiting IFRA recommendation) (see Sec. 1.5.2 Fragrances).

Ethyl heptanoate [*106-30-9*], ethyl enanthate, $CH_3(CH_2)_5COOCH_2CH_3$, $C_9H_{18}O_2$, M_r 158.24, *bp* (101.3 kPa) 187 – 188 °C, d_4^{20} 0.8680, n_D^{20} 1.4120, is a colorless liquid with a fruity odor reminiscent of cognac. It is found in fruits and alcoholic beverages and is used in appropriate aroma compositions.

2-Propenyl heptanoate [*142-19-8*], allyl enanthate, $CH_3(CH_2)_5COOCH_2CH{=}CH_2$, $C_{10}H_{18}O_2$, M_r 170.25, *bp* (101.3 kPa) 210 °C, d_4^{20} 0.8927, n_D^{20} 1.4290, has not yet been found in nature. It is used in perfume compositions for apple-like (pineapple) notes. (Llimiting IFRA recommendation) (see Sec. 1.5.2 Fragrances).

Ethyl octanoate [*106-32-1*], ethyl caprylate, $CH_3(CH_2)_6COOCH_2CH_3$, $C_{10}H_{20}O_2$, M_r 172.27, *bp* (101.3 kPa) 208 °C, d_4^{20} 0.8693, n_D^{20} 1.4178, is a liquid with a fruity-flowery odor. It occurs in many fruits and alcoholic beverages and is used in fruit flavors.

Ethyl 2-*trans*-4-*cis*-decadienoate [*3025-30-7*], $CH_3(CH_2)_4CH{=}CHCH{=}CHCOOCH_2CH_3$, $C_{12}H_{20}O_2$, M_r 196.29, *bp* (6 kPa) 70 – 72 °C, has been identified in pears and has the typical aroma of Williams pears. Synthesis of ethyl 2-*trans*-4-*cis*-decadienoate starts from *cis*-1-heptenyl bromide, which is converted into a 1-heptenyllithium cuprate complex with lithium and copper iodide. Reaction with ethyl propiolate yields a mixture of 95 % ethyl 2-*trans*-4-*cis*- and 5 % ethyl 2-*trans*-4-*trans*-decadienoate. Pure ethyl 2-*trans*-4-*cis*-decadienoate is obtained by fractional distillation [25].

Methyl 2-octynoate [*111-12-6*], $CH_3(CH_2)_4C{\equiv}CCOOCH_3$, $C_9H_{14}O_2$, M_r 154.21, *bp* (1.3 kPa) 94 °C, d_4^{20} 0.9320, n_D^{20} 1.4464. Limiting IFRA recommendation.

Methyl 2-nonynoate [*111-80-8*], $CH_3(CH_2)_5C{\equiv}CCOOCH_3$, $C_{10}H_{16}O_2$, M_r 168.24, *bp* (2.7 kPa) 121 °C, d_4^{20} 0.9162, n_D^{25} 1.4395. Both methyl 2-nonynoate and methyl 2-octynoate have a triple bond and are liquids with a fatty, violet-leaf-like odor. They are used in perfume compositions. Limiting IFRA recommendation.

2.1.6. Miscellaneous Compounds

A number of volatile aliphatic compounds that contain nitrogen or sulfur atoms are important aroma constituents. Alkyl thiols, dialkyl sulfides and disulfides, and alkyl thiocyanates belong to this group. They occur widely in foods and spices and determine the odor of, for example, onions, garlic, and mustard. Because of their potent smell, they are used in high dilution and are often produced only in small quantities. The same is true for 3-methylthiohexanol [*51755-66-9*], $CH_3(CH_2)_2CH(SCH_3)CH_2CH_2OH$, a volatile constituent of passion fruits. Allyl isothiocyanate, however, is an exception in that it is produced in large quantities.

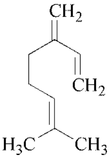
Allyl isothiocyanate [*57-06-7*], allyl mustard oil, $CH_2{=}CHCH_2N{=}C{=}S$, C_4H_5NS, M_r 99.14, *bp* (101.3 kPa) 152 °C, d_4^{20} 1.0126, is the main component of mustard oil (> 95 %). It is a colorless oil with a typical mustard odor and can be prepared by reacting allyl chloride with alkaline-earth or alkali isothiocyanates [26].

2.2. Acyclic Terpenes

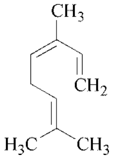
For a general description of terpenes, see → Terpenes.

2.2.1. Hydrocarbons

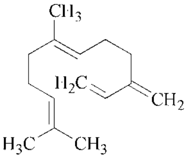
Acyclic terpene (C_{10}) and sesquiterpene (C_{15}) hydrocarbons find little use in flavor and fragrance compositions. They are relatively unstable and some have a slightly aggressive odor due to their highly unsaturated structure. Myrcene, ocimene, and farnesene, are present in many fruits and essential oils, but find only limited use in perfumery.



Myrcene



Ocimene

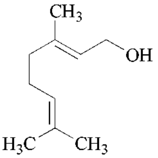


β-Farnesene

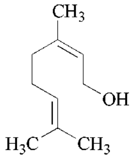
2.2.2. Alcohols

Acyclic terpene and sesquiterpene alcohols occur in many essential oils. These alcohols were formerly isolated from oils in which they are major components. Currently, large-scale synthesis of terpenoids permits production without the uncertainties associated with isolation from natural sources. However, the odor qualities of synthetic products often differ from those of compounds isolated from natural sources, since the desired natural product often cannot be separated from small amounts of compounds with similar physical properties but different odor quality.

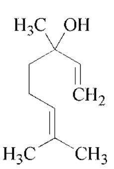
The acyclic terpene alcohols geraniol, linalool, and citronellol are the most important terpene alcohols used as fragrance and flavor substances. Geraniol and linalool are, in addition to nerol and lavandulol, primary products in terpene biosynthesis. The fully saturated alcohols tetrahydrogeraniol and tetrahydrolinalool are also used in large quantities in fragrance compositions. The fragrance materials myrcenol, identified in lavender oil, and its dihydro and tetrahydro derivatives, which have not yet been found in nature, belong structurally to the terpenes. The sesquiterpene alcohols farnesol and nerolidol are popular materials for perfume compositions.



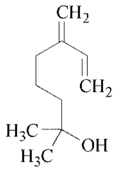
Geraniol



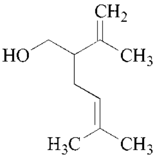
Nerol



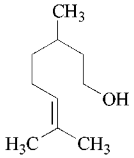
Linalool



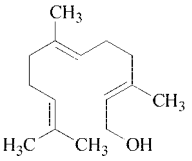
Myrcenol



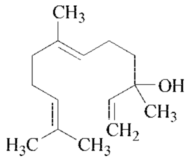
Lavandulol



Citronellol



trans,trans-Farnesol



trans-Nerolidol

Geraniol and nerol are *cis–trans*-isomers. In the rarely occurring lavandulol, the isoprene units are not coupled in the normal head-to-tail manner.

The farnesols and nerolidols are sesquiterpene analogs of geraniol–nerol and linalool. These compounds are formed by extending one of the methyl groups in the 7-position of the corresponding monoterpene with an isoprene unit. Because these compounds have an extra double bond, they also have an additional possibility for *cis–trans*-isomerism. Thus, there are four stereoisomers of farnesol and two of nerolidol.

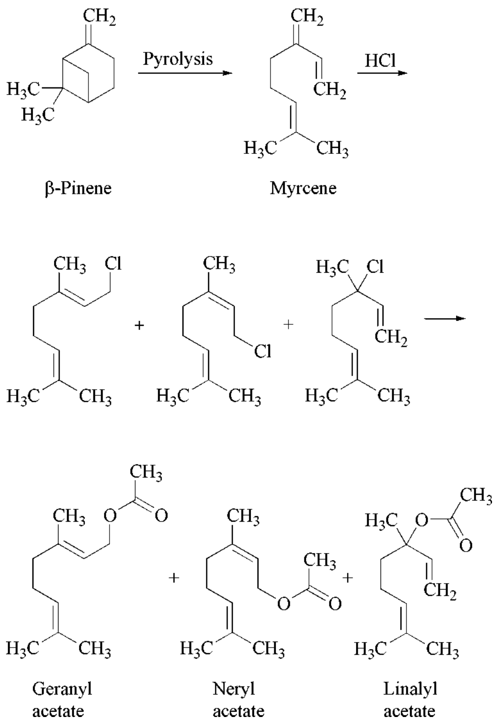
Geraniol [*106-24-1*], 3,7-dimethyl-*trans*-2,6-octadien-1-ol, $C_{10}H_{18}O$, M_r 154.25, *bp* (101.3 kPa) 230 °C, d_4^{20} 0.8890, n_D^{20} 1.4777, occurs in nearly all terpene-containing essential oils, frequently as an ester. Palmarosa oil contains 70 – 85 % geraniol; geranium oils and rose oils also contain large quantities. Geraniol is a colorless liquid, with a flowery-roselike odor.

Since geraniol is an acyclic, doubly unsaturated alcohol, it can undergo a number of reactions, such as rearrangement and cyclization. Rearrangement in the presence of copper catalysts yields citronellal. In the presence of mineral acids, it cyclizes to form monocyclic terpene hydrocarbons, cyclogeraniol being obtained if the hydroxyl function is protected. Partial hydrogenation leads to citronellol, and complete hydrogenation of the double bonds yields 3,7-dimethyloctan-1-ol (tetrahydrogeraniol). Citral is obtained from geraniol by oxidation (e.g., with chromic acid), or by catalytic dehydrogenation. Geranyl esters are prepared by esterification.

Production. Dehydrogenation of geraniol and nerol is a convenient route for synthesizing citral, which is used in large quantities as an intermediate in the synthesis of vitamin A. Large-scale processes have, therefore, been developed for producing geraniol. Currently, these are far more important than isolation from essential oils. Nevertheless, some geraniol is still isolated from essential oils for perfumery purposes.

1) *Isolation from Essential Oils.* Geraniol is isolated from citronella oils and from palmarosa oil. Fractional distillation of, for example, Java citronella oil (if necessary after saponification of the esters present) yields a fraction containing ca. 60 % geraniol, as well as citronellol and sesquiterpenes.
   A product with a higher geraniol content and slightly different odor quality for use in fine fragrances is obtained by fractionating palmarosa oil after saponification of the geranyl esters.
2) *Synthesis from β-Pinene.* Pyrolysis of β-pinene yields myrcene, which is converted into a mixture of predominantly geranyl,

neryl, and linalyl chloride by addition of hydrogen chloride in the presence of small amounts of catalyst, e.g., copper(I) chloride and an organic quaternary ammonium salt [27]. After removal of the catalyst, the mixture is reacted with sodium acetate in the presence of a nitrogen base (e.g., triethylamine) and converted to geranyl acetate, neryl acetate, and a small amount of linalyl acetate [28]. After saponification and fractional distillation of the resulting alcohols, a fraction is obtained that contains ca. 98 % geraniol.



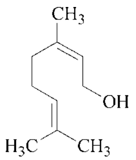
3) *Synthesis from Linalool.* Recently, a 96 % pure synthetic geraniol prepared by isomerization of linalool has become commercially available. Orthovanadates are used as catalysts, to give a > 90 % yield of a geraniol–nerol mixture [29]. Geraniol of high purity is finally obtained by fractional distillation.
A considerable portion of commercially available geraniol is produced by a modified process: linalool obtained in a purity of ca. 65 % from α-pinene is converted into linalyl borates, which rearrange in the presence of vanadates as catalysts to give geranyl and neryl borates. The alcohols are obtained by hydrolysis of the esters [30].

Uses. Geraniol is one of the most frequently used terpenoid fragrance materials. It can be used in all flowery-roselike compositions and does not discolor soaps. In flavor compositions, geraniol is used in small quantities to accentuate citrus notes. It is an important intermediate in the manufacture of geranyl esters, citronellol, and citral.

Nerol [*106-25-2*], 3,7-dimethyl-*cis*-2,6-octadien-1-ol, $C_{10}H_{18}O$, M_r 154.25, *bp* (99.3 kPa) 224 – 225 °C, d_4^{20} 0.8796, n_D^{20} 1.4744, occurs in small quantities in many essential oils where it is always accompanied by geraniol; its name originates from its occurrence in neroli oil. Nerol is a colorless liquid with a pleasant roselike odor which, unlike that of geraniol, has a fresh green note.

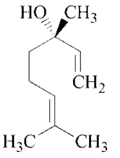
Nerol undergoes the same reactions as geraniol, but cyclizes more readily in the presence of acids.

Nerol is produced along with geraniol from myrcene in the process described for geraniol (see Geraniol). It can be separated from geraniol by fractional distillation.

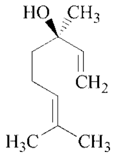


Uses. Nerol is used in perfumery not only for the same purposes as geraniol, e.g., in rose compositions, to which it lends a particular freshness, but also in other blossom compositions. In flavor work it is used for bouquetting citrus flavors. Technical-grade nerol, often in a mixture with geraniol, is used as an intermediate in the production of citronellol and citral.

Linalool [*78-70-6*], 3,7-dimethyl-1,6-octadien-3-ol, $C_{10}H_{18}O$, M_r 154.25, *bp* (101.3 kPa) 198 °C, d_4^{20} 0.8700, n_D^{20} 1.4616, occurs as one of its enantiomers in many essential oils, where it is often the main component. (−)-Linalool [*126-90-9*], for example, occurs at a concentration of 80 – 85 % in Shiu oils from *Cinnamomum camphora; Cayenne linaloe* oil contains ca. 80 %. (+)-Linalool [*126-91-0*] makes up 60 – 70 % of coriander oil.



(+)-Linalool



(−)-Linalool

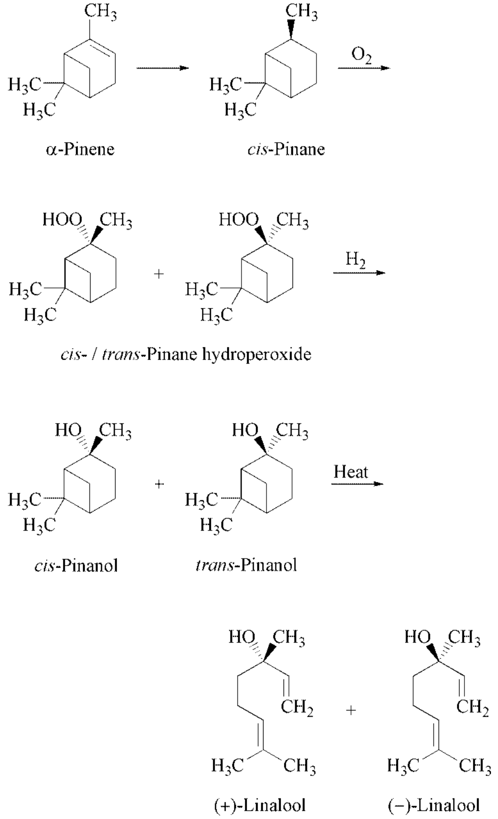
Properties. (±)-Linalool [*22564-99-4*] is, like the individual enantiomers, a colorless liquid with a flowery-fresh odor, reminiscent of lily of the valley. However, the enantiomers differ slightly in odor [31]. Together with its esters, linalool is one of the most frequently used fragrance substances and is produced in large quantities.

In the presence of acids, linalool isomerizes readily to geraniol, nerol, and α-terpineol. It is oxidized to citral by chromic acid. Oxidation with peracetic acid yields linalool oxides, which occur in small amounts in essential oils and are also used in perfumery. Hydrogenation of linalool gives tetrahydrolinalool, a stable fragrance compound. Its odor is not as strong as, but fresher than, that of linalool. Linalool can be converted into linalyl acetate by reaction with ketene or an excess of boiling acetic anhydride [32].

Production. In the 1950s nearly all linalool used in perfumery was isolated from essential oils, particularly from rosewood oil. Currently, this method is used only in countries where oils with a high linalool content are available and where the importation of linalool is restricted.

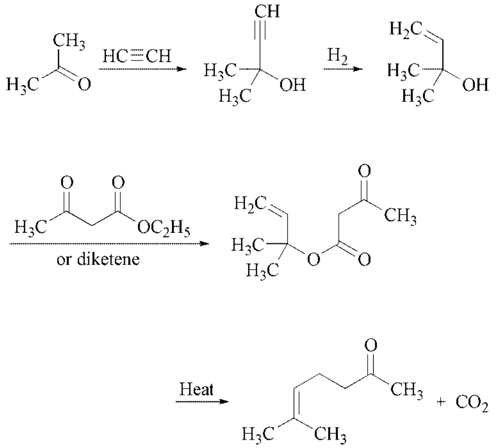
Since linalool is an important intermediate in the manufacture of vitamin E, several large-scale processes have been developed for its production. Preferred starting materials and/or intermediates are the pinenes and 2-methyl-2-hepten-6-one. Most perfumery-grade linalool is synthetic.

1) *Isolation from Essential Oils.* Linalool can be isolated by fractional distillation of essential oils, for example, rosewood oil, Shiu oil, and coriander oil, of which Brazilian rosewood oil is probably the most important.
2) *Synthesis from α-Pinene.* α-Pinene from turpentine oil is selectively hydrogenated to *cis*-pinane [33], which is oxidized with oxygen in the presence of a radical initiator to give a mixture of ca. 75 % *cis*- and 25 % *trans*-pinane hydroperoxide. The mixture is reduced to the corresponding pinanols either with sodium bisulfite ($NaHSO_3$) or a catalyst. The pinanols can be separated by fractional distillation and are pyrolized to linalool: (−)-α-pinene yields *cis*-pinanol and (+)-linalool, whereas (−)-linalool is obtained from *trans*-pinanol [34].

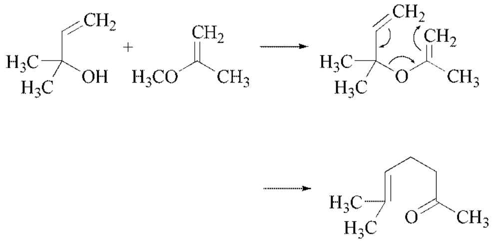


3) *Synthesis from β-Pinene.* For a description of this route, see under Geraniol. Addition of hydrogen chloride to myrcene (obtained from β-pinene) results in a mixture of geranyl, neryl, and linalyl chlorides. Reaction of this mixture with acetic acid–sodium acetate in the presence of copper(I) chloride gives linalyl acetate in 75 – 80 % yield [35]. Linalool is obtained after saponification.
4) *Synthesis from 2-Methyl-2-hepten-6-one.* The total synthesis of linalool starts with 2-methyl-2-hepten-6-one; several large-scale processes have been developed for synthesizing this compound:

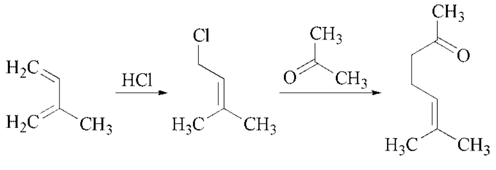
a) Addition of acetylene to acetone results in the formation of 3-methyl-1-butyn-3-ol, which is hydrogenated to 3-methyl-1-buten-3-ol in the presence of a palladium catalyst. This product is converted into its acetoacetate derivative with diketene [36] or with ethyl acetoacetate [37]. The acetoacetate undergoes rearrangement when heated (Carroll reaction) to give 2-methyl-2-hepten-6-one:



b) In another process, 2-methyl-2-hepten-6-one is obtained by reaction of 3-methyl-1-buten-3-ol with isopropenyl methyl ether followed by a Claisen rearrangement [38]:

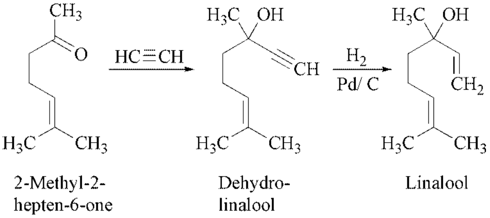


c) A third synthesis starts from isoprene, which is converted into 3-methyl-2-butenyl chloride by addition of hydrogen chloride. Reaction of the chloride with acetone in the presence of a catalytic amount of an organic base [39] leads to 2-methyl-2-hepten-6-one:



d) In another process, 2-methyl-2-hepten-6-one is obtained by isomerization of 2-methyl-1-hepten-6-one [40]. The latter can be prepared in two steps from isobutylene and formaldehyde. 3-Methyl-3-buten-1-ol is formed in the first step [41] and is converted into 2-methyl-1-hepten-6-one by reaction with acetone [42].

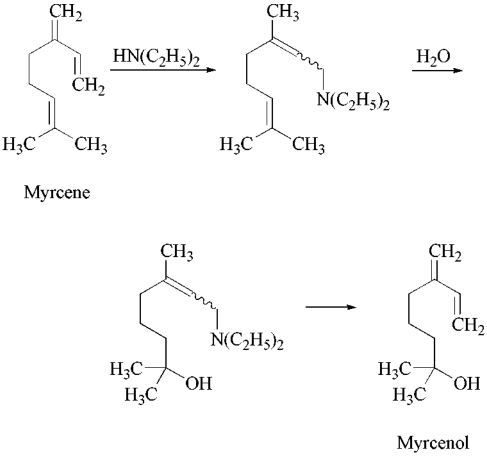
2-Methyl-2-hepten-6-one is converted into linalool in excellent yield by base-catalyzed ethynylation with acetylene to dehydrolinalool [43]. This is followed by selective hydrogenation of the triple bond to a double bond in the presence of a palladium–carbon catalyst.



Uses. Linalool is used frequently in perfumery for fruity notes and for many flowery fragrance compositions (lily of the valley, lavender, and neroli). Because of its relatively high volatility, it imparts naturalness to top notes. Since linalool is stable in alkali, it can be used in soaps and detergents. Linalyl esters can be prepared from linalool. Most of the manufactured linalool is used in the production of vitamin E.

Myrcenol [*543-39-5*], 2-methyl-6-methylene-7-octen-2-ol, $C_{10}H_{18}O$, M_r 154.25, *bp* (6.7 kPa) 78 °C, d_4^{20} 0.8764, n_D^{20} 1.4731, is an isomer of geraniol and linalool. It has been identified in Chinese lavender oil [44] and some medicinal plants. It is a colorless liquid with a fresh-flowery, slightly limelike odor. Due to its conjugated double bonds, it tends to polymerize; polymerization can be suppressed by adding inhibitors (e.g., antioxidants such as ionol).

Myrcenol can be prepared by treating myrcene with diethylamine to give a mixture of geranyl- and neryldiethylamine. These compounds are hydrated with a dilute acid to the corresponding hydroxydiethylamines. Deamination to myrcenol is effected by using a palladium–phosphine-cation complex as a catalyst [45].



Myrcenol is used in perfumery to obtain a lifting top note in citrus and lavender compositions.

Citronellol [*26489-01-0*], 3,7-dimethyl-6-octen-1-ol, $C_{10}H_{20}O$, M_r 156.27, *bp* (101.3 kPa) 244.4 °C, d_4^{20} 0.8560, n_D^{20} 1.4558, $[\alpha]_D^{20}$ + resp. − 5 to 6 °, occurs as both (+)-citronellol [*1117-61-9*] and (−)-citronellol [*7540-51-4*] in many essential oils.

(−)-Citronellol isolated from natural sources is often named rhodinol. At present, the name rhodinol is also used for the isopropenyl isomer, α-citronellol; therefore, exclusive use of the systematic name is better.

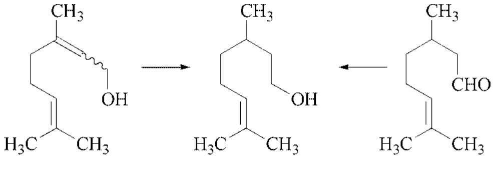
In many natural products citronellol occurs as a mixture of its two enantiomers; the pure (+) or (−) form is seldom found. (+)-Citronellol dominates in oils from *Boronia citriodora* (total citronellol content ca. 80 %) and *Eucalyptus citriodora* (citronellol content 15 – 20 %). (−)-Citronellol is the predominant enantiomer in geranium and rose oils, both of which may contain up to 50 % citronellols.

Citronellol is a colorless liquid with a sweet roselike odor. The odor of (−)-citronellol is more delicate than that of (+)-citronellol.

Citronellol undergoes the typical reactions of primary alcohols (→ Alcohols, Aliphatic, Chap. 2.2.). Compared with geraniol, which contains one more double bond, citronellol is relatively stable. Citronellol is converted into citronellal by dehydrogenation or oxidation; hydrogenation yields 3,7-dimethyloctan-1-ol. Citronellyl esters are easily prepared by esterification with acid anhydrides.

Production. (−)-Citronellol is still obtained mainly from geranium oil by saponification followed by fractional distillation. Although of high odor quality, it does not possess the true (−)-citronellol odor due to impurities. Much larger quantities of (+)- and (±)-citronellol are used and are prepared by partial or total synthesis.

1) *Synthesis of (+)- and (±)-Citronellol from the Citronellal Fraction of Essential Oils.* (+)-Citronellal is obtained by distillation of Java citronella oil and is hydrogenated to (+)-citronellol in the presence of a catalyst (e.g., Raney nickel). Similarly, (±)-citronellol is prepared from the (±)-citronellal fraction of *Eucalyptus citriodora* oil.
2) *Synthesis of (±)- or Slightly Dextrorotatory Citronellol from Geraniol Fractions of Essential Oils.* This citronellol is produced by catalytic hydrogenation of saponified geraniol fractions (also containing (+)-citronellol) obtained from Java citronella oil, followed by fractional distillation. Selective hydrogenation of the double bond in the 2-position of geraniol in geraniol–citronellol mixtures isolated from essential oils can be achieved by using Raney cobalt as a catalyst; overhydrogenation to 3,7-dimethyloctan-1-ol can be largely avoided by this method [46].

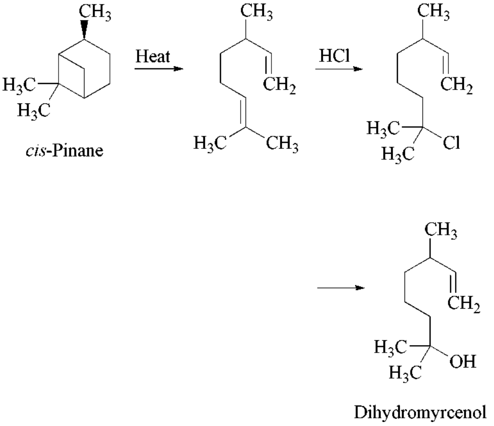


3) *Synthesis of (±)-Citronellol from Synthetic Geraniol– Nerol or Citral.* A considerable amount of commercial synthetic (±)-citronellol is produced by partial hydrogenation of synthetic geraniol and/or nerol. Another starting material is citral, which can be hydrogenated, e.g., in the presence of a catalyst system consisting of palladium, ruthenium, and trimethylamine [47].
4) *Preparation of (−)-Citronellol from Optically Active Pinenes.* (+)- *cis*-Pinane is readily synthesized by hydrogenation of (+)-α-pinene or (+)-β-pinene, and is then pyrolyzed to give (+)-3,7-dimethyl-1,6-octadiene. This

compound is converted into (−)-citronellol (97 % purity) by reaction with triisobutylaluminum or diisobutylaluminum hydride, followed by air oxidation and hydrolysis of the resulting aluminum alcoholate [48].

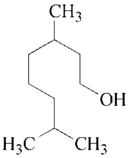
Uses. Citronellol is one of the most widely used fragrance materials, particularly for rose notes and for floral compositions in general. As flavor material, citronellol is added for bouquetting purposes to citrus compositions. It is the starting material for numerous citronellyl esters and for hydroxydihydrocitronellol, an intermediate in the production of hydroxydihydrocitronellal.

Dihydromyrcenol [*18479-58-8*], 2,6-dimethyl-7-octen-2-ol, $C_{10}H_{20}O$, M_r 156.27, *bp* (1.3 kPa) 77 – 79 °C, d_4^{20} 0.841, is a colorless liquid with a fresh citrus-like odor and a lavender note. It is prepared from 2,6-dimethyl-2,7-octadiene, the pyrolysis product of *cis*-pinane [49], by addition of hydrogen chloride and hydrolysis of the resulting 2,6-dimethyl-2-chloro-7-octene [50].

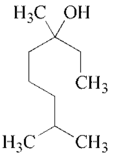


Dihydromyrcenol is used in soap perfumes for lime and blossom notes.

Tetrahydrogeraniol [*106-21-8*], 3,7-dimethyloctan-1-ol, $C_{10}H_{22}O$, M_r 158.28, *bp* (101.3 kPa) 212 – 213 °C, d_4^{20} 0.8285, n_D^{20} 1.4355, has been identified in citrus oils and is a colorless liquid with a waxy, rose-petal-like odor. It is prepared by hydrogenation of geraniol or citronellol in the presence of a nickel catalyst and is a byproduct in the synthesis of citronellol from geraniol or nerol. Because of its stability, it is often used to perfume household products.

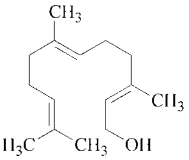


Tetrahydrolinalool [*78-69-3*], 3,7-dimethyloctan-3-ol, $C_{10}H_{22}O$, M_r 158.28, *bp* (1.3 kPa) 78 – 79 °C, d_4^{20} 0.8294, n_D^{20} 1.4335, is a constituent of honey aroma. It is a colorless liquid with a linalool-like odor that is slightly fresher but distinctly weaker than that of linalool. Tetrahydrolinalool is prepared by catalytic hydrogenation of linalool and is used as a substitute for the less stable linalool in perfuming aggressive media.



Farnesol [*4602-84-0*], 3,7,11-trimethyl-2,6,10-dodecatrien-1-ol, $C_{15}H_{26}O$, M_r 222.37, *bp* (1.6 kPa) 156 °C, d_4^{20} 0.8846, n_D^{20} 1.4890, is a component of many blossom oils. It is a colorless liquid with a linden blossom odor, which becomes more intense when evaporated, possibly due to oxidation.

Of the four possible isomers (due to the double bonds in the 2- and 6-positions), the *trans*–*trans*-isomer is the most common in nature and occurs, for example, in ambrette seed oil. 2-*cis*-6-*trans*-Farnesol has been identified in petitgrain oil Bigarade.

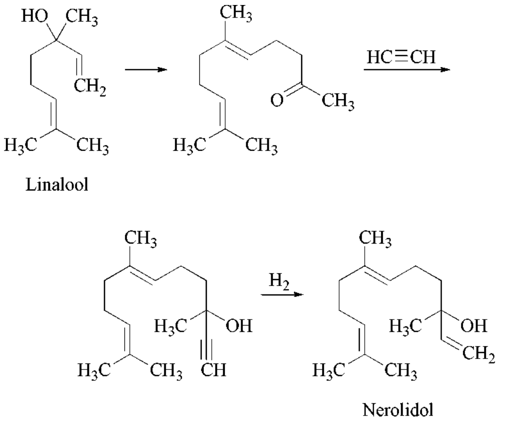


trans-trans-Farnesol

Since the odors of the isomers differ very little, natural farnesol in compositions can be replaced by synthetic farnesol, which is a mixture of isomers obtained by isomerization of nerolidol.

Farnesol is particularly suited for use in flower compositions and is valued for its fixative properties. IFRA recommends to use only qualities containing at least 96 % of the farnesol isomers.

Nerolidol [*7212-44-4*], 3,7,11-trimethyl-1,6,10-dodecatrien-3-ol, $C_{15}H_{26}O$, M_r 222.37, *bp* (1.6 kPa) 145 °C, d_4^{20} 0.8778, n_D^{20} 1.4898, is the sesquiterpene analogue of linalool. Because of the double bond at the 6-position, it exists as *cis*- and *trans*-isomers. Each of these isomers can exist as an enantiomeric pair, since the carbon atom in the 3-position is chiral.



Nerolidol is a component of many essential oils. (+)-*trans*-Nerolidol occurs in cabreuva oil; (−)-nerolidol has been isolated from *Dalbergia parviflora* wood oils.

Synthetic nerolidol consists of a mixture of (±)-*cis*- and (±)-*trans*-nerolidol and is a colorless liquid with a long-lasting, mild flowery odor.

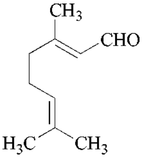
Industrial synthesis of nerolidol starts with linalool, which is converted into geranylacetone by using diketene, ethyl acetoacetate, or isopropenyl methyl ether, analogous to the synthesis of 2-methyl-2-hepten-6-one from 3-methyl-1-buten-3-ol (see page 16). Addition of acetylene and partial hydrogenation of the resultant dehydronerolidol produces a mixture of *cis*- and *trans*-nerolidol racemates.

Nerolidol is used as a base note in many delicate flowery odor complexes. It is also an intermediate in the production of vitamins E and K_1.

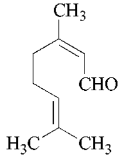
2.2.3. Aldehydes and Acetals

Among the acyclic terpene aldehydes, citral and citronellal hold key positions as fragrance and flavor chemicals, as well as starting materials for the synthesis of other terpenoids. Hydroxydihydrocitronellal is one of the most important fragrance compounds. Derivatives of these aldehydes, particularly the lower acetals, are also used as fragrance compounds. Acyclic sesquiterpene aldehydes are not very important as such, but they contribute to the characteristic fragrance and aroma of essential oils, for example, in the case of α- and β-sinensal and sweet orange oil (seepage 94).

Citral [*5392-40-5*], 3,7-dimethyl-2,6-octadien-1-al, $C_{10}H_{16}O$, M_r 152.24, occurs as *cis*- and *trans*-isomers (citral a and b, respectively) analogous to the corresponding alcohols, geraniol and nerol: citral a [*141-27-5*] (geranial), *bp* (2.7 kPa) 118 – 119 °C, d_4^{20} 0.8888, n_D^{20} 1.4898; citral b [*106-26-3*] (neral), *bp* (2.7 kPa) 120 °C, d_4^{20} 0.8869, n_D^{20} 1.4869.



Geranial (citral a)



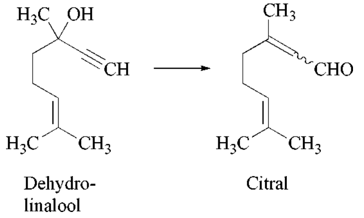
Neral (citral b)

Natural citral is nearly always a mixture of the two isomers. It occurs in lemongrass oil (up to 85 %), in *Litsea cubeba* oil (up to 75 %), and in small amounts in many other essential oils. The citrals are colorless to slightly yellowish liquids, with an odor reminiscent of lemon.

Since citral is an α,β-unsaturated aldehyde with an additional double bond, it is highly reactive and may undergo reactions such as cyclization and polymerization. Geraniol, citronellol, and 3,7-dimethyloctan-1-ol can be obtained from citral by stepwise hydrogenation. Citral can be converted into a number of addition compounds; the *cis*- and *trans*-isomers can be separated via the hydrogen sulfite addition compounds. The condensation of citral with active methylene groups is used on an industrial scale in the synthesis of pseudoionones, which are starting materials for ionones and vitamins.

Production. Since citral is used in bulk as a starting material for the synthesis of vitamin A, it is produced industrially on a large scale. Smaller quantities are also isolated from essential oils.

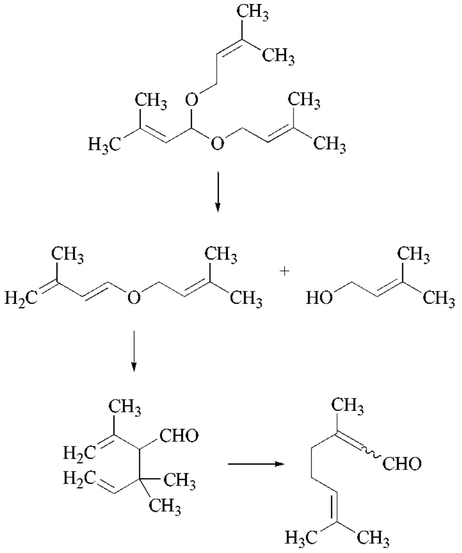
1) *Isolation from Essential Oils.* Citral is isolated by distillation from lemongrass oil (see p. page 98) and from *Litsea cubeba* oil (see p. page 106). It is the main component of these oils.
2) *Synthesis from Geraniol.* Currently, the most important synthetic procedures are vapor-phase dehydrogenation and oxidation of geraniol or geraniol–nerol mixtures. Catalytic dehydrogenation under reduced pressure using copper catalysts is preferred [51].
3) *Synthesis from Dehydrolinalool.* Dehydrolinalool is produced on a large scale from 2-methyl-2-hepten-6-one and acetylene (see page 16) and can be isomerized to citral in high yield by a number of catalysts. Preferred catalysts include organic orthovanadates [52], organic trisilyl oxyvanadates [53], and vanadium catalysts with silanols added to the reaction system [54].



Dehydro-linalool

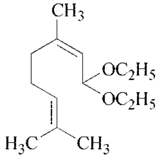
Citral

4) *Synthesis from Isobutene and Formaldehyde.* 3-Methyl-3-buten-1-ol, obtained from isobutene and formaldehyde [41], isomerizes to form 3-methyl-2-buten-1-ol [55]. However, it is also converted into 3-methyl-2-butenal by dehydrogenation and subsequent isomerization [56,57]. Under azeotropic conditions in the presence of nitric acid, 3-methyl-2-buten-1-ol and 3-methyl-2-butenal form an acetal (shown below) [58], which eliminates one molecule of 3-methyl-2-buten-1-ol at higher temperatures. The intermediate enol ether undergoes Claisen rearrangement followed by Cope rearrangement to give citral in excellent yield [59]:



Uses. Because of its strong lemon odor, citral is very important for aroma compositions such as citrus flavors. In perfumery it can be used only in neutral media due to its tendency to undergo discoloration, oxidation, and polymerization. Limiting IFRA recommendation. It is used as a starting material in the synthesis of ionones and methylionones, particularly β-ionone, which is an intermediate in vitamin A synthesis.

Citral diethyl acetal [*7492-66-2*], 3,7-dimethyl-2,6-octadien-1-al diethyl acetal, $C_{14}H_{26}O_2$, M_r 226.36, *bp* (2 kPa) 140 – 142 °C, d_4^{20} 0.8730, n_D^{20} 1.4503, is a colorless liquid with a flowery, warm-woody citrus odor. It is relatively stable in alkali and can, therefore, be used in soap.

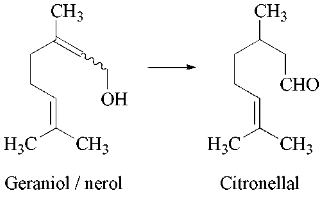


Citronellal [*106-23-0*], 3,7-dimethyl-6-octen-1-al, $C_{10}H_{18}O$, M_r 154.25, *bp* (101.3 kPa) 207 – 208 °C, d_4^{20} 0.851, n_D^{20} 1.4477, $[\alpha]_D^{20}$ + resp. − 15 °, $[\alpha]_D^{20}$ − 13.1 °, occurs in essential oils in its (+) and (−) forms, often together with the racemate. (+)-Citronellal [*2385-77-5*] occurs in citronella oil at a concentration of up to 45 %; *Backhousia citriodora* oil contains up to 80 % (−)-citronellal [*5949-05-3*]. Racemic citronellal [*26489-02-1*] occurs in a number of *Eucalyptus citriodora* oils at a concentration of up to 85 %.

Pure citronellal is a colorless liquid with a refreshing odor, reminiscent of balm mint. Upon catalytic hydrogenation, citronellal yields dihydrocitronellal, citronellol, or dihydrocitronellol, depending on the reaction conditions. Protection of the aldehyde group, followed by addition of water to the double bond in the presence of mineral acids or ion-exchange resins results in formation of 3,7-dimethyl-7-hydroxyoctan-1-al (hydroxydihydrocitronellal, see page 24). Acid-catalyzed cyclization to isopulegol is an important step in the synthesis of (−)-menthol (seepage 30).

Production. Citronellal is still isolated from essential oils in considerable quantities; it is also produced synthetically.

1) *Isolation from Essential Oils.* (+)-Citronellal is obtained from citronella oils by fractional distillation. (±)-Citronellal is isolated from *Eucalyptus citriodora* oil (see page 100); when necessary, it is purified by using an addition compound, e.g., the bisulfite derivative.
2) *Synthesis from Geraniol or Nerol.* (±)-Citronellal can be obtained by vapor-phase rearrangement of geraniol or nerol (see page 16) in the presence of, e.g., a barium-containing copper–chromium oxide catalyst [60].



3) *Synthesis from Citronellol.* (±)-Citronellal can also be obtained by dehydrogenation of citronellol (see page 19) under reduced pressure with a copper chromite catalyst [61].
4) *Synthesis from Citral.* Selective hydrogenation of citral to citronellal can be accomplished in the presence of a palladium catalyst in an alkaline alcoholic reaction medium [62].

Uses. Citronellal is used to a limited extent for perfuming soaps and detergents. Its main use is as a starting material for the production of isopulegol, citronellol, and hydroxydihydrocitronellal.

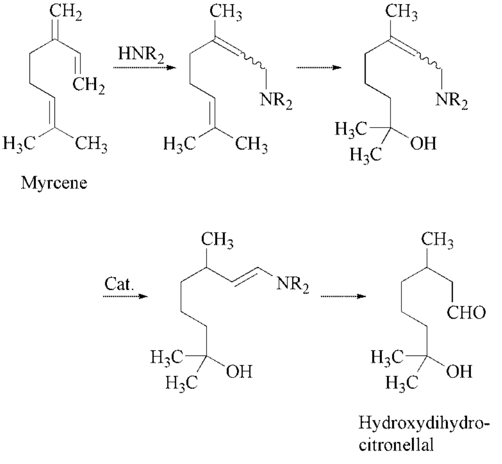
7-Hydroxydihydrocitronellal [*107-75-5*], hydroxycitronellal, 3,7-dimethyl-7-hydroxyoctan-1-al, $C_{10}H_{20}O_2$, M_r 172.27, *bp* (130 Pa) 85 – 87 °C, d_4^{20} 0.9220, n_D^{20} 1.4488, has been reported to occur in essential oils [63]. It is a colorless, slightly viscous liquid with a flowery odor reminiscent of linden blossom and lily of the valley. Commercially available hydroxycitronellal is either optically active or racemic, depending on the starting material used. Hydroxycitronellal prepared from (+)-citronellal, for example, has a specific rotation $[\alpha]_D^{20}$ + 9 to + 10 °.

Hydroxycitronellal is relatively unstable toward acid and alkali and is, therefore, sometimes converted into more alkali-resistant acetals, particularly its dimethyl acetal.

Production. The most important synthetic routes to hydroxydihydrocitronellal are listed below.

1) *Synthesis from Citronellal.* One of the oldest routes to hydroxycitronellal is the hydration of the citronellal bisulfite adduct (obtained at low temperature) with sulfuric acid, followed by decomposition with sodium carbonate. A more recent development is hydration of citronellal enamines or imines, followed by hydrolysis [64].
2) *Synthesis from Citronellol.* Citronellol (see page 19) is hydrated to 3,7-dimethyloctan-1,7-diol, for example, by reaction with 60 % sulfuric acid. The diol is dehydrogenated catalytically in the vapor phase at low pressure to highly pure hydroxydihydrocitronellal in excellent yield. The process is carried out in the presence of, for example, a copper–zinc catalyst [65]; at atmospheric pressure noble metal catalysts can also be used [66].
3) *Synthesis from 7-Hydroxygeranyl–Neryl Dialkylamine.* The starting material can be obtained by treatment of myrcene with a dialkylamine in the presence of an alkali dialkylamide, followed by hydration with sulfuric acid. The 7-hydroxygeranyl–neryl dialkylamine isomerizes to the corresponding 7-hy-

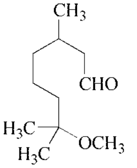
droxyaldehyde enamine in the presence of a palladium(II)–phosphine complex as catalyst. Hydrolysis of the enamine gives 7-hydroxydihydrocitronellal [67].



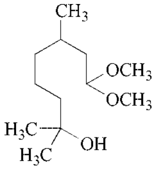
R = lower alkyl (C_1 - C_6)

Uses. Because of its fine, flowery odor, hydroxydihydrocitronellal is used in large quantities in many perfume compositions for creating linden blossom and lily of the valley notes. It is also used in other blossom fragrances such as honeysuckle, lily, and cyclamen. Limiting IFRA recommendation.

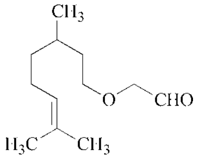
Methoxydihydrocitronellal [*3613-30-7*], 3,7-dimethyl-7-methoxyoctan-1-al, $C_{11}H_{22}O_2$, M_r 186.29, *bp* (60 Pa) 60 °C, n_D^{20} 1.4375, is a colorless liquid with a fresh, green, blossom odor and is used in perfumery in floral compositions for fresh-green nuances.



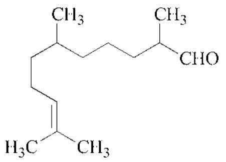
Hydroxydihydrocitronellal dimethyl acetal [*141-92-4*], 3,7-dimethyl-7-hydroxyoctan-1-al dimethyl acetal, $C_{12}H_{26}O_3$, M_r 218.34, *bp* (1.6 kPa) 131 °C, d_4^{20} 0.931, n_D^{20} 1.4419, is a colorless liquid with a weak, flowery odor. Since the acetal is stable to alkali, it is used occasionally in soap perfumes.



Citronellyloxyacetaldehyde [*7492-67-3*], $C_{12}H_{22}O_2$, M_r 198.30, *bp* (1.6 kPa) 128–130 °C, is a colorless, slightly viscous liquid with a delicate-flowery odor reminiscent of rose and lily of the valley. The aldehyde is obtained by hydrolysis (with dilute acetic acid) of its acetals, which are prepared from sodium citronellate and chloroacetaldehyde dialkyl acetals [68]. It is used in perfumery to obtain heavy-flowery effects.



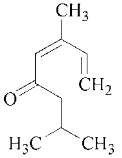
2,6,10-Trimethyl-9-undecenal [*141-13-9*], $C_{14}H_{26}O$, M_r 210.36, *bp* (1.2 kPa) 133–135 °C, d_4^{20} 0.8483, n_D^{20} 1.447–1.453, is a colorless to slightly yellow liquid with an intense aldehyde-waxy, slightly flowery odor. It is synthesized from hydrogenated pseudoionone (primarily the tetrahydro compound) and an alkyl chloroacetate by means of a glycidic ester condensation; this is followed by hydrolysis and decarboxylation.

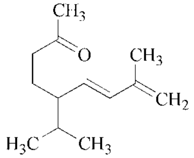


2,6,10-Trimethyl-9-undecenal is a richly fragrant compound that is used in flower compositions to obtain an aldehydic note.
Trade Names. Adoxal (Givaudan Roure), Farenal (Haarmann & Reimer).

2.2.4. Ketones

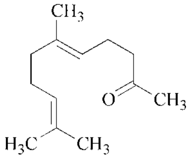
Unlike the terpene alcohols, aldehydes, and esters, acyclic terpene ketones are not particularly important as fragrance or flavor substances; thus, they are not discussed here in detail. 2-Methyl-2-hepten-6-one (see page 16) is an important intermediate in the synthesis of terpenoids. Its odor properties are not impressive. It occurs in nature as a decomposition product of terpenes. Tagetone [*6752-80-3*] is a major component of tagetes oil. Solanone [*1937-54-8*] and pseudoionone [*141-10-6*] are acyclic C_{13} ketones with a terpenoid skeleton. Solanone is one of the flavor-determining constituents of tobacco, pseudoionone is an intermediate in the synthesis of ionones (see page 36).


Tagetone


Solanone

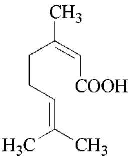
Geranylacetone [*689-67-8*], 6,10-dimethyl-5,9-undecadien-2-one, $C_{13}H_{22}O$, M_r 194.32, *bp* (1.3 kPa) 124 °C, d_4^{20} 0.8729, n_D^{20} 1.4674, occurs in *cis* as well as *trans* form and has been identified in fruits and in essential oils. It is a colorless liquid with a fresh-green, slightly penetrating, roselike odor.

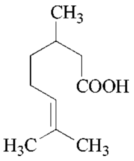
Geranylacetone is an intermediate in nerolidol synthesis (see page 21). It is used in perfumery in rose compositions, for example, in soap perfumes.


trans-Geranylacetone

2.2.5. Acids and Esters

Although a small amount of acyclic terpene acids such as geranic acid and citronellic acid occurs in many essential oils, often as esters, they are rarely used in perfume and flavor compositions.


cis-Geranic acid


Citronellic acid

Methyl geranate is an intermediate in α-damascone synthesis and is sometimes needed in the reconstitution of essential oils. However, the lower fatty acid esters (particularly the acetates) of the acyclic terpene alcohols geraniol, linalool, and citronellol are extremely important both as fragrance and as flavor substances. The acetates occur in many essential oils, sometimes in rather high amounts. Formates, propionates, and butyrates occur less frequently. As a result of the development of large-scale production processes for terpenes, the esters of acyclic terpene alcohols are nearly always made synthetically. All acyclic terpene esters that are used as fragrance and flavor materials can be prepared by direct esterification of the appropriate alcohols. However, special precautions are required for the esterification of linalool.

Because the lower fatty acid esters of geraniol, linalool, and citronellol are important contributors to the odor of many essential oils, these esters are widely used in the reconstitution of such oils, as well as in perfume and flavor compositions. The acetates, particularly linalyl acetate, are most widely used. The use of formates is limited by their relative instability. Higher esters are not important in terms of quantity, but are indispensable for creating specific nuances.

In aroma compositions, fatty acid esters of the acyclic terpene alcohols are used for obtaining citrus notes and for rounding off other flavor types.

The most important and most frequently used acyclic terpene esters are described below.

2.2.5.1. Geranyl and Neryl Esters

Geraniol is described on page 15, nerol on page 16.

Geranyl formate [*105-86-2*], $C_{11}H_{18}O_2$, M_r 182.26, *bp* (101.3 kPa) 229 °C (decomp.), d_4^{20} 0.9209, n_D^{20} 1.4659, is a liquid with a fresh, crisp-herbal-fruity rose odor. It is used as a modifier of, among others, rose, geranium, and neroli compositions.

Geranyl acetate [*105-87-3*], $C_{12}H_{20}O_2$, M_r 196.29, *bp* (1.5 kPa) 98 °C, d_4^{20} 0.9136, n_D^{20} 1.4624, occurs in varying amounts in many essential oils: up to 60 % in oils from *Callitris* and *Eucalyptus* species, and up to 14 % in palmarosa oil. A smaller amount occurs in, for example, geranium, citronella, petitgrain, and lavender oils. Geranyl acetate is a liquid with a fruity, rose note reminiscent of pear and slightly of lavender. It is used frequently in perfumery to create not only flowery-fruity nuances (e.g., rose), but also for citrus and lavender notes. A small amount is added to fruit aromas for shading.

Geranyl propionate [*105-90-8*], $C_{13}H_{22}O_2$, M_r 210.32, *bp* (101.3 kPa) 253 °C, d_4^{20} 0.9207, n_D^{20} 1.459, has a fruity rose odor and is used in perfumery in heavy blossom fragrances with a secondary fruity note.

Geranyl isobutyrate [*2345-26-8*], $C_{14}H_{24}O_2$, M_r 224.34, *bp* (101.3 kPa) 265 °C, d_4^{20} 0.9209, n_D^{20} 1.4576, is a liquid with a fruity rose odor. It is used in floral perfume compositions and in fruit flavors.

Geranyl isovalerate [*109-20-6*], $C_{15}H_{26}O_2$, M_r 238.37, *bp* (101.3 kPa) 279 °C, d_4^{20} 0.8920, n_D^{20} 1.4640, is a liquid with a strongly fruity rose odor. It is used in perfume and flavor compositions.

Neryl acetate [*141-12-8*], $C_{12}H_{20}O_2$, M_r 196.29, *bp* (3.4 kPa) 134 °C, d_4^{20} 0.9110, n_D^{20} 1.4624, is the *cis*-isomer of geranyl acetate. It is present in helichrysum oil and has also been identified in, among others, neroli oil and petitgrain oil Bigarade. It is a colorless, flowery-sweet-smelling liquid and is used in perfumery for blossom compositions (e.g., orange blossom and jasmin).

2.2.5.2. Linalyl and Lavandulyl Esters

Among the linalyl esters (linalool, see page 16), the acetate is by far the most important fragrance and flavor substance. The formate, propionate, and butyrates are used in small amounts.

Linalyl formate [*115-99-1*], $C_{11}H_{18}O_2$, M_r 182.26, *bp* (1.3 kPa) 100 – 103 °C, d_4^{20} 0.9134, n_D^{20} 1.4530, is a liquid with a fruity odor, reminiscent of bergamot. Linalyl formate is moderately stable and is used in lavender fragrances and eaux de cologne.

Linalyl acetate [*115-95-7*], $C_{12}H_{20}O_2$, M_r 196.29, *bp* (101.3 kPa) 220 °C, d_4^{20} 0.8951, n_D^{20} 1.4500, occurs as its (−)-isomer [*16509-46-9*] as the main component of lavender oil (30 – 60 %, depending on the origin of the oil), of lavandin oil (25 – 50 %, depending on the species), and of bergamot oil (30 – 45 %). It has also been found in clary sage oil (up to 75 %) and in a small amount in many other essential oils. (±)-Linalyl acetate [*40135-38-4*] is a colorless liquid with a distinct bergamot-lavender odor.

Production. Linalyl acetate is synthesized by two methods:

1) Esterification of linalool requires special reaction conditions since it tends to undergo dehydration and cyclization because it is an unsaturated tertiary alcohol. These reactions can be avoided as follows: Esterification with ketene in the presence of an acidic esterification catalyst below 30 °C results in formation of linalyl acetate without any byproducts [69]. Esterification can be achieved in good yield, with boiling acetic anhydride, whereby the acetic acid is distilled off as it is formed; a large excess of acetic anhydride must be maintained by continuous addition of anhydride to the still vessel [32]. Highly pure linalyl acetate can be obtained by transesterification of *tert*-butyl acetate with linalool in the presence of sodium methylate and by continuous removal of the *tert*-butanol formed in the process [70].
2) Dehydrolinalool, obtained by ethynylation of 2-methyl-2-hepten-6-one, can be converted into dehydrolinalyl acetate with acetic anhydride in the presence of an acidic esterification catalyst. Partial hydrogenation of the triple bond to linalyl acetate can be carried out with, for example, palladium catalysts deactivated with lead [71].

Uses. Linalyl acetate is used extensively in perfumery. It is an excellent fragrance material for, among others, bergamot, lilac, lavender, linden, neroli, ylang-ylang, and phantasy notes (particularly chypre). Smaller amounts are used in other citrus products. Since linalyl acetate is fairly stable toward alkali, it can also be employed in soaps and detergents.

Linalyl propionate [*144-39-8*], $C_{13}H_{22}O_2$, M_r 210.31, *bp* (101.3 kPa) 226 °C, d_4^{20} 0.9009, n_D^{20} 1.4505, is a liquid with a fresh bergamot note, reminiscent of lily of the valley. It is used in perfumery in, for example, bergamot, lavender, and lily of the valley compositions.

Linalyl butyrate [*78-36-4*], $C_{14}H_{24}O_2$, M_r 224.34, *bp* (101.3 kPa) 232 °C, d_4^{20} 0.8987, n_D^{20} 1.4523, is a liquid with a fruity bergamot note and a subdued animalic tone. It is used in lavender perfumes and in many blossom compositions.

Linalyl isobutyrate [*78-35-3*], $C_{14}H_{24}O_2$, M_r 224.34, *bp* (20 Pa) 63 – 65 °C, d_4^{20} 0.8991, n_D^{20} 1.4513, has a fresh-fruity lavender odor, which is more refined than that of the butyrate. It is used in lavender compositions and in several flowery notes.

Lavandulyl acetate [*25905-14-0*] (for formula of lavandulol, see Section 2.2.2), $C_{12}H_{20}O_2$, M_r 196.29, *bp* (1.7 kPa) 106 – 107 °C, d_4^{20} 0.9129, n_D^{20} 1.4561, occurs in its (−)-form at a concentration of ca. 1 % in French lavender oil and lavandin oil. It is a liquid with a fresh-herbal rose odor and is used in perfumery for lavender- and lavandin-oil reconstitutions.

One synthetic route to lavandulyl acetate starts with prenyl acetate, which dimerizes in the presence of a Friedel–Crafts catalyst, such as boron trifluoride–diacetic acid [72].

2.2.5.3. Citronellyl Esters

The following citronellyl esters (citronellol, see page 19) are used in relatively large amounts as fragrance and flavor materials:

Citronellyl formate [*105-85-1*], $C_{11}H_{20}O_2$, M_r 184.28, *bp* (2 kPa) 97 – 98 °C, d_4^{20} 0.8972, n_D^{20} 1.4556, is a liquid with a strongly fruity, roselike odor, which is suitable for fresh top notes in rose and lily of the valley fragrances.

Citronellyl acetate [*67650-82-2*], $C_{12}H_{22}O_2$, M_r 198.30, *bp* (101.3 kPa) 240 °C, d_4^{20} 0.8889, n_D^{20} 1.4515, occurs in many essential oils either as one of its optical isomers or as the racemate. The odor of racemic citronellyl acetate differs little from that of the optical isomers. (±)-Citronellyl acetate is a liquid with a fresh-fruity rose odor. It is often used as a fragrance, for example, for rose, lavender, and geranium notes as well as for eaux de cologne with citrus nuances. Since it is relatively stable to alkali, it can be used in soaps and detergents. Citrus flavors acquire specific character through the addition of citronellyl acetate; it is also used to round off other fruit flavors.

Citronellyl propionate [*141-14-0*], $C_{13}H_{24}O_2$, M_r 212.33, *bp* (2 kPa) 120 – 124 °C, d_4^{20} 0.8851, n_D^{20} 1.4452, is a fresh-fruity, roselike smelling liquid. It is used in perfume and flavor compositions in the same way as the acetate.

Citronellyl isobutyrate [*97-89-2*], $C_{14}H_{26}O_2$, M_r 226.36, *bp* (1.6 kPa) 131 – 132 °C, d_4^{20} 0.8760, n_D^{20} 1.4418, is a liquid with a sweet-fruity note and is used in perfumery for fruity-floral nuances.

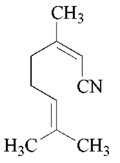
Citronellyl isovalerate [*68922-10-1*], $C_{15}H_{28}O_2$, M_r 240.39, *bp* (4 kPa) 194 – 196 °C, d_4^{20} 0.8790, n_D^{20} 1.4429, has a heavy, rosy-herbal odor and is used in oriental perfume compositions among others.

Citronellyl tiglate [*24717-85-9*] (with *trans*-$CH_3CH{=}C(CH_3)COOH$ as the acid component), $C_{15}H_{26}O_2$, M_r 238.37, *bp* (900 Pa) 144 –145 °C, d_4^{20} 0.9043, is a liquid with a flowery rosy, fruity, mushroom-like odor. It is used in geranium oil reconstitutions.

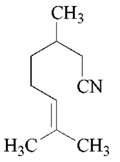
2.2.6. Miscellaneous Compounds

The number of nitrogen- and sulfur-containing derivatives of acyclic terpenoids that are known to be important fragrance and flavor substances is even smaller than in the non-terpenoid aliphatic series discussed in Section 2.1.6. However, a few nitriles are used in rather large amounts in soap perfumes because of their relatively high stability toward alkali.

Geranyl nitrile [*5146-66-7*], geranonitrile, $C_{10}H_{15}N$, M_r 149.24, *bp* (1.3 kPa) 110 °C, d_4^{20} 0.8642, n_D^{20} 1.4759, occurs as a mixture of its *cis*- and *trans*-isomers. It is a liquid with a crisp-fresh, lemon-like, green odor. The nitrile can be prepared from citral by reaction with hydroxylamine and subsequent dehydration with acetic anhydride.
Trade Name. Citralva (IFF).



Citronellyl nitrile [*51566-62-2*], $C_{10}H_{17}N$, M_r 151.25, *bp* (2 kPa) 110 – 111 °C, d_4^{20} 0.845 – 0.846, n_D^{20} 1.4485 – 1.4500, is a colorless liquid with a strong, lemon-like odor. The nitrile can be prepared from citronellal oxime in the same way as geranic acid nitrile.
Trade Name. Agrunitril (DRAGOCO).

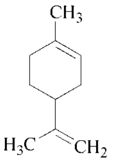


2.3. Cyclic Terpenes

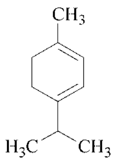
2.3.1. Hydrocarbons

Cyclic terpene hydrocarbons occur in essential oils, sometimes in large amounts. They often serve as starting materials for the synthesis of fragrance and flavor compounds. By themselves they generally contribute relatively little to fragrance and aroma. They are used mainly in household perfumery and for reconstitution of essential oils.

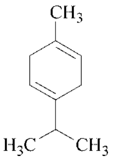
Of the various types of monocyclic terpene hydrocarbons, those with the *p*-menthadiene structure are the most important. Examples are as follows:



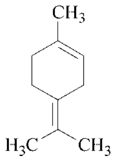
Limonene



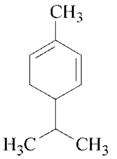
α-Terpinene



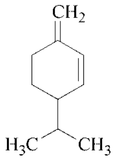
γ-Terpinene



Terpinolene

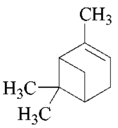


α-Phellandrene

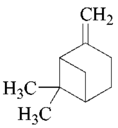


β-Phellandrene

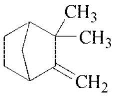
Of the bicyclic terpene hydrocarbons, the pinenes are by far the most important industrially. Camphene and 3-carene are used as starting materials for fragrance compounds.



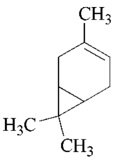
α-Pinene



β-Pinene

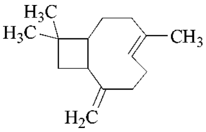


Camphene

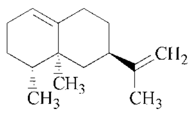


3-Carene

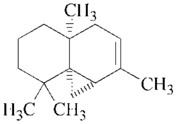
Many cyclic sesquiterpenes of various structural types have been isolated from essential oils. As in the case of the cyclic monoterpene hydrocarbons, a number of the cyclic sesquiterpenes are used as starting materials in the synthesis of fragrance and flavor compounds or for the reconstitution of essential oils. Typical examples are as follows:

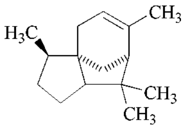


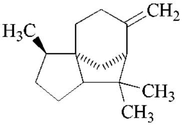
Caryophyllene

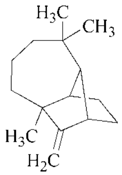


(+)-Valencene

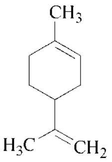

Thujopsene


α-Cedrene


β-Cedrene


Longifolene

Limonene [*138-86-3*], 1,8-*p*-menthadiene, $C_{10}H_{16}$, M_r 136.24, *bp* (101.3 kPa) 178 °C, d_4^{20} 0.8411, n_D^{20} 1.4726, $[\alpha]_D^{20}$ + or − 126.3 °; (+)-limonene [*5989-27-5*] and (−)-limonene [*5989-54-8*] as well as the racemate (dipentene) [*7705-14-8*] occur abundantly in many essential oils. The (+)-isomer is present in citrus peel oils at a concentration of over 90 %; a low concentration of the (−)-isomer is found in oils from the *Mentha* species and conifers.

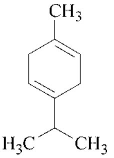


Limonene is a liquid with lemon-like odor. It is a reactive compound; oxidation often yields more than one product. Dehydrogenation leads to *p*-cymene. Limonene can be converted into cyclic terpene alcohols by hydrohalogenation, followed by hydrolysis. Nitrosyl chloride adds selectively to the endocyclic double bond; this reaction is utilized in the manufacture of (−)-carvone from (+)-limonene (see page 35).

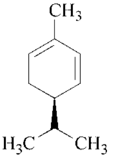
(+)-Limonene is obtained in large amounts as a byproduct in the production of orange juice; (−)-limonene is isolated in relatively small quantities from essential oils. Racemic limonenes, which are commercially available under the name dipentene, are formed as (by)products in many acid-catalyzed isomerizations of α- and β-pinene. Distillation of the so-called dipentene fraction yields limonenes in varying degrees of purity.

The limonenes are used as fragrance materials for perfuming household products and as components of artificial essential oils. (IFRA recommendation)

γ-Terpinene [*99-85-4*], 1,4-*p*-menthadiene, $C_{10}H_{16}$, M_r 136.24, *bp* (101.3 kPa) 183 °C, d_4^{20} 0.8493, n_D^{20} 1.4747, is a colorless liquid with an herbaceous citrus odor and can be prepared by isomerization of limonene.

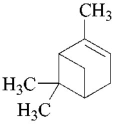


(−)-α-Phellandrene [*4221-98-1*], 1,5-*p*-menthadiene, $C_{10}H_{16}$, M_r 136.24, *bp* (99 kPa) 172 °C, d_4^{20} 0.8410, n_D^{20} 1.4708, $[\alpha]_D^{20}$ − 183 °, is a colorless liquid with a citrus odor and a slight peppery note. It is isolated, for example, from *Eucalyptus dives* oil.



Pinenes are widespread, naturally occurring terpene hydrocarbons. The α- and β-forms occur in varying ratios in essential oils.

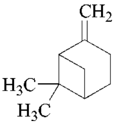
α-Pinene [*80-56-8*], 2-pinene, $C_{10}H_{16}$, M_r 136.24, *bp* (101.3 kPa) 156 °C, d_4^{20} 0.8553, n_D^{20} 1.4662, $[\alpha]_D^{20}$ + or − 51.9 °, is the most widespread pinene isomer. (+)-α-Pinene [*7785-70-8*] occurs, for example, in oil from *Pinus palustris*Mill. at a concentration up to 65 %; oil from *Pinus pinaster* Soland. and American oil from *Pinus caribaea* contain 70 % and 70 – 80 %, respectively of the (−)-isomer [*7785-26-4*].


α-Pinene

α-Pinene undergoes many reactions, of which the following are used in the fragrance industry: Upon hydrogenation α-pinene is converted to pinane, which has become an important starting material in the industrial processes used in the fragrance and flavor industry. α-Pinene can be isomerized to β-pinene with high selectivity for β-pinene formation [73]. Hydration with simultaneous ring opening yields terpineol and *cis*-terpin hydrate. Pyrolysis of α-pinene yields a mixture of ocimene and alloocimene.

Pure α-pinene is obtained by distillation of turpentine oils (see page 118). As a fragrance substance it is used to improve the odor of industrial products. However, it is far more important as a starting material in industrial syntheses, for example, terpineols (see page 33), borneol (see page 34), and camphor (see page 36).

β-Pinene [*127-91-3*], 2(10)-pinene, $C_{10}H_{16}$, M_r 136.24, *bp* (101.3 kPa) 164 °C, d_4^{20} 0.8712, n_D^{20} 1.4763, $[\alpha]_D^{20}$ + or – 22.6 °, occurs in many essential oils. Optically active and racemic β-pinenes are present in turpentine oils, although in smaller quantities than α-pinene.



β-Pinene

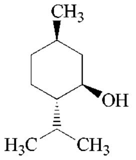
β-Pinene is similar to α-pinene in its reactions. Pyrolytic cleavage of β-pinene to myrcene, the starting material for acyclic terpenes, is used on an industrial scale. Addition of formaldehyde results in the formation of nopol; nopyl acetate is used as a fragrance material. β-Pinene is produced in large quantities by distillation of turpentine oils. It is used as a fragrance material in household perfumery. However, most β-pinene is used in the production of myrcene.

2.3.2. Alcohols and Ethers

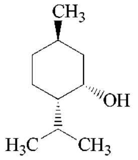
Although cyclic terpene alcohols occur widely in nature, few have the physiological properties that make them important fragrance or flavor compounds. Exceptions are α-terpineol and (–)-menthol, the latter because of its cooling/refreshing effect. Of the bicyclic monoterpene alcohols, borneol deserves mention.

Many cyclic sesquiterpene alcohols are key odor components in essential oils, for example, cedrol in cedarwood oil, the vetiverols in vetiver oil, and the santalols in sandalwood oil. Since these alcohols have not yet been synthesized on an industrial scale, they are described under the oil in which they occur (Chap. 3). Some of their derivatives, however, are discussed in this section.

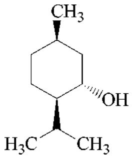
Menthol, *p*-menthan-3-ol, $C_{10}H_{20}O$, M_r 156.27, has three asymmetric carbon atoms in its cyclohexane ring and, therefore, occurs as four pairs of optical isomers. The configuration of four of these isomers is given below; the other four are their mirror images.



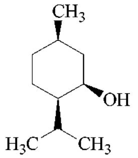
(–)-Menthol



(+)-Neomenthol



(+)-Isomenthol



(+)-Neoisomenthol

(–)-Menthol is the isomer that occurs most widely in nature. It is the main component of peppermint and cornmint oils obtained from the *Mentha piperita* and *Mentha arvensis* species. Esterified menthol also occurs in these oils (e.g., as the acetate and isovalerate). Other menthol stereoisomers may be present in these oils as well.

Physical Properties. The eight optically active menthols differ in their organoleptic properties [74]. (–)-Menthol has a characteristic peppermint odor and also exerts a cooling effect. The other isomers do not possess this cooling effect and are, therefore, not considered to be "refreshing". (±)-Menthol occupies an intermediate position; the cooling effect of the (–)-menthol present is distinctly perceptible.

The enantiomeric menthols have identical physical properties (apart from their specific rotation), but the racemates differ from the optically active forms in, for example, their melting points. Although the differences between the boiling points of the stereoisomers are small, the four racemates can be separated from each other by fractional distillation. Boiling points (in °C at 101.3 kPa) are as follows:

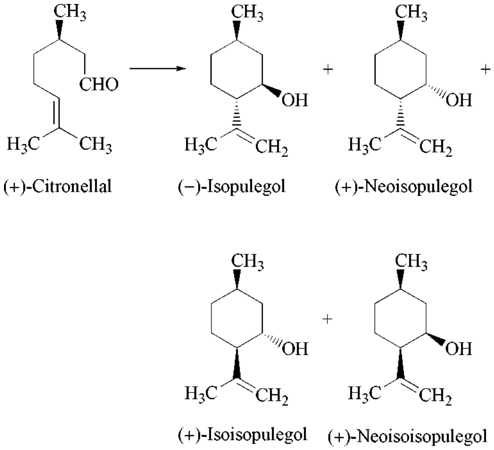
Neomenthol	211.7
Neoisomenthol	214.6
Menthol	216.5
Isomenthol	218.6

Other physical constants of commercially available levorotatory and racemic menthols are: (−)-menthol [*2216-51-5*], *mp* 43 °C, n_D^{20} 1.4600, $[\alpha]_D^{20}$ −50 °; (±)-menthol [*15356-70-4*], *mp* 38 °C, n_D^{20} 1.4615.

Chemical Properties. Hydrogenation of menthols yields *p*-menthane; oxidation with chromic acid or catalytic dehydrogenation yields menthones. Dehydration under mild conditions yields 3-*p*-menthene as the main product. Reaction with carboxylic acids or their derivatives yields menthyl esters, which are used mainly as aroma substances and in pharmaceutical preparations and formulations. The esterification of menthols with benzoic acid is used on an industrial scale in the resolution of racemic menthol.

Production. Many industrial processes exist for the production of menthols. For (−)-menthol, isolation from peppermint oil (see Mint Oils, page 107) competes with partial and total syntheses. When an optically active compound is used as a starting material, optical activity must be retained throughout the synthesis, which generally consists of several steps. Total syntheses or syntheses starting from optically inactive materials require either resolution of racemic mixtures or asymmetric synthesis of an intermediate. Recently used processes are the following:

1) *(−)-Menthol from Cornmint Oil. Mentha arvensis* oils, which may contain 70 – 80 % free (−)-menthol, are cooled and the crystals separated by centrifugation. Since the crystalline product contains traces of cornmint oil, this menthol has a slightly herbaceous-minty note. Pure (−)-menthol is obtained by recrystallization from solvents with low boiling points.
2) *(−)-Menthol from Dementholized Cornmint Oil.* Dementholized cornmint oil, from which (−)-menthol has been removed by crystallization and which still contains 40 – 50 % free menthol, can be reused for producing (−)-menthol. The fairly large quantity of (−)-menthone in the oil (30 – 50 %) is hydrogenated to form a mixture of mainly (−)-menthol and (+)- neomenthol; the (−)-menthyl esters present (chiefly (−)-menthyl acetate) are saponified. Additional (−)-menthol is then separated from other components by crystallization, distillation, or via the boric acid esters.
3) *(−)-Menthol from (+)-Citronellal.* This process uses the readily occurring cyclization of citronellal to isopulegol. (+)-Citronellal can be isolated with an optical purity of ca. 80 % from citronella oil (see page 98). Alternatively, it can be synthesized with a purity of 98 % from dialkylgeranylamine (obtained from myrcene and a dialkylamine) by enantioselective isomerization to (+)-citronellaldialkylenamine followed by hydrolytic cleavage to (+)-citronellal. Isomerization is effected in the presence of a chiral rhodium–phosphine complex as a catalyst [75]. (+)-Citronellal is cyclized in the presence of acidic catalysts (e.g., silica gel) to give a mixture of optically active isopulegol isomers containing ca. 20 % of the corresponding racemates:



(−)-Isopulegol can be isolated from this mixture and hydrogenated to (−)-menthol. The remaining isopulegol stereoisomers can be partly reconverted into (+)-citronellal by pyrolytic cleavage and reused in the cyclization procedure [76].

The isopulegol mixture can also be hydrogenated to produce a mixture of menthols; the individual stereoisomers are then separated by distillation. To obtain optically pure (−)-menthol, a resolution step involving a suitable crystalline derivative (such as the benzoate) is required. The undesired stereoisomeric menthols, mainly (+)-neomenthol and (+)-isomenthol, are epimerized to an equilibrium mixture (e.g., by heating in the presence of sodium menthylate). (−)-Menthol is then again separated from the mixture.

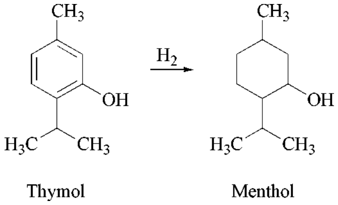
4) *(−)-Menthol from (−)-Piperitone or Piperitol.* (−)-Menthol can also be prepared from (−)-piperitone, the main component of *Eucalyptus dives* Typus oils. Hydrogenation in the presence of Raney nickel yields a mixture of menthols, from which (−)-menthol can be separated by crystallization and saponification of its chloroacetate.

   Analogously, (+)-*trans*-piperitol (obtained from α- or β-phellandrene via piperityl chloride [77]) can be hydrogenated to give a mixture of 97 % (+)-isomenthol and 3 % (+)-menthol. Pure (+)-isomenthol is obtained by crystallization and undergoes rearrangement to give an equilibrium mixture of (+)-neomenthol and (−)-menthol; the latter is separated by distillation.

5) *(−)-Menthol from (+)-3-Carene.* An Indian manufacturing process for (−)-menthol starts from 3-carene, the major component of Indian turpentine oil (55 – 65 %). (+)-3-Carene isomerizes to (+)-2-carene, which can be pyrolyzed to (+)-*trans*-2,8-*p*-menthadiene. Isomerization of the latter yields (+)-isoterpinolene, which is hydrogenated to give > 50 % (+)-3-*p*-menthene. Epoxidation and subsequent rearrangement lead to a menthone–isomenthone mixture, which gives a mixture of menthols when it is catalytically hydrogenated. Fractional distillation and crystallization yield commercially acceptable (−)-menthol [78].

6) *(−)-Menthol from* (±)-Menthol. (±)-Menthol can be prepared via several routes and subsequently resolved into the optical isomers:

   a) Racemic menthol can be synthesized by hydrogenation of thymol. This yields a mixture containing the four stereoisomeric menthols in various proportions. (±)-Menthol is separated from the other isomers by distillation.

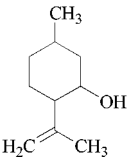


   The remaining isomeric menthols, neomenthol, isomenthol, and a trace of neoisomenthol, can be epimerized, under the conditions used for the thymol hydrogenation, to give ca. 6 : 3 : 1 equilibrium mixture of (±)-menthol, (±)-neomenthol, and (±)-isomenthol, respectively. (±)-Menthol can, again, be distilled from the equilibrium mixture.

   b) (±)-Menthol can be resolved into its optical antipodes by several routes. A large-scale industrial process utilizes selective crystallization of either (+)- or (−)-menthyl benzoate by seeding saturated solutions or supercooled melts of (±)-menthyl benzoates with crystals of (+)- or (−)-menthyl benzoate. Pure (+)- or (−)-menthol is obtained following hydrolysis of the esters [79]. The undesired (+)-menthol can be reconverted into the racemate. Biochemical resolution methods have also been developed [80].

Uses. Because of its cooling and refreshing effect, (−)-menthol is used in large quantities in cigarettes, cosmetics, toothpastes, chewing gum, sweets, and medicines. (±)-Menthol can be used in medicines and liniments.

Isopulegol, 8-*p*-menthen-3-ol, $C_{10}H_{18}O$, M_r 154.25, pure (−)-isopulegol [*89-79-2*], *bp* (1 kPa) 74 °C, d_4^{26} 0.9062, n_D^{26} 1.4690, $[\alpha]_D^{26}$ − 23.6 °. Like menthol, isopulegol has three asymmetric carbon atoms and, therefore, four stereoisomers, each occurring as a pair of optically active antipodes.

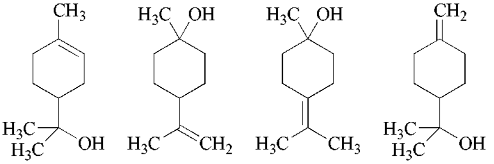


The isopulegols occur in a large number of essential oils, often in optically active or partly racemic form. Since citronellal readily cyclizes to isopulegol, the latter occurs frequently in citronellal-containing essential oils, in which it is formed during the recovery of the oil.

Isopulegol produced industrially from (+)-citronellal is a mixture of isomers containing a high percentage of (−)-isopulegol. The isopulegols are colorless liquids with a minty-herbaceous odor. They are converted into the corresponding menthols by means of hydrogenation. Cyclization of citronellal, in the presence of acidic catalysts, yields a mixture of isomeric isopulegols; (+)-citronellal obtained synthetically or from citronella oil is most frequently used as the starting material.

Isopulegol is used in perfumery in various blossom compositions, as well as for geranium notes. It is an important intermediate in (−)-menthol production.

Terpineols are unsaturated monocyclic terpene alcohols and are formed by acid-catalyzed hydration of pinenes; α-, β-, γ-, and δ-isomers exist:



α β γ δ

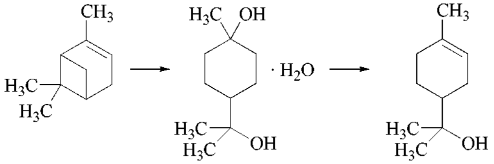
α- and β-Terpineol occur in optically active forms and as racemates. α-Terpineol is an important commercial product. It occurs in a large number of essential oils, primarily as (−)-α-terpineol (for example, in conifer and lavandin oils). Small quantities of (+)- and (±)-α-terpineol are found in many other essential oils; β-, γ-, and δ-terpineol do not occur widely in nature.

α-Terpineol [*98-55-5*], 1-*p*-menthen-8-ol, $C_{10}H_{18}O$, M_r 154.25, *mp* (pure enantiomers) 40 – 41 °C, *mp* (racemate) 35 °C, *bp* (101.3 kPa) 218 – 219 °C, d_4^{20} 0.9357, n_D^{20} 1.479, $[\alpha]_D$ + 106.4 ° (solution in ether, 4 %) is a colorless, crystalline solid, smelling of lilac. The most important commercial grade of terpineol consists of a liquid mixture of isomers, that contains mainly α-terpineol and a considerable amount of γ-terpineol. This mixture has a stronger lilac odor than does pure crystalline α-terpineol.

Hydrogenation of α-terpineol yields *p*-menthan-8-ol. Terpineol is readily dehydrated by acids, yielding a mixture of unsaturated cyclic terpene hydrocarbons. Under mildly acidic conditions, terpin hydrate is formed. The most important reaction for the fragrance industry is esterification, particularly acetylation to terpinyl acetate.

Production. Although α-terpineol occurs in many essential oils, only small quantities are isolated, e.g., by fractional distillation of pine oils.

A common industrial method of α-terpineol synthesis consists of the hydration of α-pinene or turpentine oil with aqueous mineral acids to give crystalline *cis*-terpin hydrate (*mp* 117 °C), followed by partial dehydration to α-terpineol. Suitable catalysts are weak acids or acid-activated silica gel [81].



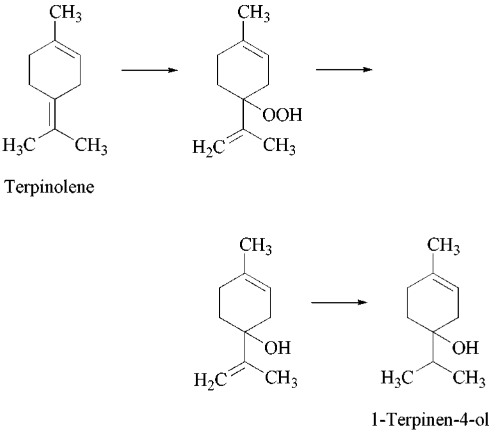
α-Pinene Terpin hydrate α-Terpineol plus isomers

Selective conversion of pinene, 3-carene, and limonene or dipentene to terpineol, without terpin hydrate formation, is also used. Addition of organic acids (weak acids require catalytic amounts of mineral acids) produces terpinyl esters, which are subsequently hydrolyzed to terpineol, sometimes in situ.

Uses. Terpineol with its typical lilac odor is one of the most frequently used fragrance compounds. It is stable and inexpensive, and is used in soaps and cosmetics.

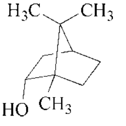
1-Terpinen-4-ol [*562-74-3*], 1-*p*-menthen-4-ol, $C_{10}H_{18}O$, M_r 154.25, *bp* (101.3 kPa) 212 °C, *bp* (500 Pa) 73.5 °C, d^{20} 0.9315, n_D^{20} 1.4799, occurs as (+)-, (−)-, and racemic 1-terpinen-4-ol in many essential oils (e.g., from *Pinus* and *Eucalyptus* species) and in lavender oil. It is a colorless liquid with a spicy, nutmeg-like, woody-earthy, and also lilac-like odor.

1-Terpinen-4-ol is a byproduct in the synthesis of terpineol from terpin hydrate, and occurs in commercial terpineol. Pure 1-terpinen-4-ol can be prepared from terpinolene by photosensitized oxidation, reduction of the resulting 1-methyl-4-isopropenyl-1-cyclohexene-4-hydroperoxide, and selective hydrogenation of the corresponding alcohol [82].

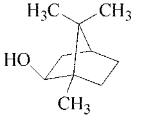


It is used, for example, in artificial geranium and pepper oils and in perfumery for creating herbaceous and lavender notes.

Borneol [*507-70-0*], 2-bornanol, $C_{10}H_{18}O$, M_r 154.25, *mp* (pure enantiomers) 208 °C, *mp* (racemate) 210.5 °C, d_4^{20} 1.011, $[\alpha]_D^{20}$ + or − 37.7 °, is a bicyclic terpene alcohol. Borneol is an *endo* isomer; the corresponding *exo* isomer is isoborneol [*124-76-5*]:



(−)-Borneol

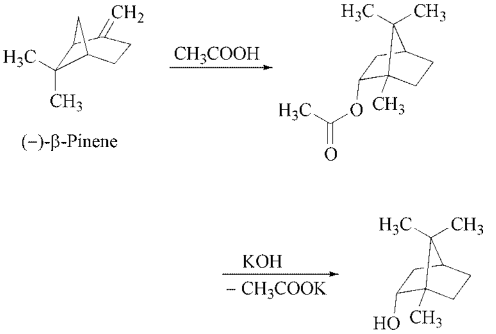


(+)-Isoborneol

Borneol occurs abundantly in nature as a single enantiomer or, less frequently, as the racemate. (−)-Borneol [*464-45-9*] occurs particularly in oils from Pinaceae species and in citronella oil. (+)-Borneol [*464-43-7*] is found, for example, in camphor oil (Hon-Sho oil), in rosemary, lavender, and olibanum oils.

Borneol is a colorless, crystalline solid. (+)-Borneol has a camphoraceous odor, with a slightly sharp, earthy-peppery note, which is less evident in (−)-borneol. Commercial borneol is often levorotatory ($[\alpha]_D^{20}$ − 18 to − 28 ° in ethanol), and contains (−)-borneol and up to 40 % isoborneol.

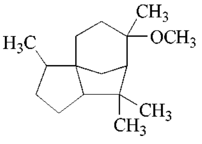
Borneol is oxidized to camphor with chromic or nitric acid; dehydration with dilute acids yields camphene. Borneol is readily esterified with acids, but on an industrial scale bornyl esters are prepared by other routes. For example, levorotatory borneol is synthesized industrially from levorotatory pinenes by Wagner-Meerwein rearrangement with dilute acid, followed by hydrolysis of the resulting esters [83].



Borneol is used in the reconstitution of the essential oils in which it occurs naturally.

Cedryl methyl ether [*19870-74-7*], 1*H*-3a,7-methanoazulene, octahydro-6-methoxy-3,6,8,8-tetramethyl-(6*β*), and [*67874-81-1*], 1*H*-3a,7-methanoazulene, octahydro-6-methoxy-3,6,8,8-tetramethyl-(6*α*), $C_{16}H_{18}O$, M_r 236.40, d_{25}^{25} 0.974 – 0.979, n_D^{20} 1.494 – 1.498, is a colorless liquid with a fine cedarwood odor and a distinct amber nuance. It is prepared by methylation of cedrol and is used in perfumes, soaps, and cosmetics.

Trade Name. Cedramber (IFF).

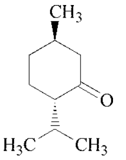


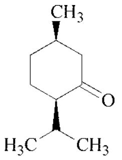
2.3.3. Aldehydes and Ketones

Cyclic terpene aldehydes occur in essential oils only in low concentration. These aldehydes are seldom used as single fragrance compounds.

A few of the cyclic terpene ketones are commercially important as fragrance and flavor compounds, for example, menthone and carvone, which have the *p*-menthane skeleton, and the ionones, which have a (trimethylcyclohexenyl)alkenone skeleton. The ionones and their methyl-substituted homologues are some of the most valuable fragrance materials. Some cyclic terpene ketones are the main components of essential oils (e.g., camphor in camphor oil); others, although not main components, may be essential for a fragrance (e.g., β-damascenone, which is an important component of Bulgarian rose oil; see Rose Oils, page 114). The cyclic sesquiterpene ketone, nootkatone, is one of the characteristic components of grapefruit aroma.

Menthone, *p*-menthan-3-one, $C_{10}H_{18}O$, M_r 154.25, exists as two stereoisomers, menthone and isomenthone, each of which occurs as a pair of enantiomers, due to the two asymmetric centers present in the molecule.


(−)-Menthone


(+)-Isomenthone

Both stereoisomers occur in many essential oils, often as a single enantiomer species. A particularly high concentration (sometimes $> 50\,\%$) is found in oils from *Mentha* species. The menthones are colorless liquids that possess a typically minty odor; the odor of isomenthone is slightly musty. They have a strong tendency to interconvert and are, therefore, difficult to obtain in high purity. Industrial products are mixtures of varying composition. Physical constants of industrially important menthone isomers are listed in Table 1.

The menthones are converted into the corresponding menthols by hydrogenation; for example, (−)-menthone yields (+)-neomenthol and (−)-menthol. (−)-Menthone can be obtained by distillation of dementholized cornmint oil or by oxidation of (−)-menthol (e.g., with chromic acid). Dehydrogenation of (−)-menthol (e.g., with copper chromite) yields a mixture of (−)-menthone and (+)-isomenthone. (±)-Menthone is prepared analogously from (±)-menthol. However, it can also be synthesized by hydrogenation of thymol in the presence of palladium–carbon catalysts [84].

Menthone and isomenthone are used for synthetic peppermint oils and bases.

Carvone, 1,8-*p*-menthadien-6-one, $C_{10}H_{14}O$, M_r 150.22, *bp* (101.3 kPa) 230 °C, d_4^{20} 0.960, n_D^{20} 1.499, $[\alpha]_D^{18}$ (+)-carvone $+64.3\,°$, $[\alpha]_D^{20}$ (−)-carvone $-62.5\,°$, occurs as (+)-carvone [*2244-16-8*], (−)-carvone [*6485-40-1*], or racemic carvone [*22327-39-5*]. The optical isomers differ considerably in their organoleptic properties. They occur in high percentages in a number of essential oils. (+)-Carvone is the main component of caraway oil (ca. 60 %) and dill oil; (−)-carvone occurs in spearmint oil at a concentration of 70 – 80 %.

Properties. The carvones are colorless to slightly yellow liquids. (+)-Carvone has an herbaceous odor reminiscent of caraway and dill seeds, whereas (−)-carvone has a herbaceous odor reminiscent of spearmint. Depending on the reaction conditions, hydrogenation of carvone yields either carveols or dihydrocarvone, which are also used as flavor compounds. When treated with strong acids, carvone isomerizes to carvacrol.

Production. In the past, (+)- and (−)-carvones were isolated by fractional distillation of caraway oil and spearmint oil, respectively. However, these carvones are now prepared syn-

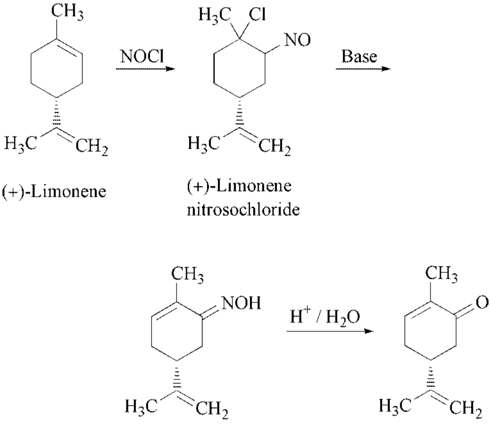
Table 1. Physical properties of industrially important menthone isomers

Compound	CAS registry number	*bp* (101.3 kPa), °C	d_t^{20}	n_D^{20}	$[\alpha]_D$
(−)-Menthone	[*14073-97-3*]	210	0.896*	1.450	− 28.5 °
(±)-Menthone	[*1074-95-9*]	210	0.896*	1.450	
(+)-Isomenthone	[*1196-31-2*]	212	0.900**	1.453	+ 95.0 °
(±)-Isomenthone	[*36977-92-1*]	212	0.900**	1.453	

$*t = 20\,°C$; $**t = 4\,°C$

thetically, the preferred starting material being (+)- and (−)- limonenes, which are converted into the corresponding optically active carvones. Since optical rotation is reversed in the process, (+)-limonene is the starting material for (−)-carvone.

The preferred industrial method of carvone synthesis utilizes the selective addition of nitrosyl chloride to the endocyclic double bond of limonene. If a lower aliphatic alcohol is used as solvent, limonene nitrosochloride is obtained in high yield. It is converted into carvone oxime by elimination of hydrogen chloride in the presence of a weak base. Acid hydrolysis in the presence of a hydroxylamine acceptor, such as acetone, yields carvone [85].



(+)-Limonene

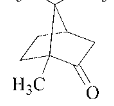
(+)-Limonene nitrosochloride

(−)-Carvone oxime

(−)-Carvone

Uses. Both (+)- and (−)-carvone are used to flavor a number of foods and beverages. (−)-Carvone is produced in much larger quantities and is also used in oral hygiene products.

Camphor [*21368-68-3*], 1,7,7-trimethylbicyclo[2.2.1]heptan-2-one, $C_{10}H_{16}O$, M_r 152.24, (+)-camphor: *bp* (101.3 kPa) 204 °C, *mp* 178.8 °C, $[\alpha]_D^{20}$ +44.3 °; both optical isomers are found widely in nature, (+)-camphor [*464-49-3*] being the more abundant. It is, for example, the main component of oils obtained from the camphor tree *Cinnamomum camphora.*

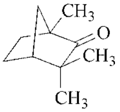


(+)-Camphor

Camphor is produced by fractional distillation and crystallization of camphor oil (see page 90) or, synthetically, by dehydrogenation of isoborneol (from isobornyl acetate, see page 41) over a copper catalyst.

Due to its characteristic penetrating, slightly minty odor, camphor is only used in perfuming industrial products. It is far more important as a plasticizer.

Fenchone [*1195-79-5*], 1,3,3-trimethylbicyclo[2.2.1]heptan-2-one, $C_{10}H_{16}O$, M_r 152.24, *bp* (101.3 kPa) 193 °C, d_4^{20} 0.9484, n_D^{20} 1.4628, $[\alpha]_D^{20}$ + or − 66.8 °, occurs as its (−)-isomer in a number of fennel oils. It is a colorless, slightly viscous liquid with a camphoraceous odor.

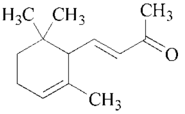


(+)-Fenchone

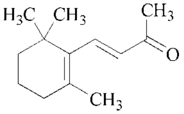
(+)-Fenchone [*7787-20-4*] containing a small amount of the (−)-isomer [*4695-62-9*] is prepared by dehydrogenation of (−)-fenchol. (−)-Fenchyl esters are obtained, along with other compounds, by addition of carboxylic acids to α-pinene. Hydrolysis of the esters yields (−)-fenchol.

Fenchone is used to prepare artificial fennel oils and to perfume household products.

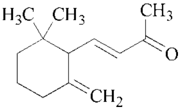
Ionones and Homologous Compounds. The C_{13} ketones α- and β-ionone are cyclic terpenoids that occur in many essential oils. However, being metabolites of the corresponding carotenoids [86], they occur in only small amounts. A third isomer, γ-ionone, has not yet been observed in nature.



α-Ionone



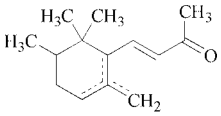
β-Ionone



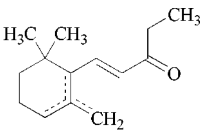
γ-Ionone

Both optical isomers of α-ionone are found in nature. Generally, ionones have a *trans* configuration. *trans*-α-Ionone can be converted into the *cis*-isomer by exposure to ultraviolet light. Under the same conditions, *trans*-β-ionone rearranges to the retro compound.

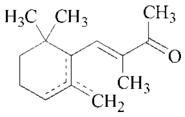
The *irones* are ionone homologues that have an additional methyl group adjacent to the twin methyl groups in the cyclohexane ring. The number of possible irone isomers is larger than that of the ionones due to the additional methyl group on the ring. Some of these irone isomers occur in essential oils from the roots of *Orris* species (see Orris Root Oil, page 111).



Irone, α-, β-, γ-



n-Methylionone, α-, β-, γ-



Isomethylionone, α-, β-, γ-

Other ionone homologues are the *methylionones,* in which the oxoalkenyl group carries an extra methyl substituent. The methylionones also exist as α-, β-, and γ-isomers, each of which can occur in the *cis* or *trans* form; the isomers may also be optically active. Their natural occurrence is debated [87].

All ionones, irones, and methylionones, as well as the corresponding pseudocompounds (their synthetic acyclic precursors) are slightly viscous yellowish liquids. Commercial irones and methylionones are mixtures of isomers that are named according to their main component. Their composition varies with the method used to prepare and cyclize the pseudocompound and fluctuates considerably between different manufacturers.

Physical and Chemical Properties. Physical and odor properties of the best known ionones are listed in Table 2.

β-Ionone is converted into intermediates for vitamin A synthesis (→ Vitamins, Chap. 2.7.2.). The hydrogenation of ionones and methylionones is of some importance. Dihydro or tetrahydro derivatives or ionols can be obtained depending on reaction conditions.

Table 2. Physical properties of ionones

Name	Formula	CAS registry number	M_r	*bp* °C (*p*, kPa)	d_4^{20}	n_D^{20}	Odor
α-Ionone	$C_{13}H_{20}O$	[*127-41-3*]	192.30	121 – 122 (1.3)	0.9319	1.4982	sweet-floral, reminiscent of violet
β-Ionone	$C_{13}H_{20}O$	[*79-77-6*]	192.30	121.5 (0.93)	0.9461	1.5202	reminiscent of cedarwood, violet-like upon dilution
γ-Ionone	$C_{13}H_{20}O$	[*79-76-5*]	192.30	82 (0.16)	0.9317	1.4985	violet-like with woody-resinous tonality (intermediate in the synthesis of γ-dihydroionone, a component of ambergris)
α-Irone	$C_{14}H_{22}O$	[*79-69-6*]	206.33	109 (0.36)	0.9340	1.4998	responsible for the fragrance of natural orris oil
β-Irone	$C_{14}H_{22}O$	[*79-70-9*]	206.33	108 – 109 (0.21)	0.9465	1.5183	reminiscent of β-ionone, but slightly more intense
α-*n*-Methylionone	$C_{14}H_{22}O$	[*127-42-4*]	206.33	97 (0.35)	0.9210 [a]	1.4938 [b]	reminiscent of α-ionone, but milder and more delicate
β-*n*-Methylionone	$C_{14}H_{22}O$	[*127-43-5*]	206.33	102 (0.35)	0.9370	1.5155	β-ionone-like, but with a distinct leather note
α-Isomethylionone	$C_{14}H_{22}O$	[*127-51-5*]	206.33	130 – 131 (1.3)	0.9345	1.5019	reminiscent of orris and violets, possesses the finest odor of all ionones
β-Isomethylionone	$C_{14}H_{22}O$	[*79-89-0*]	206.33	94 (0.4)	0.9376	1.5053	interesting, powdery, orris-like odor with slightly woody aspects
Allylionone [c]	$C_{16}H_{24}O$	[*79-78-7*]	232.35	102 – 104 (0.02)	0.9289	1.5040	floral violet odor with a fruity pineapple note and high tenacity

[a] d_4^{25}

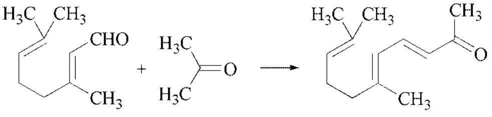
[b] n_D^{25}

[c] Obtained by cyclization of allylpseudoionone (from citral and allylacetone)

With Raney nickel–copper chromite catalysts, methylionones are converted into tetrahydromethylionols, which are also used as fragrance materials [88].

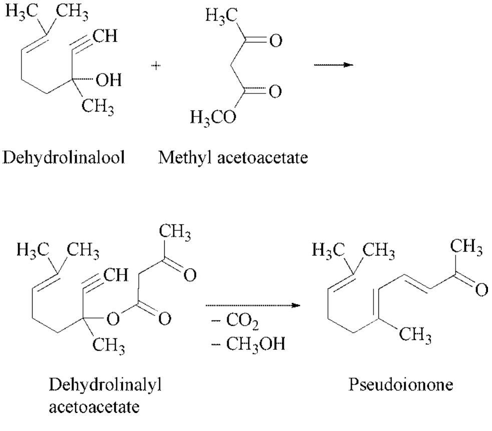
Production. Ionones, irones, and methylionones, as well as allylionone, are all produced by analogous routes. Special procedures must be used to obtain a particular isomer, either pure or as the main component. These are described where appropriate.

In all processes an acyclic precursor, called a pseudoionone, pseudoirone, etc., is prepared by base-catalyzed condensation of citral or 6-methylcitral with acetone, methyl ethyl ketone, or allylacetone, as appropriate.

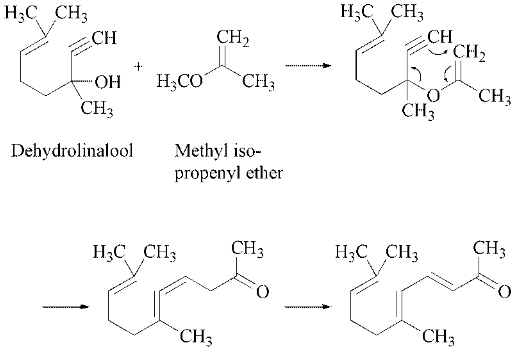


Citral Acetone Pseudoionone

In the synthesis of vitamin A, the dependence on natural sources as well as steadily increasing production via β-ionone as an intermediate have led to the development of a method for synthesizing citral from dehydrolinalool (see page 21). More recent routes employ dehydrolinalool as the starting material for pseudoionone. Dehydrolinalool is converted into pseudoionone by using either diketene [89] or a suitably substituted acetoacetate (Carroll reaction) [90]:

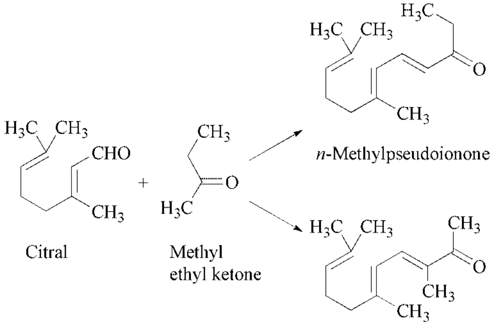


A milder reaction for synthesizing pseudoionone from dehydrolinalool is transetherification with an alkoxyalkene [91]:



Pseudoionone

In the methylionone synthesis, condensation of citral with methyl ethyl ketone results in a mixture of *n*-methyl- and isomethylpseudoionone, each of which may occur as one of four possible *cis–trans*-isomers.



Isomethylpseudoionone

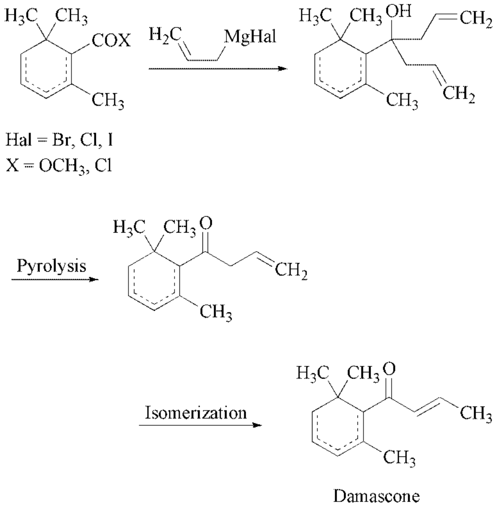
The ratio of the major isomers in the mixture depends on the condensation catalyst and the reaction conditions. In the presence of common alkaline catalysts (e.g., sodium hydroxide), straight-chain isomers are formed preferentially. Strongly alkaline catalysts, such as quaternary ammonium bases, favor the formation of isomethylpseudoionone [92]. This compound is a precursor for the highly valued fragrance substance α-isomethylionone and can be obtained as the main component by reacting dehydrolinalool with the enol ether of methyl ethyl ketone and methanol [93]. Acidic and Lewis catalysts are employed in the cyclization of the pseudocompounds to the cyclic ketones. The primary cyclization products are α-ionone or its homologues, which are isomerized to the β-compounds by strong acids. Concentrated sulfuric acid converts pseudoionone almost exclusively into β-ionone; 85 % phosphoric acid yields α-ionone in ca. 80 % purity. γ-Ionone can be obtained together with a small amount of α- and β-ionone when boron trifluoride etherate is used as the catalyst and dimethylformamide as the solvent [94]; γ-ionone is of little commercial importance. Since α- and β-ionone can be separated on an industrial scale by fractional distillation in high-performance columns, other methods of separation are seldom used.

Uses. The volume of the production of β-ionone, which serves as an intermediate in vitamin A synthesis, shows that it is by far the most important. The ionones and their homologues are components of blossom and phantasy perfume compositions. The ionones and irones are used in aroma compositions as well, although on a much smaller scale. α-Ionone is a highly valued fragrance material. The methylionones are among the most important fragrance substances, α-isomethylionone being the most important. The irones, isomers of the methylionones, are produced in limited quantities, mainly due to their high cost. Likewise, allylionone is manufactured in small amounts.

Damascones, 1-(2,6,6-trimethylcyclohexenyl)-2-buten-1-ones, $C_{13}H_{20}O$, M_r 192.30, are ionone isomers. Damascone exists in α-, β-, γ-, δ-, and ε-forms, depending on the position of the double bond in the cyclohexane ring. Commercially important are α-damascone [*43052-87-5*], β-damascone ([*23726-91-2*] for (E) and δ-damascone [*57378-68-4*] as mixtures of their *cis*- and *trans*-isomers.

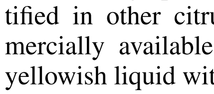
The α- and β-damascones have been identified as components of tea aroma. They are liquids with a fruity, roselike odor. One synthetic route to the damascones starts with an appropriate cyclogeranic acid derivative (halide, ester, etc.). This is reacted with an allyl magnesium halide to give 2,6,6-trimethylcyclohexenyl diallyl carbinol, which on pyrolysis yields the desired 1-(2,6,6-trimethylcyclohexenyl)-3-buten-1-one. Damascone is otained by rearrangement of the double bond in the side-chain [95].

The damascones are used in perfume compositions, especially rose perfumes, and in flavor compositions, to which they impart naturalness and body. (IFRA recommendation)



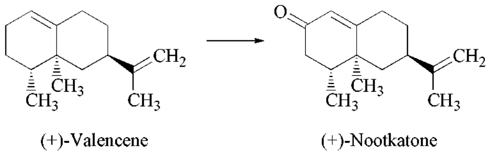
β-Damascenone [*23726-93-4*], 1-(2,6,6-trimethyl-1,3-cyclohexadienyl)-2-buten-1-one, $C_{13}H_{18}O$, M_r 190.28, is a constituent of Bulgarian rose oil, which has a powerful fragrance although it is only present at a concentration of 0.05 %.

It is used in small quantities in flavor and perfume compositions to impart naturalness and brilliance. (IFRA recommendation)



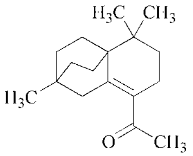
Nootkatone [*4674-50-4*], 5,6-dimethyl-8-isopropenylbicyclo[4.4.0]-1-decen-3-one, $C_{15}H_{22}O$, M_r 218.33, *mp* 35 °C, has been isolated from grapefruit peel and juice and identified in other citrus oils as well. The commercially available product is a colorless to yellowish liquid with a typical grapefruit odor.

Nootkatone can be prepared by oxidation of valencene, a sesquiterpene hydrocarbon isolated from orange oils. (IFRA recommendation)



Nootkatone is used for flavoring beverages.

Cedryl methyl ketone, $C_{17}H_{26}O$, M_r 246.39, is a long-lasting wood fragrance which is prepared by acetylation of cedarwood oil fractions that contain sesquiterpene hydrocarbons, mainly α-cedrene and thujopsene (for structures, see Section 2.3.1). Acetylation is carried out in the presence of an acidic catalyst (e.g., polyphosphoric acid). Commercially available cedryl methyl ketone is a multicomponent mixture. The main component is 1-(2,6,6,8-tetramethyltricyclo[5.3.1.0^{1,5}]undec-8-en-9-yl)ethan-1-one [*32388-55-9*]. One of its odor-determining compounds is 1-(2,2,8-trimethyltricyclo[6.2.2.0^{1,6}]dodec-5-en-5-yl)ethan-1-one [*32388-56-0*]:



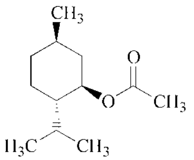
Trade Names. Lignofix (Dragoco), Lixetone (Quest), Vertofix (IFF).

2.3.4. Esters

Esters derived from cyclic terpene alcohols, especially the acetates, are common fragrance and flavor components. Menthanyl, menthenyl, bicyclic bornyl acetates, and a few acetates of sesquiterpene alcohols are extensively used in perfume and aroma compositions.

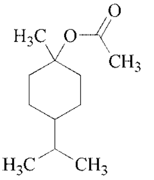
(−)-Menthyl acetate [*2623-23-6*], (−)-*p*-menthan-3-yl acetate, $C_{12}H_{22}O_2$, M_r 198.30, *bp* (3 kPa) 116 °C, d_4^{20} 0.9253, n_D^{20} 1.4467 – 1.4468, $[\alpha]_D^{20}$ − 81.1 °, occurs in peppermint oils. It is a colorless liquid with a fresh-fruity, peppermint odor.

(−)-Menthyl acetate is prepared by acetylation of (−)-menthol (e.g., with acetic anhydride). It is used mainly in peppermint flavors and reconstituted peppermint oils, but also to a small extent in perfumery.



(±)-Menthyl acetate [*29066-34-0*] occurs in essential oils. It is synthesized by esterification of racemic menthol. Its odor is crisper and less fruity than that of (−)-menthyl acetate. It is used for essential oil compositions and occasionally in household perfumery.

***p*-Menthanyl acetate,** $C_{12}H_{22}O_2$, M_r 198.30, *bp* (200 Pa) 67 – 70 °C, d_{25}^{25} 0.931 – 0.937, n_D^{20} 1.446 – 1.451, is commercially available as a *cis–trans* mixture of *p*-menthan-1-yl acetate [*26252-11-9*] (**1**) and *p*-menthan-8-yl acetate [*80-25-1*] (**2**). It is a colorless liquid with a citrus-fresh, pine-needle odor and a secondary, slightly herbaceous note. Menthanyl acetate is produced by hydrogenation of terpinyl acetates (mixtures of isomers) (e.g., in the presence of Raney nickel [96]) or by esterification of a mixture of isomeric *p*-menthanols.



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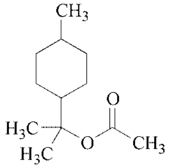
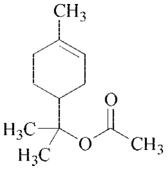


2

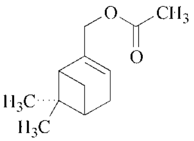
The ester mixture is highly stable and is, therefore, used in perfumery for detergents and other household products.

α-Terpinyl acetate [*80-26-2*], 1-*p*-menthen-8-yl acetate, $C_{12}H_{20}O_2$, M_r 196.29, *bp* (5.3 kPa) 140 °C, d_4^{20} 0.9659, n_D^{21} 1.4689, $[\alpha]_D^{20}$ of the enantiomers + or − 79 °; the enantiomers and the racemate occur in many essential oils (e.g., Siberian pine needle oil and cypress oil), but generally not as the main component. Pure α-terpinyl acetates are colorless liquids with a fresh bergamot-lavender odor. Commercially available terpinyl acetate consists mainly of α-terpinyl acetate, but also contains a number of other isomeric compounds. It can be prepared by acetylating the terpineol mixture obtained from terpin hydrate, using a customary procedure for tertiary alcohols.

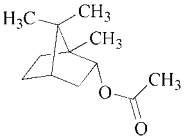
Because of its odor properties, stability, and low price, large quantities of terpinyl acetate are used in perfumery for lavender and bergamot types, as well as in essential oil reconstitutions.



Nopyl acetate [*35836-72-7*], (−)-2-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethyl acetate, $C_{13}H_{20}O_2$, M_r 208.30, *bp* (1.5 kPa) 122 °C, d_4^{20} 0.9811, n_D^{20} 1.4733, $[\alpha]_D$ − 30.9 ° (CAS registry no. of racemate [*128-51-8*], is not found in nature and has a fresh-fruity-woody odor. (−)-Nopyl acetate is prepared by acetylation of (−)-nopol with acetic anhydride. (−)-Nopol is obtained from (−)-β-pinene and paraformaldehyde in a Prins reaction. Nopyl acetate is used in perfumes for soap and household products.



Bornyl acetate, 2-*endo*-bornanyl acetate, $C_{12}H_{20}O_2$, M_r 196.29, *bp* (101.3 kPa) 223–224 °C, d_4^{20} 0.9838, n_D^{20} 1.4630, $[\alpha]_D^{20}$ + or − 44.4 °, *mp* (+)- and (−)-form 29 °C, occurs in its optically active forms and as a racemate in many essential oils.

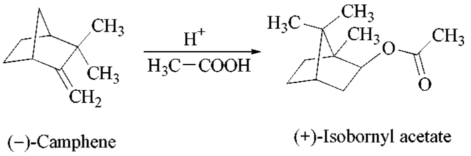


(−)-Bornyl acetate

(−)-Bornyl acetate [*5655-61-8*] is a characteristic component of most conifer oils. It has a camphoraceous, pine-needle-like odor. Both (+)-bornyl acetate [*20347-65-3*] and (−)-bornyl acetate form colorless crystals; the racemate [*36386-52-4*] is a colorless liquid. Bornyl acetate is prepared by esterification of borneol with acetic anhydride or via the process described under borneol (see page 34).

Due to its characteristic pine needle odor, bornyl acetate is frequently used in conifer needle compositions, soap, bath products, room sprays, and pharmaceutical products.

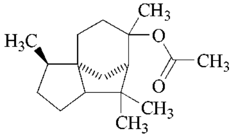
Isobornyl acetate [*125-12-2*], 2-*exo*-bornanyl acetate, $C_{12}H_{20}O_2$, M_r 196.29, *bp* (1.6 – 1.7 kPa) 102–103 °C, d_4^{20} 0.9841, n_D^{20} 1.4640, has been identified in a number of essential oils. It is a colorless liquid with a pleasant, pine-needle odor. Isobornyl acetate is prepared from camphene and acetic acid in the presence of acidic catalysts (e.g., sulfuric acid) [97], or ion-exchange resins (e.g., sulfonated styrene–divinylbenzene polymers) [98].



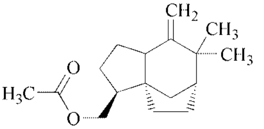
Isobornyl acetate is used in large amounts for perfuming soap, bath products, and air fresheners. However, the major use of isobornyl acetate is as an intermediate in the production of camphor.

Guaiyl acetate, $C_{17}H_{28}O_2$, M_r 264.41, *bp* (300 Pa) 118–123 °C, d_{25}^{25} 0.965–0.990, n_D^{20} 1.489–1.495, is obtained by esterification of guaiac wood oil with acetic anhydride and consists of the acetates of the natural sesquiterpene alcohols guaiol and bulnesol (see Guaiac Wood Oil, page 103). Guaiyl acetate is a yellow to amber-yellow liquid with a weak but lasting, woody odor. It is used in perfumery for tea-rose and wood nuances.

Cedryl acetate [*77-54-3*], $C_{17}H_{28}O_2$, M_r 264.41, *bp* (400 Pa) 146–150 °C, d_{25}^{25} 0.966–1.012, n_D^{20} 1.495–1.506, occurs in cedarwood oils. The pure compound is crystalline (*mp* 80 °C). Commercial cedryl acetate is a colorless to amber-yellow liquid, with a cedarwood-like odor. It is prepared by esterification of the cedrol-rich fraction from cedarwood oil and is used in perfumery for wood and leather notes, and as a fixative.



Vetiveryl acetate [*62563-80-8*], *bp* (300 Pa) 125 – 128 °C, d_{25}^{25} 0.979 – 1.015, n_D^{20} 1.5050 – 1.5180, is not a single compound; its main component is khusimyl acetate [*61474-33-7*]. Vetiveryl acetate is prepared by esterification of the sesquiterpene alcohols isolated from vetiver oils.



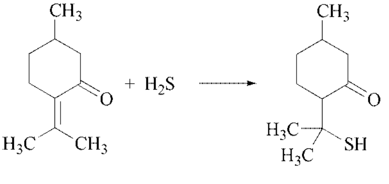
Khusimyl acetate

Vetiveryl acetate is a light yellow liquid with a dry, fresh-woody odor. It is a popular fragrance mixture that is frequently used in luxury perfumery; it is also used as a fixative in many fine fragrances. (Limiting IFRA recommendation)

2.3.5. Miscellaneous Compounds

Of the few known terpene compounds that contain heteroatoms such as nitrogen or sulfur, the thiol 8-mercapto-*p*-menthan-3-one described below has qualitatively important applications as a fragrance and flavor substance. The second thiol, 1-*p*-menthene-8-thiol, is described because its odor threshold value is far lower than that of most other fragrance and flavor compounds.

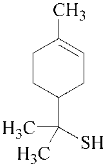
8-Mercapto-*p*-menthan-3-one [*38462-22-5*], $C_{10}H_{18}OS$, M_r 186.31, *bp* (13 Pa) 57 °C, is an essential odoriferous constituent of buchu leaf oil. The commercial product is synthesized from pulegone and is a liquid mixture of *cis–trans*-isomers with a typical blackcurrant odor. 8-Mercapto-*p*-menthan-3-one is prepared by reacting pulegone with hydrogen sulfide in the presence of a base (e.g., triethylamine) [99]:



Pulegone 8-Mercapto-*p*-menthan-3-one

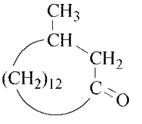
This powerful fragrance and flavor substance is used in perfume and aroma compositions.

1-*p*-Menthene-8-thiol [*71159-90-5*], $C_{10}H_{18}S$, M_r 170.31, *bp* (45 Pa) 40 °C, d_4^{20} 0.948, n_D^{20} 1.503, has been identified in grapefruit juice. It is a liquid with an extremely powerful, obnoxious odor; when diluted it has the typical aroma of fresh grapefruit juice. Its odor threshold value is extremely low: 2×10^{-5} µg/kg for the (+)-R and 8×10^{-5} µg/kg for the (−)-S isomer [100].

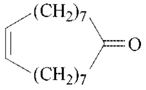


2.4. Other Cycloaliphatic Compounds

In addition to cyclic terpenoids, several other cycloaliphatic compounds have above-average importance as fragrance materials; some of them are structurally related to the terpenes. Ketones are most widely represented and include cyclopentanone derivatives, such as the jasmin fragrance compounds, and cyclic ketones with 15 – 17-membered carbon rings, such as muscone [*541-91-3*] and civetone [*542-46-1*], which are constituents of the extremely expensive animal products, musk and civet.



Muscone



Civetone

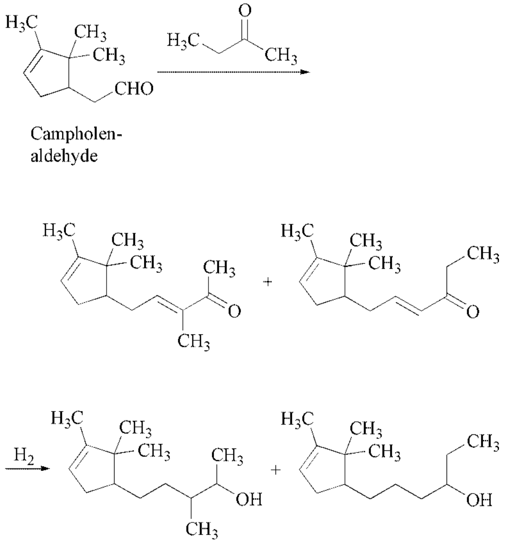
Many syntheses have been devised for these macrocyclic ketones. However, due to the many steps involved and poor yields, they are not used widely on an industrial scale. Cyclopentadecanone, a natural musk fragrance, and the unsaturated 5-cyclohexadecen-1-one, which has not yet been found in nature, are more easily synthesized. Their odor characteristics are similar to those of muscone and civetone and are, therefore, used instead of them.

A few alicyclic aldehydes are valuable perfume materials and are obtained by Diels – Alder reactions using terpenes and acrolein. Esters derived from hydrogenated aromatic compounds, such as *tert*-butylcyclohexyl and decahydro-β-naphthyl acetates, are also used in large amounts as fragrance materials.

2.4.1. Alcohols

Some alicyclic alcohols are important as synthetic sandalwood fragrances. The annual world production of natural sandalwood oil is about 100 t with a current price of about $ 400 per kilogram. Due to the limitations of the harvest and this highly fluctuating price, chemists have been searching for cheap synthetic substitutes for this important perfumery ingredient. Since the 1970s a new class of sandalwood products has been developed, which all originate from campholenic aldehyde, an easily available product of the rearrangement of α-pinene epoxide, catalyzed by zinc chloride or zinc bromide.

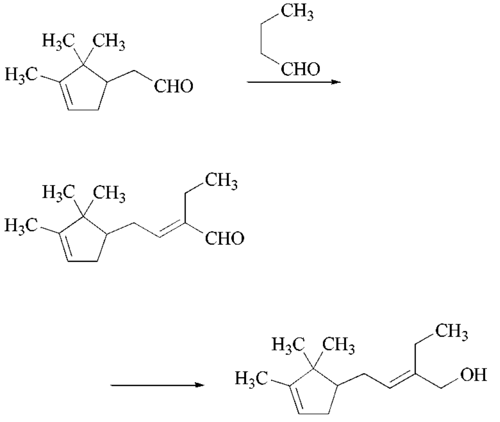
5-(2,2,3-Trimethyl-3-cyclopenten-1-yl)-3-methylpentan-2-ol [*65113-99-7*] (**3**), $C_{14}H_{26}O$, M_r 210.36, d_4^{20} 0.896 – 0.904, n_D^{20} 1.470 – 1.476, is a fragrance ingredient that does not occur in nature. It is prepared by condensation of campholenic aldehyde with methyl ethyl ketone, followed by selective hydrogenation of the resulting unsaturated ketone [101].



3 **4**

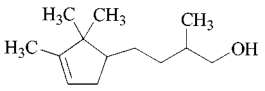
Compound **3** can be used either in a pure state or as a mixture with its byproduct **4** in perfume compositions and soap perfumes.
Trade Name. Sandalore (Givaudan Roure).

2-Ethyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-buten-1-ol [*8219-61-6*], $C_{14}H_{26}O$, M_r 208.35, *bp* (3 kPa) 114 – 116 °C, d_4^{20} 0.9160 – 0.9168, n_D^{20} 1.4870 – 1.4880, is another sandelwood-like fragrance also derived from campholenic aldehyde. Aldol condensation of this aldehyde with butyric aldehyde gives an α,β-unsaturated carbonyl compound that can be reduced to an unsaturated alcohol.

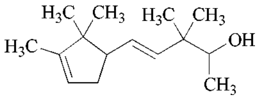


Trade Names. Bacdanol (IFF), Bangalol (Quest), Sandolene (Haarmann & Reimer), Sandranol (DRAGOCO).

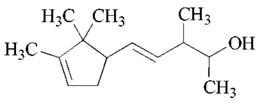
In addition some other materials of this type are on the market:



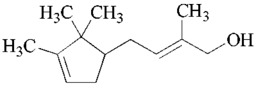
Trade Name. Brahmanol (DRAGOCO).



Trade Name. Polysantol (Firmenich).

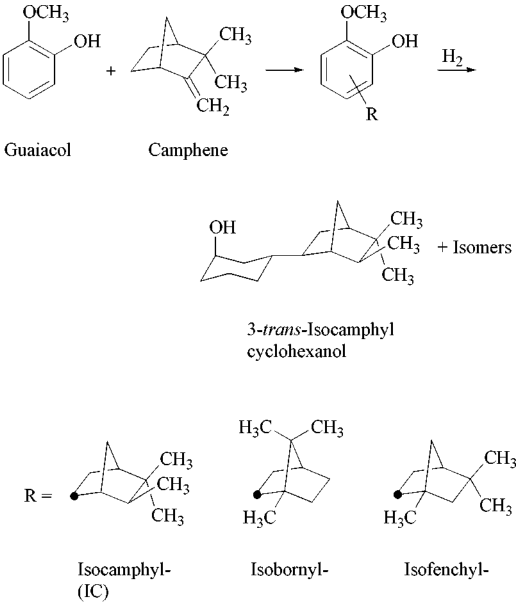


Trade Name. Ebanol (Givaudan Roure).

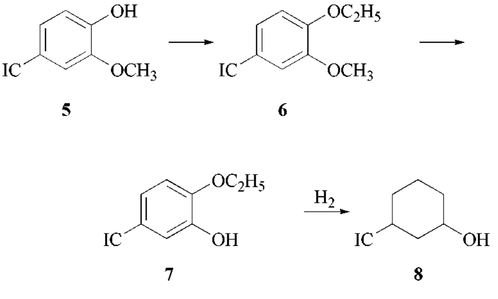


Trade Names. Madrol (DRAGOCO), Sandelice (Cognis).

3-*trans*-Isocamphylcyclohexanol [*3407-42-9*], $C_{16}H_{28}O$, M_r 236.40, does not occur in nature. A synthetic mixture of terpenylcyclohexanol isomers has a sandalwood odor. A commercially available mixture containing 3-*trans*-isocamphylcyclohexanol is prepared by reacting camphene and guaiacol in the presence of an acidic catalyst (e.g., boron trifluoride), followed by catalytic hydrogenation of the resulting terpenylguaiacols. In the alkylation reaction, camphene rearranges to the isobornyl, isofenchyl, and isocamphyl skeletons. These substituents may be introduced in guaiacol at four positions. In the subsequent hydrogenation with simultaneous elimination of the methoxy group, additional possibilities for isomerism arise because the hydroxyl group may be either axial or equatorial to the terpenyl moiety. Therefore, the actual content of the desired isomer, 3-*trans*-isocamphylcyclohexanol, is low in most products. The other isomers are either weak in odor or odorless.



A process starting from catechol, instead of guaiacol, yields a mixture with a higher content of 3-*trans*-isocamphylcyclohexanol [102]. Moreover, the process starting from guaiacol has been improved by converting the main component formed in the first step, *p*-isocamphylguaiacol (**5**), into a mixed ether (**6**) by reaction with diethyl sulfate. Nucleophilic cleavage of the ether with alcoholates or Grignard reagents results in a high yield of *m*-isocamphylguethol (**7**), which is hydrogenated catalytically, with concomitant loss of the ethoxy group, to give a high yield of 3-*trans*-isocamphylcyclohexanol (**8**) [103].



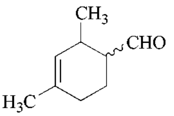
IC = Isocamphyl

The mixture is used as such in large amounts as a replacement for sandalwood oil in soaps, cosmetics, and perfume compositions.

Trade Names. Sandela (Givaudan Roure), Sandel H + R (Haarmann & Reimer), Sandiff (IFF), Rhodanthial (Rhodia), Santalex (Takasago).

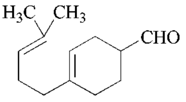
2.4.2. Aldehydes

2,4-Dimethyl-3-cyclohexene carboxaldehyde [*68039-49-6*], $C_9H_{14}O$, M_r 138.21, *bp* (4 kPa) 94 – 96 °C, n_D^{25} 1.4696, is prepared as a mixture of its *cis*- and *trans*-isomers by a Diels – Alder reaction of 2-methyl-1,3-pentadiene and acrolein. It is a liquid with a strongly green, slightly herbaceous, citrus note. It is used for perfuming cosmetic preparations as well as household products.



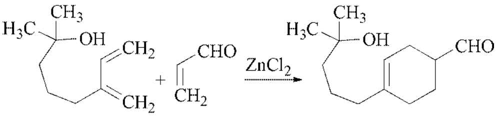
Trade Names. CyclalC (Givaudan Roure), Ligustral (Quest), Triplal (IFF), Vertocitral (Haarmann & Reimer).

4-(4-Methyl-3-penten-1-yl)-3-cyclohexene carboxaldehyde [*37677-14-8*], $C_{13}H_{20}O$, M_r 192.30, is prepared, together with its 3-isomer, by a Diels – Alder reaction of myrcene and acrolein. The mixture has a fresh-fruity, slightly citrus-like odor and is used to perfume household products.



Trade Names. Empetal (Quest), Myrac aldehyde (IFF), Vertomugal (Haarmann & Reimer).

4-(4-Hydroxy-4-methylpentyl)-3-cyclohexene carboxaldehyde [*31906-04-4*] (**9**), $C_{13}H_{22}O_2$, M_r 210.32, *bp* (130 Pa) 120 – 122 °C, d_4^{20} 0.9941, n_D^{20} 1.4915, is a fragrance substance that does not occur in nature. It is a colorless, viscous liquid with a sweet odor reminiscent of lily of the valley. The aldehyde can be prepared by a Diels – Alder reaction of myrcenol and acrolein in the presence of a Lewis catalyst (e.g., zinc chloride) [104]:

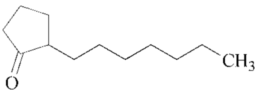


Myrcenol Acrolein **9**

Reaction of myrcenol with acrolein at elevated temperatures, without a catalyst, yields a 70 : 30 mixture of the 4- and 3-substituted cyclohexene carboxaldehydes [105]. This mixture is a commercial product. Compound **9** has excellent fixative properties and is used especially in soap and cosmetics perfumery.
Trade Names. Lyral (IFF), Kovanol (Takasago).

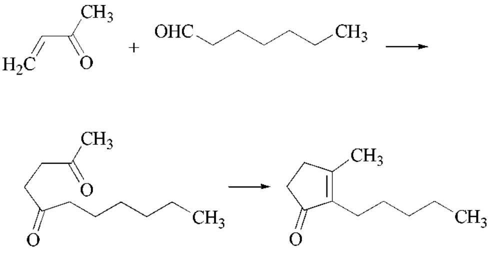
2.4.3. Ketones

2-Heptylcyclopentanone [*137-03-1*], $C_{12}H_{22}O$, M_r 182.31, *bp* (1.3 kPa) 130 °C, d^{20} 0.890, n_D^{20} 1.4530, is a fragrance material with a fruity, slightly herbaceous, jasmin odor; it has not yet been found in nature. It is a colorless, viscous liquid prepared by condensation of cyclopentanone with heptanal to give 2-heptylidenecyclopentanone, with subsequent hydrogenation of the double bond.



2-Heptylcyclopentanone and its lower mass homologues 2-pentyl- and 2-hexylcyclopentanone are used in, for example, jasmin, honeysuckle, and lavender compositions.
Trade Names. Fleuramone (IFF), Projasmon P (Haarmann & Reimer).

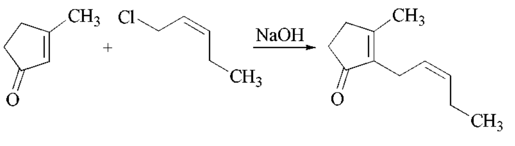
Dihydrojasmone [*1128-08-1*], 3-methyl-2-pentyl-2-cyclopenten-1-one, $C_{11}H_{18}O$, M_r 166.26, *bp* (2.7 kPa) 87 – 88 °C, d^{25} 0.9157, n_D^{25} 1.4771, is a colorless, slightly viscous liquid with a typical jasmin odor, resembling that of the naturally occurring *cis*-jasmone. Dihydrojasmone can be synthesized by various routes. A preferred method is intramolecular aldol condensation of 2,5-undecanedione, which can be prepared from heptanal and 3-buten-2-one in the presence of a thiazolium salt, such as 5-(2-hydroxyethyl)-4-methyl-3-benzylthiazolium chloride [106]:



Dihydrojasmone

Dihydrojasmone is used in perfumery in jasmin bases and, more generally, in blossomy and fruity fragrances.

***cis*-Jasmone** [*488-10-8*], 3-methyl-2-(2-*cis*-penten-1-yl)-2-cyclopenten-1-one, $C_{11}H_{16}O$, M_r 164.25, *bp* (1.6 kPa) 78 – 79 °C, d^{20} 0.9423, n_D^{20} 1.4989, occurs in jasmin absolute and contributes to its typical jasmin odor. It is a pale yellow, viscous liquid with a strong jasmin odor. Various stereospecific syntheses for *cis*-jasmone have been reported. A patented method involves alkylation of 3-methyl-2-cyclopenten-1-one with *cis*-2-pentenyl chloride in an alkaline medium in the presence of a phase-transfer catalyst (e.g., tricaprylmethylammonium chloride) [107]:

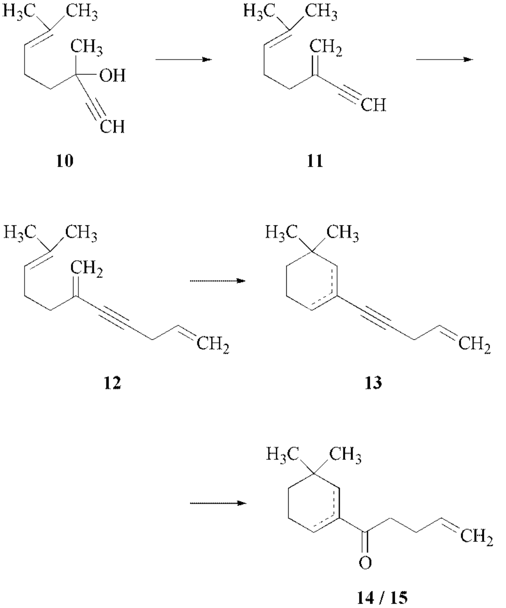


cis-Jasmone

cis-Jasmone is used in perfumery in fine jasmin bases and floral compositions.

1-(5,5-Dimethylcyclohex-1-en-1-yl)pent-4-en-1-one [*56973-85-4*], and 1-(3,3-dimethylcyclohex-1-en-1-yl)pent-4-en-1-one [*56973-84-3*], $C_{13}H_{20}O$, M_r 192.30, d_4^{20} 1.490, n_{20}^{20} 0.930. The isomeric mixture is a colorless to pale yellow liquid with an extremely powerful and diffusive odor reminiscent of galbanum, with a pineapple and hyacinth character.

The cyclic ketone can be formed by dehydratization of dehydrolinalool (**10**), subsequent alkylation of **11** with allyl chloride to form **12**, acid-catalyzed cyclization of (**12**) and hydrolysis of the product **13** to give a mixture of **14** and **15** [108].

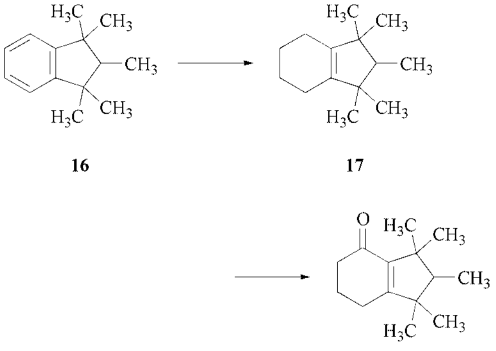


10 **11** **12** **13** **14 / 15**

Trade Name. Dynascone (Firmenich).

1,2,3,5,6,7-Hexahydro-1,1,2,3,3-pentamethyl-4*H*-inden-4-one [*33704-61-9*], $C_{14}H_{22}O$, M_r 206.32, d_4^{20} 0.962, n_D^{20}1.500, has not yet been found in nature. It is colorless to pale yellow solid to semi-solid mass with a diffusive, spicy, musk-like odor with strong floral reinforcement and powdery, velvet nuances.

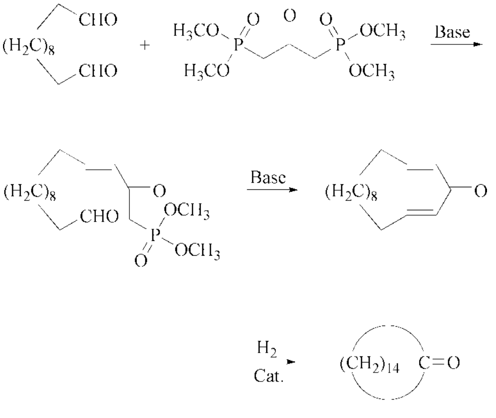
The indenone **18** can be prepared by hydrogenation of pentamethylindan (**16**) and subsequent oxidation of the intermediate **17** with air over copper acetate to yield the corresponding ketone **18** [109, 110].



16 **17** **18**

Trade Name. Cashmeran (IFF).

Cyclopentadecanone [*502-72-7*], $C_{15}H_{28}O$, M_r 224.39, *mp* 65 – 67 °C, *bp* (7 Pa) 85 °C, is a musk fragrance found in the scent gland of the male civet cat.

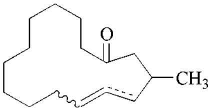


Cyclopentadecanone

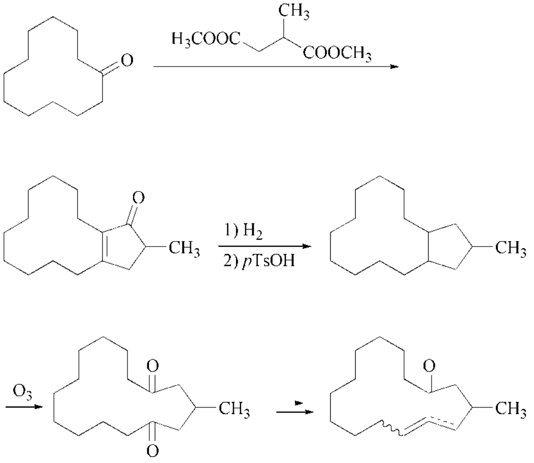
A number of syntheses have been developed for its manufacture. In a more recent method, 1,12-dodecanedial is reacted with 1,3-bis(dimethylphosphono)propan-2-one in the presence of a base, preferably in two steps via the intermediates 15-(dimethylphosphono)pentadec-12-en-14-on-1-al and 2,14-cyclopentadecadien-1-one. Subsequent hydrogenation yields cyclopentadecanone [111].

Cyclopentadecanone is used in fine fragrances.
Trade Name. Exalton (Firmenich).

3-Methylcyclopentadec-4/5-en-1-one, (*E*/*Z*) [*82356-51-2*], $C_{16}H_{28}O$, M_r 236.40, d_{20}^{20} 0.925 – 0.935, has a powerful musk odor, reminiscent of musk ketone.



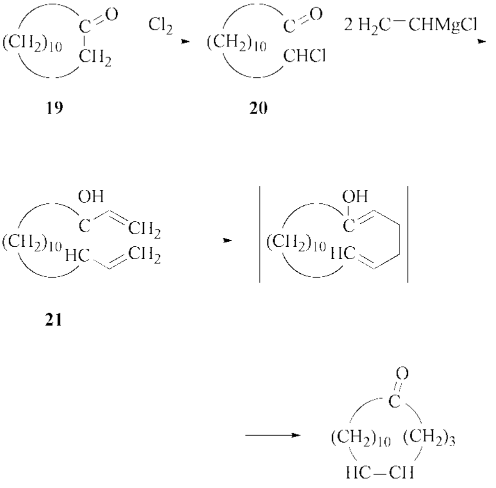
The synthesis of muscenone starts with a condensation of cyclododecanone and dimethyl methylsuccinate, followed by cyclization with polyphosphoric acid. Hydrogenation and elimination yields methylbicyclo[10.3.0]-pentadec-1(12)-ene. Ozonolyses results in a diketone, which is converted via hydrogenation and elimination to the unsaturated muscone [112].



3-Methylcyclopentadec-4/5-en-1-one is used as nitromusk replacer, at low dosage (0.05 – 0.5 %) as a fragrance enhancer, at higher dosage it is "used for its musky character in addition to its boosty effect".
Trade Name. Muscenone (Firmenich).

5-Cyclohexadecen-1-one [*37609-25-9*], $C_{16}H_{28}O$, M_r 236.40, *bp* (10 Pa) 121 °C, n_D^{25} 1.4865, is commercially available as a 40 : 60 mixture of its *cis*- and *trans*-isomers. It is a colorless liquid with an intense musk odor.

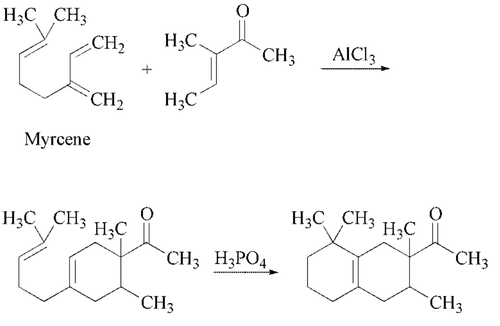
A three-step synthesis starts from cyclododecanone (**19**). Reaction with chlorine gives 2-chlorocyclododecanone (**20**) which is reacted with 2 mol of vinylmagnesium chloride to give 1,2-divinylcyclododecan-1-ol (**21**). This is finally converted into 5-cyclohexadecen-1-one by an oxy-Cope rearrangement [113]:



5-Cyclohexadecen-1-one

5-Cyclohexadecen-1-one can be added to perfume compositions as a substitute for the natural macrocyclic ketone musks.
Trade Name. TM II SP (Soda Aromatic), Ambretone (Takasago).

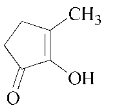
2,3,8,8-Tetramethyl-1,2,3,4,5,6,7,8-octahydro-2-naphthalenyl methyl ketone [*54464-57-2*] (**22**), $C_{16}H_{26}O$, M_r 234.38, *bp* (370 Pa) 134 – 135 °C, n_D^{20} 1.4975 – 1.500, is a synthetic amber fragrance. It is prepared by a Diels – Alder reaction of myrcene and 3-methyl-3-penten-2-one in the presence of aluminum chloride and cyclization of the substituted cyclohexenyl methyl ketone intermediate with phosphoric acid. Some 3-acetyl isomer is also formed [114].



22

The ketone is used in perfume bases for soaps, eaux de cologne, and detergent compositions.
Trade Name. Iso E Super (IFF).

3-Methyl-2-cyclopenten-2-ol-1-one [*80-71-7*], $C_6H_8O_2$, M_r 112.13, *mp* (monohydrate) 106 °C, occurs in beechwood tar and has a caramel-like odor. It has been identified as a flavor component in food. Crystals of the compound usually contain 1 mol of water. Synthetic routes of production are of limited importance in comparison with isolation from beechwood tar.

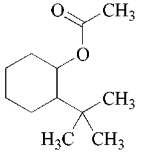


The compound is frequently used in flavor compositions for its caramel note, e.g., in beverages and in confectionery. It is rarely used in perfumery, and then mainly as an intensifier.

2.4.4. Esters

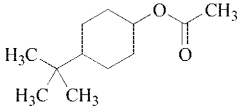
2-*tert*-Butylcyclohexyl acetate [*88-41-5*], $C_{12}H_{22}O_2$, M_r 198.30, *mp* (pure *cis*-isomer) 34.5 – 35.4 °C; commercial product: d_{25}^{25} 0.938 – 0.944, n_D^{20} 1.4500 – 1.4560; this compound does not occur in nature and exists in *cis* and *trans* forms. Pure 2-*cis*-*tert*-butylcyclohexyl acetate is a crystalline solid, with a fruity, agrumen-like odor. The commercial product is a colorless liquid and consists of a mixture of *cis* and *trans*-isomers, which contains 60 – 95 % of the *cis* ester. With an increasing percentage of the *trans*-isomer, the odor becomes more woody-camphory.

The acetate is prepared by esterification of 2-*tert*-butylcyclohexanol, which is obtained from 2-*tert*-butylphenol. It is highly stable and is used for perfuming soap as well as bath and household products.



Trade Names. Agrumex (Haarmann & Reimer), Verdox (IFF).

4-*tert*-Butylcyclohexyl acetate [*32210-23-4*], $C_{12}H_{22}O_2$, M_r 198.30, *bp* (1 kPa) 89 – 95 °C, d_{25}^{25} 0.933 – 0.939, n_D^{20} 1.450 – 1.454, does not occur in nature and exists in *cis* and *trans* forms. The *trans*-isomer has a rich, woody odor, while the odor of the *cis*-isomer is more intense and more flowery. Considerable variations in *cis*–*trans* ratios in commercial mixtures have little effect on the physical constants. Therefore, the composition of mixtures should be determined by gas chromatography.

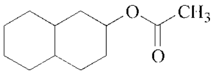


The ester is prepared by catalytic hydrogenation of 4-*tert*-butylphenol followed by acetylation of the resulting 4-*tert*-butylcyclohexanol [115]. If Raney nickel is used as the catalyst, a high percentage of the *trans*-isomer is obtained. A rhodium–carbon catalyst yields a high percentage of the *cis*-isomer. The *trans* alcohol can be isomerized by alkaline catalysts; the lower-boiling *cis* alcohol is then removed continuously from the mixture by distillation [116].

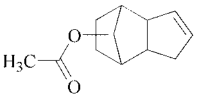
4-*tert*-Butylcyclohexyl acetate is used particularly in soap perfumes.
*Trade Names.*4-*tert*-Butylcyclohexylacetate (Degussa), Oryclon extra (Haarmann & Reimer), Vertenex (IFF).

Decahydro-β-naphthyl acetate [*10519-11-6*], $C_{12}H_{20}O_2$, M_r 196.29, *bp* (650 Pa) 120 °C, d^{25} 1.005 – 1.015, n_D^{25} 1.475 – 1.482, is a fragrance substance that does not occur in nature. It consists of a mixture of several stereoisomers and is a colorless liquid with a sweet-fruity-herbaceous odor and a slight jasmin note.

Decahydro-β-naphthyl acetate is prepared by esterification of technical-grade decahydro-β-naphthol (e.g., with acetic anhydride). The acetate is used for perfuming household products.

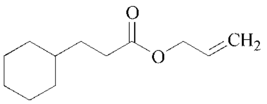


4,7-Methano-3a,4,5,6,7,7a-hexahydro-5(or 6)-indenyl acetate [*2500-83-6*] (or [*5413-60-5*]), $C_{12}H_{16}O_2$, M_r 192.26, *bp* (1 kPa) 119 – 121 °C, d_4^{25} 1.0714, n_D^{25} 1.4935, is a colorless liquid with a herbal, fresh-woody odor. It consists of a mixture of isomers that is obtained by addition of acetic acid to dicyclopentadiene in the presence of an acid catalyst. It is used for perfuming soaps, detergents, and air fresheners.

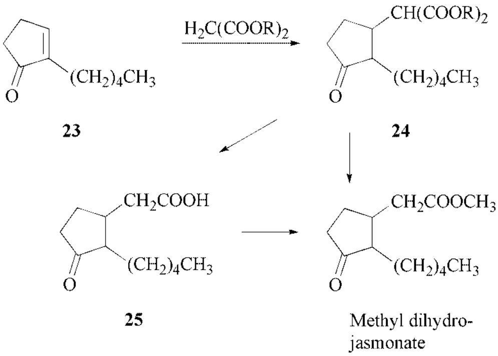


Trade Names. Cyclacet (IFF), Herbaflorat (Haarmann & Reimer), Verdylacetate (Givaudan Roure).

Allyl 3-cyclohexylpropionate [*2705-87-5*], $C_{12}H_{20}O_2$, M_r 196.29, *bp* (130 Pa) 91 °C, has not yet been found in nature. It is a colorless liquid with a sweet-fruity odor, reminiscent of pineapples. The ester is prepared by esterification of 3-cyclohexylpropionic acid (obtained by hydrogenation of cinnamic acid) with allyl alcohol. It is used in perfumery to obtain fruity top notes as well as pineapple and chamomile nuances. (Limiting IFRA recommendation)

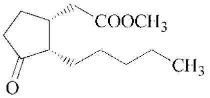


Methyl dihydrojasmonate [*24851-98-7*], methyl (3-oxo-2-pentylcyclopentyl)acetate, $C_{13}H_{22}O_3$, M_r 226.32, *bp* (1 Pa) 85 – 90 °C, $d_4^{21.6}$ 1.003, $n_D^{20.2}$ 1.4589, is a jasmin fragrance that is closely related to methyl jasmonate, which occurs in jasmin oil. Methyl dihydrojasmonate has been identified in tea. It is a liquid with a typical fruity, jasmin-like blossom odor. Methyl dihydrojasmonate is prepared as *cis/trans*-isomeric mixture by Michael addition of malonic esters to 2-pentyl-2-cyclopenten-1-one (**23**), followed by hydrolysis and decarboxylation of the resulting 2-pentyl-3-oxocyclopentyl malonate (**24**), and esterification of the (2-pentyl-3-oxocyclopentyl)acetic acid (**25**) [117]. Dealkoxycarbonylation of **24** can also be accomplished directly with water at elevated temperature [118].

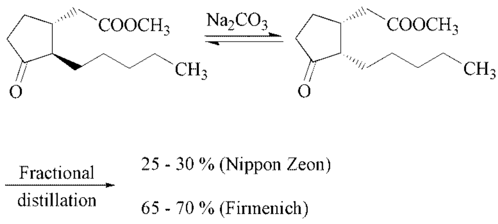


Methyl dihydrojasmonate is used in perfumery for blossom fragrances, particularly in jasmin types.
Trade Names. Hedione (Firmenich).

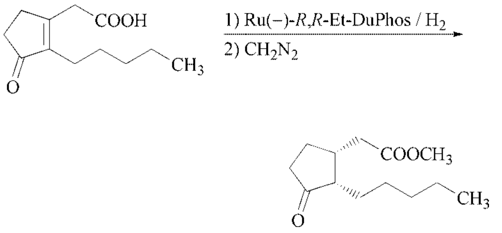
***cis*-Methyldihydrojasmonate** [*24851-98-7*], methyl (3-oxo-2-pentylcyclopentyl)acetate, $C_{13}H_{22}O_3$, M_r 226.32, *bp* (7 Pa) 180 °C, d_{20}^{20} 1.001 – 1.009, has an extremely powerful hedionic, jasminic odor.



Although *cis*-methyldihydrojasmonate is the minor isomer of hedione (see page 49), it is the much more intensive one. Its odor threshold is about 20 times lower than that of the *trans*-isomer. Several attempts have been made to synthesize the pure *cis*-isomer. One approach is heating of the *trans*-isomer with sodium carbonate followed by fractional distillation [119, 120]:

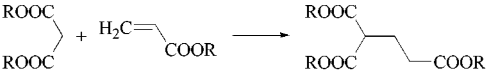


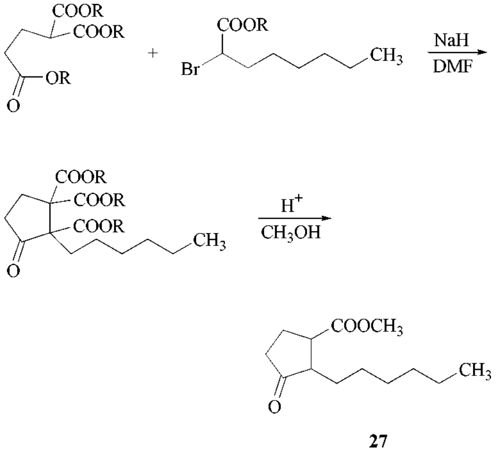
A *cis* : *trans* ratio of 96 : 4 was obtained by catalytic asymmetric hydrogenation of the acid in the presence of the chiral ruthenium catalyst DuPhos (**26**):



Due to its thermodynamic instability *cis*-methyldihydrojasmonate is only stable in media having a pH value of 5.5 to 6.5.
Trade Names. Hedione HC (Firmenich), Cepionate (Nippon Zeon).

Methyl 2-hexyl-3-oxocyclopentanecarboxylate [*37172-53-5*] (**27**), $C_{13}H_{22}O_3$, M_r 226.32, *bp* (8 Pa) 85 °C, n_D^{20} 1.4562, is a colorless liquid with a long-lasting, floral, jasmin-like odor, that has only little of the fatty aspect characteristic of many jasmin fragrances. The product has not yet been found in nature.





27

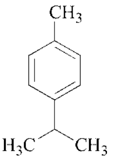
Compound **27** can be prepared by condensing an alkyl α-bromocaprylate with a trialkyl propane-1,1,3-tricarboxylate to give a substituted cyclopentanone. Hydrolysis, decarboxylation, and esterification of the resulting monocarboxylic acid with methanol yields the desired ester [121]. Trialkyl propane-1,1,3-tricarboxylates can be prepared by Michael addition of dialkyl malonates to alkyl acrylates.

Compound **27** is used in perfumery in floral compositions.
Trade Name. Jasmopol (Haarmann & Reimer).

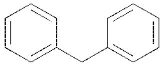
2.5. Aromatic Compounds

2.5.1. Hydrocarbons

A few alkyl- and aralkyl-substituted aromatic hydrocarbons find limited use in perfumery. Examples include *p*-cymene [*99-87-6*], which is a component of many essential oils and when pure has a weak, citrus odor, as well as diphenylmethane [*101-81-5*] which has an odor like geranium:



p-Cymene



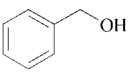
Diphenylmethane

2.5.2. Alcohols and Ethers

Phenethyl alcohol is qualitatively and quantitatively one of the most important fragrance substances that belongs to the class of araliphatic alcohols. Its lower homologue (benzyl alcohol) and higher homologue (dihydrocinnamic alcohol) also have characteristic odor properties, but are more frequently used in the form of their esters. Cinnamic alcohol, the most important unsaturated araliphatic alcohol, is valuable for both fragrances and flavors.

The araliphatic alcohols mentioned above occur in many natural fragrances and flavors, but are generally not the main components. These alcohols are nearly always prepared synthetically for use in compositions. The branched-chain homologues of phenethyl and dihydrocinnamic alcohols (dimethyl benzyl carbinol and dimethyl phenethyl carbinol, respectively) are used in fairly large amounts as fragrance materials, but have not been found in nature.

Benzyl alcohol [*100-51-6*], C_7H_8O, M_r 108.14, *bp* (101.3 kPa) 205.4 °C, d_4^{20} 1.0419, n_D^{20} 1.5396, occurs in many essential oils and foods. It is a colorless liquid with a weak, slightly sweet odor. For further details on the chemical properties and synthesis of benzyl alcohol, see→ Benzyl Alcohol, Chap. 3.



Because of its relatively weak odor, benzyl alcohol is used in fragrance and flavor compositions mainly as a solvent and for dilution. It is the starting material for a large number of benzyl esters, which are important fragrance and flavor substances.

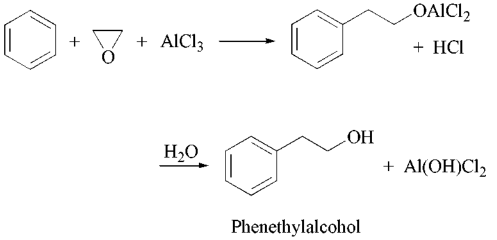
Phenethyl alcohol [*60-12-8*], 2-phenylethyl alcohol, $C_8H_{10}O$, M_r 122.17, *bp* (101.3 kPa) 219.8 °C, d_4^{20} 1.0202, n_D^{20} 1.5325, is the main component of rose oils obtained from rose blossoms. It occurs in smaller quantities in neroli oil, ylang-ylang oil, carnation oil, and geranium oils. Since the alcohol is rather soluble in water, losses occur when essential oils are produced by steam distillation.

Properties. Phenethyl alcohol is a colorless liquid with a mild rose odor. It can be dehydrogenated catalytically to phenylacetaldehyde and oxidized to phenylacetic acid (e.g., with chromic acid). Its lower molecular mass fatty acid esters as well as some alkyl ethers, are valuable fragrance and flavor substances.

Production. Many synthetic methods are known for preparing phenethyl alcohol; the following are currently of industrial importance:

Friedel–Crafts Reaction of Benzene and Ethylene Oxide.

In the presence of molar quantities of aluminum chloride, ethylene oxide reacts with benzene to give an addition product, which is hydrolyzed to phenethyl alcohol:

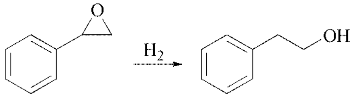


Phenethylalcohol

Formation of byproducts, such as 1,2-diphenylethane, is largely avoided by using an excess of benzene and low temperature. Special purification procedures are required to obtain a pure product that is free of chlorine and suitable for use in perfumery.

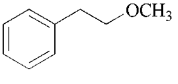
Hydrogenation of Styrene Oxide.

According to a patent, excellent yields of phenethyl alcohol are obtained when styrene oxide is hydrogenated at low temperature, using Raney nickel as a catalyst and a small amount of sodium hydroxide [122].

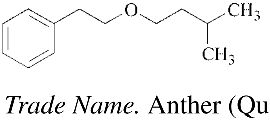


Uses. Phenethyl alcohol is used frequently and in large amounts as a fragrance compound. It is a popular component in rose type compositions, but it is also used in other blossom notes. It is stable to alkali and, therefore, ideally suited for use in soap perfumes.

Phenethyl methyl ether [*3558-60-9*], $C_9H_{12}O$, M_r 136.19, *bp* (94.6 kPa) 185–186 °C, d^{27} 0.9417, n_D^{24} 1.4970, is a colorless liquid with a sharp, rosy-green odor. It is used in oriental type perfumes as well as in artificial keora oil.

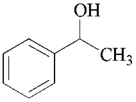


Phenethyl isoamyl ether [*56011-02-0*], $C_{13}H_{20}O$, M_r 192.30, d_{25}^{25} 0.901 – 0.904, n_D^{20} 1.481 – 1.484, is a colorless liquid with a green, sweet-flowery odor of chamomile blossoms and a secondary, soapy note; it is used in perfumes.



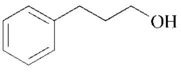
Trade Name. Anther (Quest).

1-Phenylethyl alcohol [*98-85-1*], styrallyl alcohol, $C_8H_{10}O$, M_r 122.17, *mp* 20 °C, *bp* (101.3 kPa) 203 °C, d_4^{20} 1.0135, n_D^{20} 1.5275, has been identified as a volatile component of food (e.g., in tea aroma and mushrooms). The alcohol is a colorless liquid with a dry, roselike odor, slightly reminiscent of hawthorn. It can be prepared by catalytic hydrogenation of acetophenone. 1-Phenylethyl alcohol is used in small quantities in perfumery and in larger amounts for the production of its esters, which are more important as fragrance compounds.



Dihydrocinnamic alcohol [*122-97-4*], 3-phenylpropanol, hydrocinnamic alcohol, $C_9H_{12}O$, M_r 136.19, *bp* (100 kPa) 237.5 °C, d_4^{20} 1.008, n_D^{20} 1.5278, occurs both in free and esterified form in resins and balsams (e.g., benzoe resin and Peru balsam). It has been identified in fruit and cinnamon.

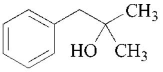
Hydrocinnamic alcohol is a slightly viscous, colorless liquid with a blossomy-balsamic odor, slightly reminiscent of hyacinths. Esterification with aliphatic carboxylic acids is important because it leads to additional fragrance and flavor compounds.



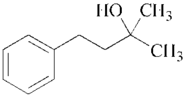
Hydrocinnamic alcohol is prepared by hydrogenation of cinnamaldehyde. A mixture of hydrocinnamic alcohol and the isomeric 2-phenylpropanol can be obtained from styrene by a modified oxo synthesis. The two isomers can be separated by distillation [123].

Hydrocinnamic alcohol is used in blossom compositions for balsamic and oriental notes.

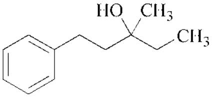
α,α-Dimethylphenethyl alcohol [*100-86-7*], 1-phenyl-2-methyl-2-propanol, α,α-dimethyl benzyl carbinol, DMBC, $C_{10}H_{14}O$, M_r 150.22, *mp* 24 °C, *bp* (101.3 kPa) 214 – 216 °C, d_4^{20} 0.9840, n_D^{20} 1.5170, has not yet been found in nature. The alcohol has a floral-herbaceous odor, reminiscent of lilac, and is prepared by a Grignard reaction of benzylmagnesium chloride and acetone. It is used in perfumery for various flower notes (e.g., lilac, hyacinth, mimosa). The alcohol is stable to alkali and, thus, is suited for soap perfumes. It is used to prepare a number of esters, which are also used as fragrance compounds.



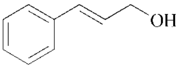
4-Phenyl-2-methyl-2-butanol [*103-05-9*], α,α-dimethylphenethyl carbinol, $C_{11}H_{16}O$, M_r 164.25, *bp* (1.9 kPa) 124 – 125 °C, $d_4^{20.7}$ 0.9626, $n_D^{20.7}$ 1.5077, is a colorless liquid with a dry-flowery, lily-like odor. It has been identified in cocoa aroma and is prepared by a Grignard reaction of benzylacetone and methylmagnesium chloride. It is used in blossom compositions.



1-Phenyl-3-methyl-3-pentanol [*10415-87-9*], phenethyl methyl ethyl carbinol, $C_{12}H_{18}O$, M_r 178.28, *bp* (1.7 kPa) 129 – 130 °C, d_4^{25} 0.9582, n_D^{20} 1.509 – 1.513, has not yet been found in nature. It is a colorless liquid with a delicate peony, slightly fruity odor. Phenethyl methyl ethyl carbinol can be prepared from benzylacetone and ethylmagnesium chloride by a Grignard reaction. It is used to perfume soap, cosmetics, and detergents.



Cinnamic alcohol [*104-54-1*], 3-phenyl-2-propen-1-ol, $C_9H_{10}O$, M_r 134.18; *trans*-isomer [*4407-36-7*]: *mp* 34 °C, *bp* (101.3 kPa) 257.5 °C, d_4^{20} 1.0440, n_D^{20} 1.5819; this alcohol can exist in *cis* and *trans* forms. Although both isomers occur in nature, the *trans*-isomer is far more abundant and is present, for example, in styrax oil. *trans*-Cinnamic alcohol is a colorless, crystalline solid with a hyacinth-like balsamic odor.



trans-Cinnamic alcohol

Cinnamic alcohol can be dehydrogenated to give cinnamaldehyde and oxidized to give cinnamic acid. Hydrogenation yields 3-phenylpropanol and/or 3-cyclohexylpropanol. Reaction with carboxylic acids or carboxylic acid derivatives results in the formation of cinnamyl esters, some of which are used as fragrance compounds.

Production. Cinnamic alcohol is prepared on an industrial scale by reduction of cinnamaldehyde. Three methods are particularly useful:

1) In the *Meerwein–Ponndorf reduction,* cinnamaldehyde is reduced to cinnamic alcohol (yield, ca. 85 %) with isopropyl or benzyl alcohol in the presence of the corresponding aluminum alcoholate.
2) A 95 % yield of cinnamic alcohol is obtained by selective hydrogenation of the carbonyl group in cinnamaldehyde with, for example, an *osmium–carbon* catalyst [124].
3) High yields of cinnamic alcohol can be obtained by reduction of cinnamaldehyde with *alkali borohydrides.* Formation of dihydrocinnamic alcohol is thus avoided [125].

Uses. Cinnamic alcohol is valuable in perfumery for its odor and fixative properties. It is a component of many flower compositions (lilac, hyacinth, and lily of the valley) and is a starting material for cinnamyl esters, several of which are valuable fragrance compounds. In aromas, the alcohol is used for cinnamon notes and for rounding off fruit aromas. It is used as an intermediate in many syntheses (e.g., for pharmaceuticals such as the antibiotic chloromycetin). (Limiting IFRA recommendation)

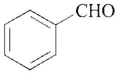
2.5.3. Aldehydes and Acetals

Many of the aldehydes discussed in this section are treated in detail elsewhere (→ Aldehydes, Aliphatic and Araliphatic).

Several araliphatic aldehydes are of special commercial importance as fragrance and flavor materials. These include cinnamaldehyde and its homologues in which the side-chain carries an alkyl substituent; α-amyl- and α-hexylcinnamaldehyde are particularly important. Other important members of this group are the substituted phenylpropanals, 4-isopropyl- and 4-*tert*-butyl-α-methyldihydrocinnamaldehyde. Arylacetaldehydes and arylpropionaldehydes are, in comparison, seldom used in compositions. The corresponding acetals are more stable and are used as well, although their odor is slightly different and significantly weaker.

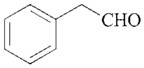
The simplest araliphatic aldehyde, benzaldehyde and its 4-isopropyl homologue, cuminaldehyde, are used to a limited extent as fragrance and flavor compounds. However, both compounds are used in large quantity for the production of cinnamic and dihydrocinnamic aldehydes, respectively.

Benzaldehyde [*100-52-7*], C_7H_6O, M_r 106.12, *bp* (101.3 kPa) 178.1 °C, d_4^{15} 1.0415, n_D^{20} 1.5463, is the main, characteristic component of bitter almond oil. It occurs in many other essential oils and is a colorless liquid with a bitter almond odor. For further details on the chemical properties and synthesis of benzaldehyde, see → Benzaldehyde, Chap. 3.



Benzaldehyde is used in aroma compositions for its bitter almond odor. It is the starting material for a large number of araliphatic fragrance and flavor compounds.

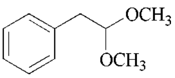
Phenylacetaldehyde [*122-78-1*], C_8H_8O, M_r 120.15, *bp* (101.3 kPa) 195 °C, d_4^{20} 1.0272, n_D^{20} 1.5255, has been identified in many essential oils and as a volatile constituent of foods. It is a colorless liquid with a sweet-green odor, reminiscent of hyacinth. Since it readily undergoes oxidation and polymerizes, it must be stabilized by addition of antioxidants and by dilution with, for example, diethyl phthalate before use in compositions.



Phenylacetaldehyde can be obtained in high yield by vapor-phase isomerization of styrene oxide, for example, with alkali-treated silica–alumina [126]. Another process starts from phenylethane-1,2-diol, which can be converted into phenylacetaldehyde in high yield. The reaction is performed in the vapor phase in the presence of an acidic silica–alumina catalyst [127].

Phenylacetaldehyde is used in perfume compositions, in particular for hyacinth and rose notes. (IFRA recommendation)

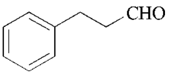
Phenylacetaldehyde dimethyl acetal [*101-48-4*], $C_{10}H_{14}O_2$, M_r 166.22, *bp* (100.2 kPa) 219 – 221 °C, d^{18} 1.004, is a colorless liquid with a strong, rose-petal odor. The dimethyl acetal is more stable than phenylacetaldehyde itself. It imparts a herbal green note to many flower compositions.



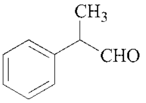
Trade Names. Lilas Vert (Firmenich), Viridine (Givaudan Roure).

Dihydrocinnamaldehyde [*104-53-0*], 3-phenylpropanal, $C_9H_{10}O$, M_r 134.18, *bp* (2.7 kPa) 112 °C, d_4^{20} 1.019, n_D^{20} 1.5266, occurs in Sri Lanka cinnamon oil, among others. The aldehyde is a colorless liquid with a strong, flowery, slightly balsamic, heavy hyacinth-like odor. It tends to undergo self-condensation.

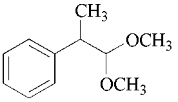
Dihydrocinnamaldehyde can be obtained with scarcely any byproducts by selective hydrogenation of cinnamaldehyde. It is used in perfumery for hyacinth and lilac compositions.



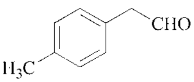
Hydratropaldehyde [*93-53-8*], 2-phenylpropanal, $C_9H_{10}O$, M_r 134.18, *bp* (1.5 kPa) 92 – 94 °C, d_4^{20} 1.0089, n_D^{20} 1.5176, is a colorless liquid with a green hyacinth odor. Hydratropaldehyde can be hydrogenated to hydratropic alcohol, which is also used to a limited extent as a fragrance compound. Hydratropaldehyde is obtained from styrene by oxo synthesis; small quantities of the isomeric dihydrocinnamaldehyde are formed as a byproduct. Hydratropaldehyde is used in perfumery in blossom compositions.



Hydratropaldehyde dimethyl acetal [*90-87-9*], $C_{11}H_{16}O_2$, M_r 180.25, n_D^{20} 1.4938, is a liquid with a mushroom-like, earthy odor. It is used for green nuances in flower compositions.



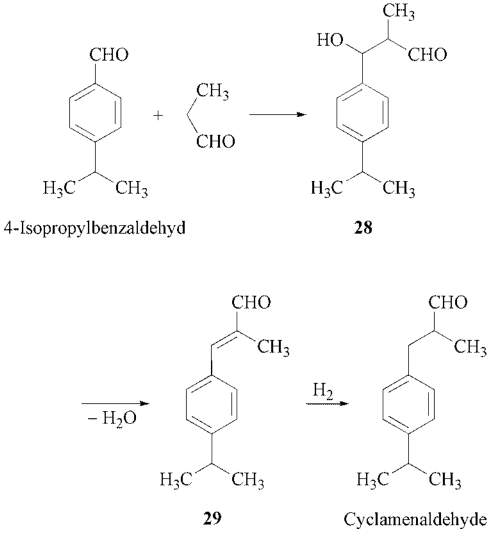
4-Methylphenylacetaldehyde [*104-09-6*], $C_9H_{10}O$, M_r 134.18, *bp* (101.3 kPa) 221 – 222 °C, d_4^{20} 1.0052, n_D^{20} 1.5255, which has been identified in corn oil, is a colorless liquid with a strong green odor. It can be prepared by reaction of 4-methylbenzaldehyde with chloroacetates, followed by hydrolysis of the resulting glycidates and decarboxylation. The aldehyde is used in flower compositions for green notes.



Cyclamenaldehyde [*103-95-7*], 2-methyl-3-(4-isopropylphenyl)propanal, $C_{13}H_{18}O$, M_r 190.28, *bp* (300 Pa) 108 – 108.5 °C, d_4^{20} 0.9502, n_D^{20} 1.5068, has been reported in nutmeg [128]. The commercially available racemate is a colorless to yellowish liquid with an intense flowery odor reminiscent of *Cyclamen europaeum* (cyclamen, sowbread).

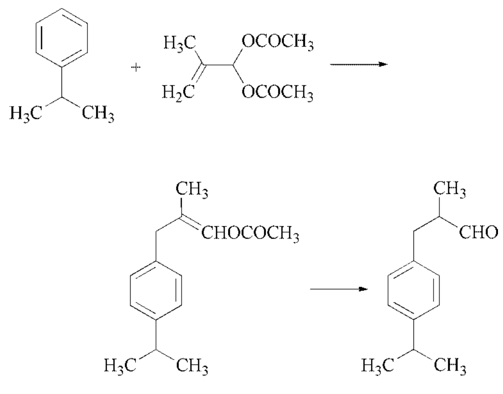
Production. Two main processes are used for the industrial synthesis of cyclamenaldehyde:

1) Alkaline condensation of 4-isopropylbenzaldehyde and propanal results, via the aldol **28**, in the formation of 2-methyl-3-(4-isopropylphenyl)-2-propenal (**29**). The unsaturated



aldehyde is hydrogenated selectively to the saturated aldehyde in the presence of potassium acetate and a suitable catalyst, such as palladium–alumina [129]: see previous page.

2) Friedel–Crafts reaction of isopropylbenzene and 2-methylpropenal diacetate (methacrolein diacetate) in the presence of titanium tetrachloride/boron trifluoride etherate gives cyclamenaldehyde enolacetate, which is hydrolyzed to the aldehyde [130]:

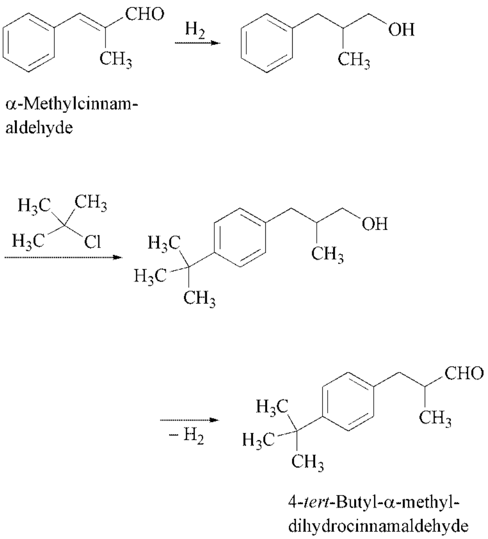

Cyclamenaldehyde

Uses. Cyclamenaldehyde is an important component for obtaining special blossom notes in perfume compositions, particularly the cyclamen type. Because of its fresh-flowery aspect, it is also used as the top note in many other blossom fragrances.

4-*tert*-Butyl-α-methyldihydrocinnamaldehyde [*80-54-6*], 2-methyl-3-(4-*tert*-butylphenyl)propanal, $C_{14}H_{20}O$, M_r 204.31, *bp* (800 Pa) 126 – 127 °C, d_4^{20} 0.9390, n_D^{20} 1.5050, is a homologue of cyclamenaldehyde, but is not found in nature. The racemic compound is a colorless to slightly yellow liquid with a mild-flowery odor, reminiscent of cyclamen and lily of the valley.

The aldehyde is prepared by the same routes as cyclamenaldehyde (see under Cyclamenaldehyde, page 54).

A patent describes the following preparation from α-methylcinnamaldehyde. α-Methylcinnamaldehyde (from benzaldehyde and propionaldehyde) is hydrogenated to α-methyldihydrocinnamic alcohol. The alcohol is alkylated with *tert*-butyl chloride or isobutene to 4-*tert*-butyl-α-methyldihydrocinnamic alcohol, which is subsequently dehydrogenated to the desired aldehyde [131].


α-Methylcinnamaldehyde

4-*tert*-Butyl-α-methyldihydrocinnamaldehyde

The compound is more stable than cyclamenaldehyde and is a popular component of flower compositions, particularly lily of the valley and linden types, because of its mild, pleasant, blossom fragrance. Large quantities are used in soap and cosmetic perfumes.

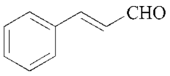
Trade Names. Lilestral (IFF), Lilial (Givaudan Roure).

Cinnamaldehyde [*14371-10-9*], 3-phenyl-2-propenal, C_9H_8O, M_r 132.16, *trans*-isomer *bp* (101.3 kPa) 253 °C, d_4^{20} 1.0497, n_D^{20} 1.6195, is the main component of cassia oil (ca. 90 %) and Sri Lanka cinnamon bark oil (ca. 75 %). Smaller quantities are found in many other essential oils. In nature, the *trans*-isomer is predominant.

trans-Cinnamaldehyde is a yellowish liquid with a characteristic spicy odor, strongly reminiscent of cinnamon. Being an α,β-unsaturated aldehyde, it undergoes many reactions, of which hydrogenation to cinnamic alcohol, dihydrocinnamaldehyde, and dihydrocinnamic alcohol are important. Cinnamic acid is formed by autoxidation.

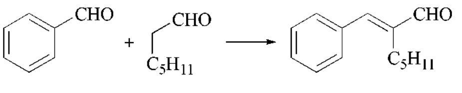
On an industrial scale, cinnamaldehyde is prepared almost exclusively by alkaline condensation of benzaldehyde and acetaldehyde. Self-condensation of acetaldehyde can be avoided by using an excess of benzaldehyde and by slowly adding acetaldehyde [132].

Cinnamaldehyde is used in many compositions for creating spicy and oriental notes (e.g., soap perfumes). It is the main component of artificial cinnamon oil. In addition, it is an important intermediate in the synthesis of cinnamic alcohol and dihydrocinnamic alcohol.



α-Amylcinnamaldehyde [*122-40-7*], 2-pentyl-3-phenyl-2-propenal, $C_{14}H_{18}O$, M_r 202.30, *bp* (0.7 kPa) 140 °C, d_4^{20} 0.9710, n_D^{20} 1.5381. Its natural occurrence as a genuine product is debatable. It is a light yellow liquid with a flowery, slightly fatty odor, which becomes reminiscent of jasmin when diluted. The aldehyde is relatively unstable and must be stabilized by antioxidants.

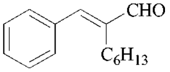
It is prepared from benzaldehyde and heptanal in the same way as cinnamaldehyde.



α-Amylcinnamaldehyde

α-Amylcinnamaldehyde is a very popular fragrance substance for creating jasmin notes. It is stable to alkali and long-lasting; large quantities are used, particularly in soap perfumes.

α-Hexylcinnamaldehyde [*101-86-0*], 2-hexyl-3-phenyl-2-propenal, $C_{15}H_{20}O$, M_r 216.32, *bp* (2 kPa) 174 – 176 °C, d^{24} 0.9500, n_D^{25} 1.5268, has not yet been identified in nature. It is a yellow liquid with a mild, slightly fatty, flowery, somewhat herbal odor and a distinct jasmin note. Like the α-amyl homologue, α-hexylcinnamaldehyde must be protected against oxidation by the addition of stabilizers. It is prepared in a manner similar to α-amylcinnamaldehyde by alkaline condensation of excess benzaldehyde with octanal (instead of heptanal). α-Hexylcinnamaldehyde is widely used in flower compositions (e.g., jasmin and gardenia) and, because of its stability to alkali, in soap perfumes.



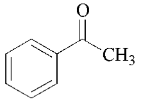
2.5.4. Ketones (→ Ketones)

The aromatic ketones that occur or are used as fragrance and flavor materials are predominantly aryl methyl ketones, which include acetophenones and β-naphthyl methyl ketone. Several acetylpolymethylindanes and -tetralins are commercially important as musk fragrances. Musk ketone, a substituted nitroacetophenone, is discussed in page 62.

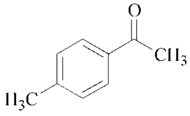
Acetophenone [*98-86-2*], methyl phenyl ketone, C_8H_8O, M_r 120.15, *mp* 20.5 °C, *bp* (101.3 kPa) 202.0 °C, d_4^{20} 1.0281, n_D^{20} 1.5372, is a naturally occurring component of a large number of foods and essential oils. It is a colorless liquid with a penetrating sweet odor, reminiscent of orange blossom.

Acetophenone can be hydrogenated catalytically to 1-phenylethanol. It is obtained as a byproduct in the Hock phenol synthesis and is purified from the high-boiling residue by distillation (→ Ketones, Chap. 7.1.). The quantitites obtained from this source satisfy the present demand.

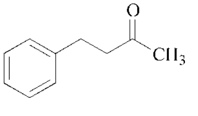
Acetophenone is used for perfuming detergents and industrial products and is an intermediate in the synthesis of other fragrance compounds.



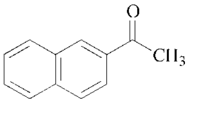
4-Methylacetophenone [*122-00-9*], *p*-tolyl methyl ketone, $C_9H_{10}O$, M_r 134.18, *mp* 28 °C, *bp* (101.3 kPa) 226 °C, d_4^{20} 1.0051, n_D^{20} 1.5335, has been identified in Brazilian rosewood oil and in pepper. It occurs as colorless crystals with a flowery-sweet odor that is milder than that of acetophenone. 4-Methylacetophenone is prepared from toluene and acetic anhydride or acetyl chloride by a Friedel–Crafts reaction. It is used for blossom notes in mimosa and hawthorn type perfumes, especially in soap perfumes.



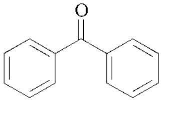
Benzylacetone [*2550-26-7*], 1-phenyl-3-butanone, $C_{10}H_{12}O$, M_r 148.20, *bp* (101.3 kPa) 233 – 234 °C, d_4^{22} 0.9849, n_D^{22} 1.5110, has been identified as a volatile component of cocoa. Benzylacetone is a sweet-flowery smelling liquid, which can be prepared by selective hydrogenation of benzylidene acetone (from benzaldehyde and acetone). It is used in soap perfumes.



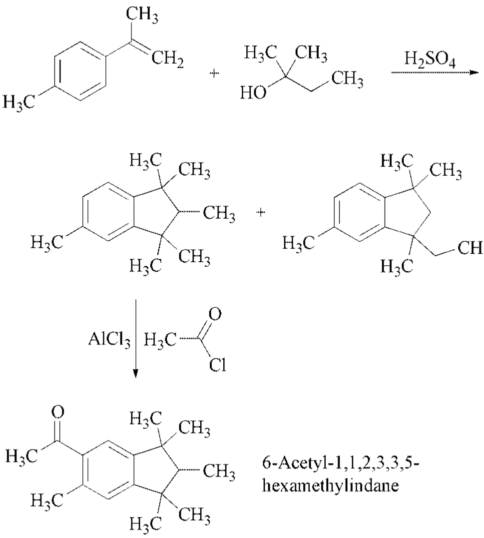
Methyl β-naphthyl ketone [*93-08-3*], $C_{12}H_{10}O$, M_r 170.21, *bp* (1.7 kPa) 171 – 173 °C, *mp* 56 °C, d_4^{20} 1.171, n_D^{20} 1.6752, has been identified in some essential oils. It smells like orange blossom and is a colorless crystalline solid. It is usually prepared by Friedel–Crafts acetylation of naphthalene (with acetylchloride, acetic anhydride, etc.) in the presence of aluminum chloride. In polar solvents (e.g., nitrobenzene), the percentage of the simultaneously formed α-isomer is lower. Methyl β-naphthyl ketone is used in eaux de cologne, soap perfumes, and detergents. It is a good fixative.



Benzophenone [*119-61-9*], diphenyl ketone, $C_{13}H_{10}O$, M_r 182.22, *bp* (6.3 kPa) 200.5 °C, *mp* 48.1 °C, d^{50} 1.976, has been identified as a flavor component of grapes. It is a colorless crystalline solid with a rosy, slightly geranium-like odor. It can be prepared in several ways (→ Ketones, Chap. 7.3.), for example, by Friedel–Crafts reaction of benzene and benzoyl chloride with aluminum chloride, or of benzene and carbon tetrachloride, and subsequent hydrolysis of the resulting α,α-dichlorodiphenylmethane. Benzophenone can also be prepared by oxidation of diphenylmethane. It is used in flower compositions and as a fixative.

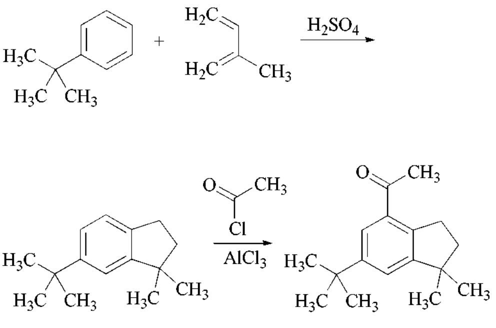


6-Acetyl-1,1,2,3,3,5-hexamethylindane [*15323-35-0*], $C_{17}H_{24}O$, M_r 244.38, *mp* 35 °C, is a synthetic musk fragrance. It is prepared by Friedel–Crafts acetylation of 1,1,2,3,3,5-hexamethylindane, which can be obtained as a 70 : 30 mixture with 1,1,3,5-tetramethyl-3-ethylindane by reacting α,p-dimethylstyrene with amylenes or 2-methyl-2-butanol in a mixture of acetic acid and concentrated sulfuric acid [133]:



The indane ketone is a musk fragrance that is stable to light and in soap. It is used in perfumes and cosmetics for its fixative properties as well as its fragrance.
Trade Name. Phantolide (Haarmann & Reimer).

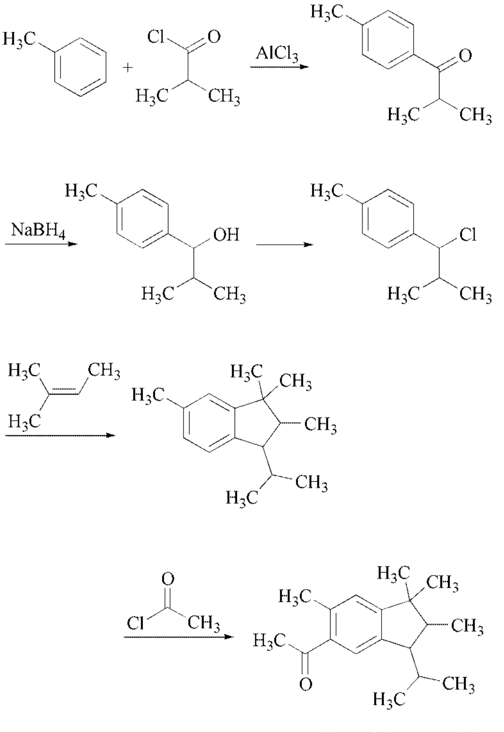
4-Acetyl-1,1-dimethyl-6-*tert*-butylindane [*13171-00-1*], $C_{17}H_{24}O$, M_r 244.38, *mp* 76.7 – 77.2 °C, is a musk fragrance that does not occur in nature. It is prepared by reacting *tert*-



butylbenzene with isoprene in the presence of sulfuric acid, followed by acetylation of the resulting 1,1-dimethyl-6-*tert*-butylindane [134]: see previous page.

The indane is light-stable and is mainly used for perfuming soaps and cosmetics.
Trade Names. Celestolide (IFF), Crysolide (Givaudan Roure).

5-Acetyl-1,1,2,6-tetramethyl-3-isopropylindane [*68140-48-7*], $C_{18}H_{26}O$, M_r 258.40, *bp* (130 Pa) 144 – 146 °C, n_{D}^{20} 1.5301, is also a musk fragrance that does not occur in nature. It is prepared from toluene and isobutyryl chloride by a Friedel–Crafts reaction that yields *p*-tolyl isopropyl ketone; the ketone is reduced to the corresponding alcohol. Chlorination and treatment with 2-methyl-2-butene yield 1-isopropyl-2,3,3,5-tetramethylindane, which by a Friedel–Crafts reaction with acetyl chloride gives the title compound [135]:

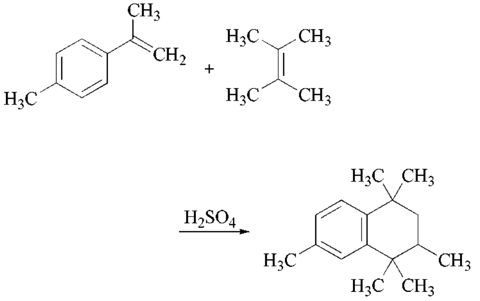


5-Acetyl-1,1,2,6-tetramethyl-3-isopropylindane

It is used in perfume compositions for soaps and detergents.
Trade Name. Traseolide (Quest).

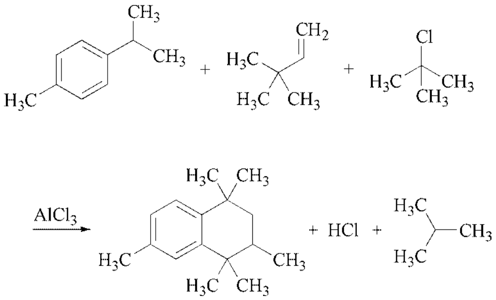
6-Acetyl-1,1,2,4,4,7-hexamethyltetralin [*1506-02-1*], $C_{18}H_{26}O$, M_r 258.40, *mp* 55.5 °C, *bp* (250 Pa) 119 °C, is a synthetic musk fragrance. It is prepared from 1,1,2,4,4,7-hexamethyltetralin, which is obtained by one of the following routes:

1) Reaction of α,*p*-dimethylstyrene with tetramethylethene [136] or 2,3-dimethylbutan-2-ol [133] in an acetic acid–sulfuric acid mixture yields the desired hexamethyltetralin, in addition to polymerized starting materials:



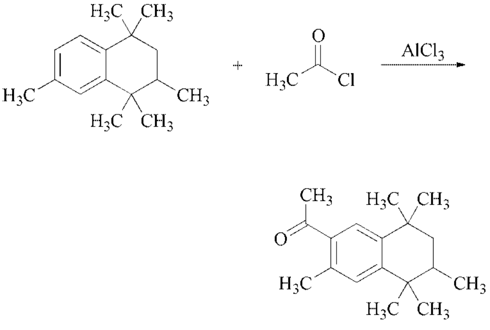
1,1,2,4,4,7-Hexamethyltetralin

2) Reaction of *p*-cymene with 2,2-dimethyl-3-butene (neohexene) and a tertiary alkylhalide (as a hydrogen scavenger) in the presence of catalytic amounts of anhydrous aluminum halide in inert solvents produces a high yield of the hexamethyltetralin [137].



1,1,2,4,4,7-Hexamethyltetralin is subsequently acetylated to 6-acetyl-1,1,2,4,4,7-hexamethyltetralin, e.g., with acetyl chloride and aluminum chloride (see next page).

The product is a light-stable, versatile musk fragrance that is used in soap and cosmetics.
Trade Names. Fixolide (Givaudan Roure), Tonalide (Haarmann & Reimer).



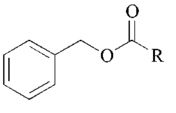
6-Acetyl-1,1,2,4,4,7-hexamethyltetralin

2.5.5. Esters of Araliphatic Alcohols and Aliphatic Acids

Esters of araliphatic alcohols and aliphatic acids are interesting as flavors and fragrances because of their characteristic odor properties. Acetates are the most popular esters. Benzyl acetate is particularly important commercially and occupies a prominent position in the fragrance and flavor industry.

Esters of other fatty acids are used to a lesser extent. In addition to benzyl esters and phenethyl esters, isomeric homologues with substituted side-chains are used in fairly large amounts in perfume compositions because of their special blossom odors. Not all have yet been found in nature. The esters are prepared from the corresponding alcohols via the customary routes (→ Esters, Organic).

Benzyl esters of lower molecular mass fatty acids occur widely in nature. The following are important fragrance and flavor materials:

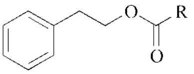


Benzyl acetate [*140-11-4*], R = CH_3, $C_9H_{10}O_2$, M_r 150.18, *bp* (101.3 kPa) 215 °C, d_4^{20} 1.0550, n_D^{20} 1.5232, is the main component of jasmin and gardenia oils. It occurs as a minor component in a large number of other essential oils and extracts. It is a colorless liquid with a strong, fruity, jasmin odor. Benzyl acetate is prepared by esterification of benzyl alcohol with acetic anhydride (e.g., with sodium acetate as a catalyst) or by reaction of benzyl chloride with sodium acetate (→ Benzyl Alcohol, Chap. 8.2.). In terms of volume, benzyl acetate is one of the most important fragrance and flavor chemicals.

Benzyl propionate [*122-63-4*], R = CH_2CH_3, $C_{10}H_{12}O_2$, M_r 164.20, *bp* (101.3 kPa) 219–220 °C, d_4^{20} 1.0335, n_D^{20} 1.4996, is a liquid with a sweet-fruity odor, which is used in perfumery for floral-fruity notes and in fruit flavor compositions.

Benzyl isovalerate [*103-38-8*], R = $CH_2CH(CH_3)_2$, $C_{12}H_{16}O_2$, M_r 192.26, *bp* (101.3 kPa) 245 °C, d_4^{20} 0.9900, n_D^{20} 1.4878, is a liquid with a heavy, flowery odor, which is used in perfumery for oriental and heavy blossom odors.

Phenethyl Esters. The most commonly used *phenethyl esters* are the following:

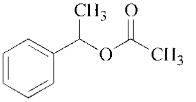


Phenethyl acetate [*103-45-7*], R = CH_3, $C_{10}H_{12}O_2$, M_r 164.20, *bp* (101.3 kPa) 232.6 °C, d_4^{20} 1.0883, n_D^{20} 1.5171, occurs in a number of essential oils and is a volatile aroma component of many fruits and alcoholic beverages. Phenethyl acetate is a colorless liquid with a fine rose scent and a secondary, sweet, honey note. It is used in perfumery as a modifier of phenethyl alcohol, e.g., in rose and lilac compositions. In addition, it is used in a large number of aromas, in keeping with its natural occurrence.

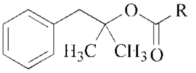
Phenethyl isobutyrate [*103-48-0*], R = $CH(CH_3)_2$, $C_{12}H_{16}O_2$, M_r 192.26, *bp* (2 kPa) 122–124 °C, d^{15} 0.9950, n_D^{20} 1.4871, occurs in peppermint oils. It has a heavy, fruity, blossom odor and is used accordingly in perfume and flavor compositions.

Phenethyl isovalerate [*140-26-1*], R = $CH_2CH(CH_3)_2$, $C_{13}H_{18}O_2$, M_r 206.28, *bp* (7.2 kPa) 141–145 °C, d^{15} 0.9845, n_D^{20} 1.4855, has been identified as a volatile aroma component of peppermint oils. The fruitiness of its odor is even more pronounced than that of the isobutyrate. It is used in small quantities for the same purposes as phenethyl isobutyrate.

1-Phenylethyl acetate [*93-92-5*], styrallyl acetate, $C_{10}H_{12}O_2$, M_r 164.20, *bp* (1.3 kPa) 92.5 °C, d_4^{20} 1.0277, n_D^{20} 1.4954, is a liquid with a dry, fruity-green, blossom odor, reminiscent of gardenia. It can occur in the form of optically active enantiomers, but only the racemate is used in perfumery. Styrallyl acetate is a key ingredient in gardenia fragrances and is added to many other blossom compositions, particularly for dry top notes.



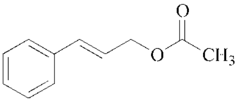
α,α-Dimethylphenethyl Esters. The following α,α-dimethylphenethyl esters are commercially important:



α,α-Dimethylphenethyl acetate [*151-05-3*], R = CH_3, $C_{12}H_{16}O_2$, M_r 192.26, *mp* ca. 30 °C, *bp* (400 Pa) 90 °C, d_{25}^{25} 0.998 – 1.000, n_D^{20} 1.4923, is a colorless liquid with a flowery-woody odor. The ester is used in blossom compositions, e.g., lily of the valley, rose, and geranium.

α,α-Dimethylphenethyl butyrate [*10094-34-5*], R = $(CH_2)_2CH_3$, $C_{14}H_{20}O_2$, M_r 220.31, *bp* (400 Pa) 96 °C, d_{25}^{25} 0.971 – 0.974, n_D^{20} 1.4860 – 1.4900, is a colorless liquid with a slightly herbal, strongly fruity odor, reminiscent of prune and apricot. It is used in perfumery as a modifier of the alcohol and for oriental notes.

Cinnamyl acetate [*103-54-8*], $C_{11}H_{12}O_2$, M_r 176.21, *bp* (1.3 kPa) 139 – 140 °C, d^{22} 1.0520, n_D^{20} 1.5420, is the only ester of cinnamic alcohol of any importance. *trans*-Cinnamyl acetate occurs in cassia oil and is a colorless liquid with a sweet-flowery-fruity, slightly balsamic odor. It is a good fixative and is used in blossom compositions (e.g., lilac and jasmin) and for oriental notes. In aroma compositions, it is used for cinnamon-fruity effects.

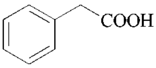


2.5.6. Aromatic Acids

Aromatic acids (e.g., benzoic acid) and araliphatic acids (e.g., phenylacetic, cinnamic, and dihydrocinnamic acids) occur in numerous essential oils and have also been identified in the aromas of many foods. However, phenylacetic acid is the only acid that is used in significant quantities as a fragrance and flavor substance.

Phenylacetic acid [*103-82-2*], $C_8H_8O_2$, M_r 136.15, *bp* (101.3 kPa) 265.5 °C, *mp* 78 °C, $d_4^{79.8}$ 1.0809, occurs in Japanese peppermint oil, in neroli oil, and in traces in rose oils. It is a volatile aroma constituent of many foods (e.g., honey). It forms colorless crystals that have a honey odor. For further details on chemical properties and synthesis, see → Phenylacetic Acid.

Because of its intense odor, phenylacetic acid is added to perfumes in small quantities for rounding off blossom odors. Addition to fruit aromas imparts a sweet honey note.

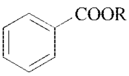


2.5.7. Esters Derived from Aromatic and Araliphatic Acids

The acid moiety generally determines the odor of esters derived from aromatic or araliphatic acids. Unless stated otherwise, the esters are prepared from the corresponding acids or acid derivatives and alcohols by the customary methods (→ Esters , Organic).

2.5.7.1. Benzoates

The following benzoates are used in fairly large quantities as perfumery materials.



Methyl benzoate [*93-58-3*], R = CH_3, $C_8H_8O_2$, M_r 136.15, *bp* (101.3 kPa) 199.6 °C, d_4^{20} 1.0888, n_D^{20} 1.5164, has been found in essential oils (e.g., ylang-ylang and tuberose blossom oil). It is a colorless liquid with a strong, dry-fruity, slightly phenolic odor. For further properties and synthesis, seeBenzoic Acid and Derivatives, Chap. 8.5. .

Methyl benzoate is used in perfume bases, such as ylang-ylang and tuberose types.

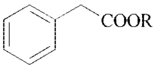
Hexyl benzoate [*6789-88-4*], R=$(CH_2)_5CH_3$, $C_{13}H_{18}O_2$, M_r 206.28, *bp* (102.6 kPa) 272 °C, is a liquid with a balsamic-green, melon-like odor. It is used in perfumery.

Benzyl benzoate [*120-51-4*], R = $CH_2C_6H_5$, $C_{14}H_{12}O_2$, M_r 212.25, *bp* (2.0 kPa) 170 – 171 °C, *mp* 21 – 22 °C, d_4^{25} 1.1121, n_D^{20} 1.5680, is the main component of Peru balsam. It occurs in fairly large amounts in a number of blossom concretes and absolutes (e.g., tuberose and hyacinth). It forms either a viscous liquid or solid flakes and has a weak, sweet-balsamic odor. For further properties and synthesis, see Benzoic Acid and Derivatives, Chap. 8.5.

Benzyl benzoate is used in perfumery as a fixative and as a modifier in heavy blossom fragrances.

2.5.7.2. Phenyl acetates

Of the phenyl acetates, the following are particularly important fragrance and flavor substances:



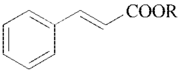
Ethyl phenyl acetate [*101-97-3*], R = CH_2CH_3, $C_{10}H_{12}O_2$, M_r 164.20, *bp* (101.3 kPa) 227 °C, d_4^{20} 1.0333, n_D^{20} 1.4980, is a volatile aroma component of fruit and honey. It is a colorless liquid with a strong, sweet odor reminiscent of honey. Small amounts are used in flower perfumes and in fruit flavors.

Geranyl phenyl acetate [*102-22-7*], R =$CH_2CH{=}C(CH_3)CH_2CH_2CH{=}C(CH_3)_2$, $C_{18}H_{24}O_2$, M_r 272.39, has not been found in nature. It is a yellow liquid with a mild rose odor and a secondary honey note. It is used as a fixative in rose compositions and heavy perfumes.

Phenethyl phenyl acetate [*102-20-5*], R = $CH_2CH_2C_6H_5$, $C_{16}H_{16}O_2$, M_r 240.30, *bp* (600 Pa) 177 – 178 °C, *mp* 26.5 °C, d_{25}^{25} 0.880, n_D^{20} 1.5496 – 1.5504, has not yet been identified in natural sources. It occurs as a colorless liquid or crystals, which have a heavy, sweet, rose or hyacinth odor and a distinct honey note. The ester is used particularly in flowery fragrance compositions and as a fixative.

2.5.7.3. Cinnamates

Three cinnamates are of some importance in perfumery:



Methyl cinnamate [*103-26-4*], R = CH_3, $C_{10}H_{10}O_2$, M_r 162.19, *bp* (101.3 kPa) 261.9 °C, *mp* 36.5 °C, d_4^{20} 1.0911, n_D^{21} 1.5766, occurs in essential oils, mostly as the *trans*-isomer. It is the main component of oils isolated from *Alpinia* species (content up to 80 %) and *Ocimum canum* varieties (> 50 %). It has also been identified as a volatile aroma component of cinnamon and strawberries.

Methyl cinnamate is a colorless crystalline solid with a fruity, sweet-balsamic odor. In addition to the common esterification methods, it can be prepared by Claisen condensation of benzaldehyde and methyl acetate in the presence of sodium. Methyl cinnamate is used in soap perfumes, as well as in blossom and oriental perfumes, and is sometimes added to aromas.

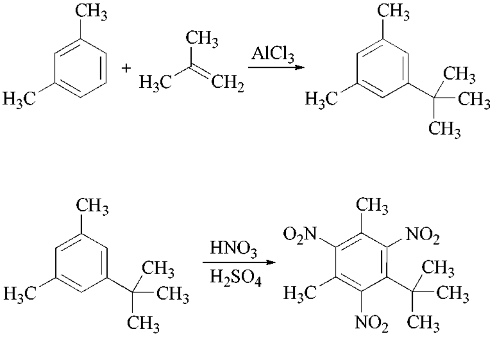
Benzyl cinnamate [*103-41-3*], R = $CH_2C_6H_5$, $C_{16}H_{14}O_2$, M_r 238.29, *mp* 35 – 36 °C, occurs in balsams and balsam oils. It forms white, sweet-balsamic-smelling crystals. Benzyl cinnamate is used as a fixative in perfumes and as a component of heavy, oriental perfumes.

Phenethyl cinnamate [*103-53-7*], R = $CH_2CH_2C_6H_5$, $C_{17}H_{16}O_2$, M_r 252.31, *mp* 65 – 68 °C, occurs in extracts from *Populus balsamifera* buds. It is a crystalline solid with a heavy, rosy-balsamic odor. It is used as a fixative in blossom fragrances.

2.5.8. Miscellaneous Compounds

Of the few aromatic, nitrogen-containing fragrance substances, the nitro musks are by far the most important. They are still considerably important commercially as substitutes for the natural macrocyclic musks that are difficult to synthesize, but nitro musks are being increasingly replaced by lightfast musk fragrances. Methyl anthranilate and its *N*-methyl derivative are also aromatic, nitrogen-containing compounds that are used as fragrances and flavors in fairly large amounts. A number of aromatic nitriles have been introduced; they are stable to alkali and, therefore, are used in soap perfumes.

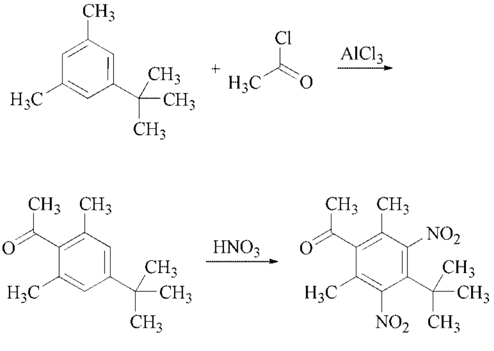
Musk xylol [*81-15-2*], 2,4,6-trinitro-1,3-dimethyl-5-*tert*-butylbenzene, $C_{12}H_{15}N_3O_6$, M_r 297.27, *mp* 114 °C, does not occur in nature. It forms yellow crystals with a persistent musk odor. Musk xylol is prepared by alkylation of *m*-xylene with isobutene and subsequent nitration with a sulfuric acid–nitric acid mixture.



Musk xylol

Musk xylol is used in large quantities in inexpensive perfumes for soap and household products.

Musk ketone [*81-14-1*], 3,5-dinitro-2,6-dimethyl-4-*tert*-butylacetophenone, $C_{14}H_{18}N_2O_5$, M_r 294.31, *mp* 137 °C, does not occur in nature. It forms yellowish crystals with a sweet, very persistent, slightly animal musk odor. Musk ketone is prepared by Friedel–Crafts acetylation of 1,3-dimethyl-5-*tert*-butylbenzene, and nitration of the resulting 2,6-dimethyl-4-*tert*-butylacetophenone with nitric acid.

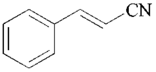


Musk ketone

Musk ketone is widely used as a fixative in blossom and phantasy compositions.

Cinnamonitrile [*4360-47-8*], C_9H_7N, M_r 129.16, *bp* (1.7 kPa) 135 – 135.5 °C, *mp* 23.5 – 24 °C, d^{25} 1.0244, n_D^{25} 1.6001; *trans*-cinnamonitrile is a colorless crystalline solid or a colorless viscous liquid with a spicy, slightly flowery odor.

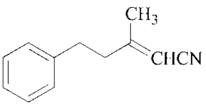
Cinnamonitrile can be prepared by one of the common routes to nitriles, e.g., by dehydration of cinnamaldoxime. It is stable to alkali and is used for perfuming soap and detergents.



Trade Name. Cinnamalva (IFF).

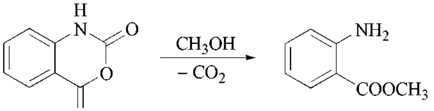
5-Phenyl-3-methyl-2-pentenonitrile [*93893-89-1*], $C_{12}H_{13}N$, M_r 171.24, *bp* (20 Pa) 82 – 88 °C, d^{25} 0.979, n_D^{20} 1.5340, is a colorless liquid with a citrus-fruity, slightly balsamic odor. The commercial product is a 2 : 3 mixture of the *cis* and *trans*-isomers.

The nitrile is prepared by condensation of benzylacetone with cyanoacetic acid in the presence of pyridine and by elimination of carbon dioxide. The mixture is used as such in soap and detergent perfumes [140].



Trade Name. Citronitril (Haarmann & Reimer).

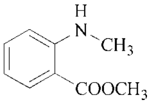
Methyl anthranilate [*134-20-3*], $C_8H_9NO_2$, M_r 151.16, *bp* (2 kPa) 135.5 °C, *mp* 24–25 °C, d_4^{19} 1.1682, n_D^{20} 1.5815, occurs in a large number of blossom essential oils (e.g., neroli, ylang-ylang, and jasmin oils), grapes, and citrus oils. It occurs as white crystals or a yellowish liquid, that show blue fluorescence and have an orange blossom odor. Methyl anthranilate is prepared by esterification of anthranilic acid with methanol or by reaction of isatoic anhydride with methanol [141].



Methyl anthranilate

It is used in a large number of blossom fragrances. However, its use in perfumes for soaps and cosmetics is limited because it causes discoloration. It is used in aroma compositions (e.g., in grape and citrus flavors).

Methyl *N*-methylanthranilate [*85-91-6*], $C_9H_{11}NO_2$, M_r 165.19, *bp* (1.6 kPa) 130–131 °C, d_4^{20} 1.1295, n_D^{20} 1.5796, is the main component of petitgrain oil from mandarin leaves and is also found in mandarin peel oil. It is a pale yellow, fluorescent liquid with a delicate mandarin odor. The ester can be prepared by methylation of methyl anthranilate. It is used in soap and cosmetic perfumes as well as in aromas, particularly for mandarin flavors. (IFRA recommendation)



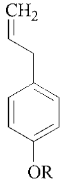
Some Schiff's bases of methyl anthranilate are interesting fragrance materials, e.g., those formed with hydroxydihydrocitronellal [*89-43-0*] and 2,4-dimethyl-3-cyclohexene carboxaldehyde [*68845-02-3*]. Both have a heavy blossom odor and a high tenacity.

2.6. Phenols and Phenol Derivatives

For a detailed description of phenols and their derivatives, see → Phenol, → Phenol Derivatives.

2.6.1. Phenols, Phenyl Esters, and Phenyl Ethers

Of the phenols and phenyl ethers used as fragrance and flavor compounds, 4-allyl- (**30**, R = H) and 4-propenylphenols (**31** and **32**, R = H) and their methyl ethers (**30**–**32**, R = CH_3) occur particularly frequently in essential oils.



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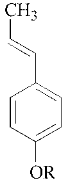

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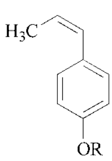

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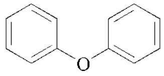
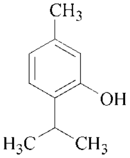
A second hydroxyl or methoxyl substituent is often present; 2-methoxy-4-allylphenol and 2-methoxy-4-propenylphenol are the most important compounds belonging to this category.

Diphenyl ether [*101-84-8*], $C_{12}H_{10}O$, M_r 170.21, *bp* (1.34 kPa) 121 °C, *mp* 26.8 °C, d^{20} 1.0748, has not been observed in nature. It is a colorless liquid or a crystalline solid with an odor reminiscent of geranium leaves. Diphenyl ether is obtained as a byproduct in the production of phenol by high-pressure hydrolysis of chlorobenzene. For further details of properties and synthesis, see → Phenol Derivatives, Chap. 6.3. Because of its stability and low price, diphenyl ether is used in large quantities in soap perfumes. However, its main application is as a heat-transfer medium (eutectic mixture with diphenyl).

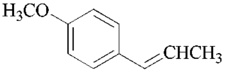


Thymol [*89-83-8*], 2-isopropyl-5-methylphenol, $C_{10}H_{14}O$, M_r 150.22, *bp* (101.3 kPa) 232.5 °C, *mp* 51.5 °C, d_4^{20} 0.9756, n_D^{20} 1.5227, is the main constituent of thyme and some origanum oils; it also occurs in many other essential oils. It forms colorless crystals with a spicy-herbal, slightly medicinal odor reminiscent of thyme. For further details of properties and synthesis, see → Phenol Derivatives, Chap. 1.5.3.

Thymol is used as a dry top note in lavender compositions, in men's fragrances, and as a disinfectant in oral hygiene products. It is also important as a starting material for the production of racemic menthol (see page 30).



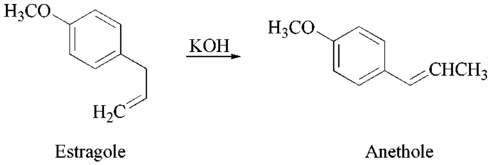
Anethole [*104-46-1*], 1-methoxy-4-propenylbenzene, $C_{10}H_{12}O$, M_r 148.20, *trans*-isomer: *bp* °C, d_4^{20} 0.9883, n_D^{20} 1.5615, occurs both as its *cis*- and *trans*-isomers in nature; however, *trans*-anethole is always the main isomer. Anethole occurs in anise oil (80 – 90 %), star anise oil (> 90 %), and fennel oil (80 %).



trans-Anethole [*4180-23-8*] forms colorless crystals (*mp* 21.5 °C) with an anise-like odor and a sweet taste. Anethole is oxidized to anisaldehyde (e.g., with chromic acid); when hydrogenated it is converted into 1-methoxy-4-propylbenzene.

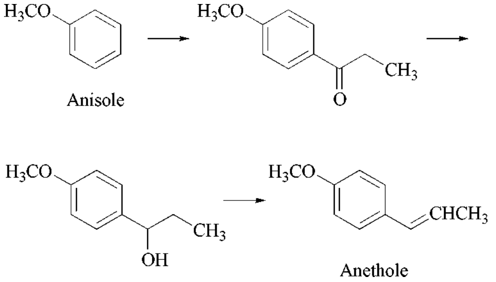
Production. Isolation of anethole from anethole-rich essential oils has lost its significance in favor of isolation from sulfate turpentine oils (see page 118).

1) Anethole can be crystallized from oils in which it occurs as a major component (anise, star anise, and fennel oils).
2) A fraction of American sulfate turpentine oil (0.5 % of the total) consists mainly of an azeotropic mixture of anethole and caryophyllene. *trans*-Anethole can be isolated from this mixture by crystallization.
3) Another fraction of American sulfate turpentine oil (1 % of the total) consists essentially of an azeotropic mixture of estragole (1-methoxy-4-allylbenzene, *bp* (101.3 kPa) 216 °C) and α-terpineol. Treatment with potassium hydroxide yields a mixture of anethole isomers and α-terpineol, which can be separated by fractional distillation.



Since isolation from oils does not always satisfy demand, synthetic processes starting from anisole have been developed.

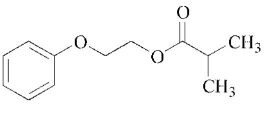
4) *Synthesis from Anisole and Propionic Acid Derivatives.* Anisole is converted into 4-methoxypropiophenone by Friedel–Crafts acylation with propionyl chloride or propionic anhydride. The ketone is hydrogenated to the corresponding alcohol with a copper chromite catalyst. The alcohol is dehydrated in the presence of acidic catalysts to a mixture of *cis*- and *trans*-anethole [142].



5) *Synthesis from Anisole and Propanal.* Anisole is converted into a mixture of 1,1-bis(4-methoxyphenyl)propane and small amounts of isomeric compounds by condensation with propionaldehyde in the presence of catalytic amounts of acid. 1,1-Bis(4-methoxyphenyl) propane is cleaved when heated to give anethole and anisole [143].

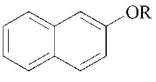
Uses. Anethole is used in large quantities in the alcoholic beverage industry (Pernod, Ouzo) and in oral hygiene products. Some crude anethole is converted into anisaldehyde.

2-Phenoxyethyl isobutyrate [*103-60-6*], $C_{12}H_{16}O_3$, M_r 208.26, *bp* (530 Pa) 125 – 127 °C, d_{25}^{25} 1.044 – 1.050, n_D^{20} 1.492 – 1.496, is a fragrance compound that does not occur in nature. It is a colorless liquid with a sweet, flowery-fruity odor.



The ester is prepared by esterification of 2-phenoxyethanol with isobutyric acid and is used as a fixative in perfumes (rose and lavender types) as well as for fruity notes.
Trade Name. Phenirat (Haarmann & Reimer).

β-Naphthyl Alkyl Ethers. The β-naphthyl alkyl ethers described below are used in perfumery, especially in soap perfumes. The ethers are prepared by O-alkylation of β-naphthol. They have not been observed in nature.



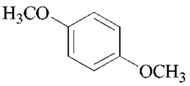
β-Naphthyl methyl ether [*93-04-9*], R = CH_3, $C_{11}H_{10}O$, M_r 158.20, *bp* (1.3 kPa) 138 °C, *mp* 73 – 74 °C, forms white crystals with an intense orange blossom odor.

β-Naphthyl ethyl ether [*93-18-5*], R = CH_2CH_3, $C_{12}H_{12}O$, M_r 172.23, *bp* (1.3 kPa) 148 °C, *mp* 37 – 38 °C, forms white crystals with a mild, long-lasting, orange blossom fragrance.

β-Naphthyl isobutyl ether [*2173-57-1*], R = $CH_2CH(CH_3)_2$, $C_{14}H_{16}O$, M_r 200.28, *mp* 33 – 33.5 °C, forms white crystals with a fruity, orange blossom odor.

Hydroquinone dimethyl ether [*150-78-7*], 1,4-dimethoxybenzene, $C_8H_{10}O_2$, M_r 138.17, *bp* (2.7 kPa) 109 °C, *mp* 57 – 58 °C, occurs in hyacinth oil and has also been identified in tea. It is a white crystalline solid with an intensely sweet, somewhat herbal, nutlike odor.

Hydroquinone dimethyl ether is prepared by etherification of hydroquinone and is used in soap perfumes.

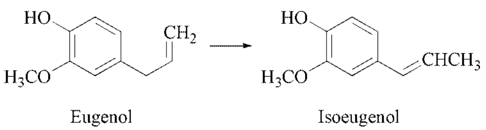


Isoeugenol [*97-54-1*], 2-methoxy-4-(1-propenyl)phenol, $C_{10}H_{12}O_2$, M_r 164.22; *cis*-isomer [*5912-86-7*]: *bp* (1.7 kPa) 134 – 135 °C, d_4^{20} 1.0837, n_D^{20} 1.5726; *trans*-isomer [*5932-68-3*]: *mp* 33 – 34 °C, *bp* (1.7 kPa) 141 – 142 °C, d_4^{20} 1.0852, n_D^{20} 1.5784. Isoeugenol occurs in many essential oils, mostly with eugenol, but not as the main component. Commercial isoeugenol is a mixture of *cis*- and *trans*-isomers, in which the *trans*-isomer dominates because it is thermodynamically more stable. Isoeugenol is a yellowish, viscous liquid with a fine clove odor, that of the crystalline *trans*-isomer being the more delicate.

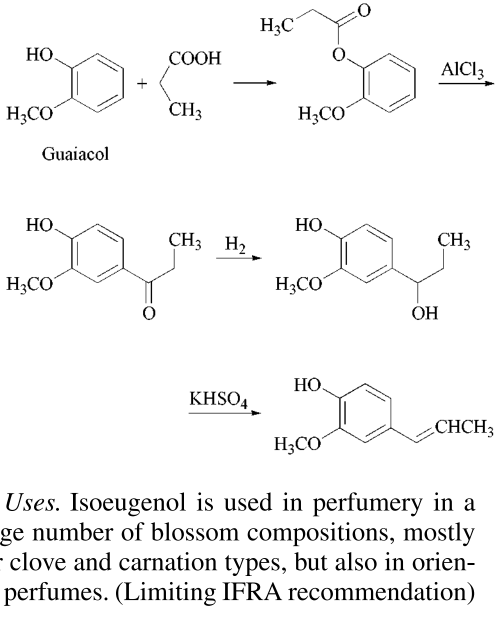
Isoeugenol can be hydrogenated catalytically to form dihydroeugenol. Vanillin was formerly prepared by oxidation of isoeugenol. Additional fragrance compounds are prepared by esterification or etherification of the hydroxyl group.

Production. Starting materials for the synthesis of isoeugenol are eugenol and guaiacol.

1) *Synthesis from Eugenol.* The sodium or potassium salt of eugenol is isomerized to isoeugenol by heating. Isomerization can also be carried out catalytically in the presence of ruthenium [144] or rhodium [145] compounds.



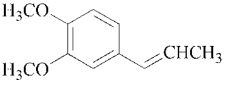
2) *Synthesis from Guaiacol.* Guaiacol is esterified with propionic acid, and the resulting guaiacyl propionate rearranges in the presence of aluminum chloride to give 4-hydroxy-3-methoxypropiophenone. Reduction of the ketone to the corresponding secondary alcohol and dehydration finally yield isoeugenol [146–148].



Uses. Isoeugenol is used in perfumery in a large number of blossom compositions, mostly for clove and carnation types, but also in oriental perfumes. (Limiting IFRA recommendation)

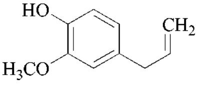
Small amounts are employed in aromas and in reconstituted essential oils.

Isoeugenol methyl ether [*93-16-3*], $C_{11}H_{14}O_2$, M_r 178.23, *cis*-isomer [*6380-24-1*]: *bp* (900 Pa) 137 – 137.5 °C, d_4^{20} 1.0530, n_D^{20} 1.5628; *trans*-isomer [*6379-72-2*]: *bp* (700 Pa) 126 °C, d_4^{20} 1.0556, n_D^{20} 1.5699, occurs in small quantities in several essential oils. It is a colorless to pale yellow liquid with a mild clove odor.



Isoeugenol methyl ether is used in perfumery in clove and carnation bases and as a fixative in spicy-floral compositions.

Eugenol [*97-53-0*], 2-methoxy-4-allylphenol, $C_{10}H_{12}O_2$, M_r 164.20, *bp* (1.3 kPa) 121 °C, d_4^{20} 1.0652, n_D^{20} 1.5409, is the main component of several essential oils; clove leaf oil and cinnamon leaf oil may contain > 90 %. Eugenol occurs in small amounts in many other essential oils. It is a colorless to slightly yellow liquid with a spicy, clove odor.

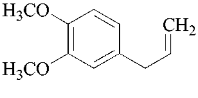


Catalytic hydrogenation (e.g., in the presence of noble-metal catalysts) yields dihydroeugenol. Isoeugenol is obtained from eugenol by shifting the double bond (see Isoeugenol, page 65). Esterification and etherification of the hydroxyl group of eugenol yield valuable fragrance and flavor materials (e.g., eugenyl acetate and eugenyl methyl ether).

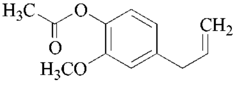
Production. Since sufficient eugenol can be isolated from cheap essential oils, synthesis is not industrially important. Eugenol is still preferentially isolated from clove leaf and cinnamon leaf oil (e.g., by extraction with sodium hydroxide solution). Nonphenolic materials are then removed by steam distillation. After the alkaline solution is acidified at low temperature, pure eugenol is obtained by distillation.

Uses. Eugenol is used in perfumery in clove and carnation compositions as well as for oriental and spicy notes. It is a common component of clove and other aroma compositions. In dentistry, it is used as an antiseptic.

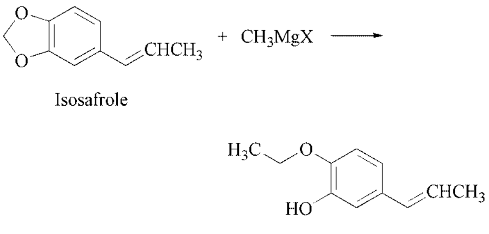
Eugenol methyl ether [*93-15-2*], $C_{11}H_{14}O_2$, M_r 178.23, *bp* (1.5 kPa) 127 – 129 °C, d_4^{20} 1.0396, n_D^{20} 1.5340, occurs in numerous essential oils, sometimes at a very high concentration; leaf and wood oil from *Dacrydium franklinii* Hook. (Huon pine oil) contain more than 90 %. The ether is an almost colorless liquid with a mild-spicy, slightly herbal odor. It is prepared by methylation of eugenol and is used in perfumery (e.g., in carnation and lilac compositions) and in flavor compositions.



Eugenyl acetate [*93-28-7*], $C_{12}H_{14}O_3$, M_r 206.24, *bp* (400 Pa) 120 – 121 °C, *mp* 29 °C, d_4^{20} 1.0806, n_D^{20} 1.5205, occurs in clove oil, together with eugenol. It is a crystalline solid or yellowish liquid with a slightly fruity, clove odor. Eugenyl acetate is prepared by acetylation of eugenol with acetic anhydride and is used in clove compositions to accentuate flowery character.

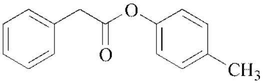


Propenylguethol [*94-86-0*], 2-ethoxy-5-(1-propenyl)phenol, $C_{11}H_{14}O_2$, M_r 178.23, exists in *cis* (*mp* 35 – 36 °C) and in *trans* (*mp* 86 °C) forms. The *trans*-isomer has a sweet vanilla-like odor. Propenylguethol can be prepared from isosafrole by reaction with methylmagnesium chloride or by ethylation of isoeugenol followed by selective demethylation with alkali [149].



It is used in perfumery, for example, in soaps and cosmetics, to create or enhance vanilla notes.

***p*-Cresyl phenylacetate** [*101-94-0*], $C_{15}H_{14}O_2$, M_r 226.27, is prepared by esterification of *p*-cresol with phenylacetic acid. It forms crystals (*mp* 75 – 76 °C) with a narcissus odor and a honey note. It is used in blossom compositions with a slight animal note.

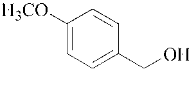


2.6.2. Phenol Alcohols and their Esters

In comparison with the araliphatic alcohols discussed in Section 2.5.5, very few phenol alcohols are used as fragrance and flavor materials. None of the alcohol derivatives of vanillin, ethylvanillin, and heliotropin or their esters have special organoleptic properties. Anise alcohol and its acetate are the only products that are used to some extent in perfume and aroma compositions.

Anisyl alcohol [*105-13-5*], 4-methoxybenzyl alcohol, $C_8H_{10}O_2$, M_r 138.17, *bp* (1.3 kPa) 136 °C, d_4^{20} 1.1140, n_D^{25} 1.5420, occurs in vanilla pods and in anise seeds. It is a colorless liquid with a sweet-flowery, slightly balsamic odor.

Pure anise alcohol for perfumery and flavor purposes is prepared by hydrogenation of anisaldehyde. It is used in perfumery in blossom compositions (e.g., lilac and gardenia types) and in flavors for confectionery and beverages.

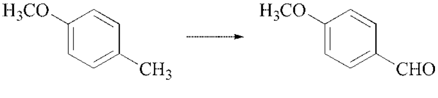


Anisyl acetate [*104-21-2*], $C_{10}H_{12}O_3$, M_r 180.20, *bp* (1.5 kPa) 133 °C, d_4^{20} 1.1084, has been found in several types of berries. It is a colorless liquid with a fruity, slightly balsamic blossom odor and is used occasionally in sweet-flowery compositions, but more frequently in flavor compositions for fruity notes.

2.6.3. Phenol Aldehydes

Phenol aldehydes are generally pleasant-smelling products. Some of them are particularly important as fragrance and flavor compounds. Anisaldehyde and certain derivatives of protocatechu aldehyde (3,4-dihydroxybenzaldehyde) are well-known representatives. The monomethyl ether of protocatechu aldehyde, vanillin, is perhaps the most widely used flavor compound. Other important derivatives of this aldehyde are veratraldehyde (dimethyl ether) and piperonal (formaldehyde acetal derivative); they are not only used as fragrance and flavor substances, but also are intermediates in many industrial processes.

***p*-Anisaldehyde** [*123-11-5*], 4-methoxybenzaldehyde, $C_8H_8O_2$, M_r 136.15, *bp* (1.85 kPa) 132 °C, d_4^{25} 1.1192, n_D^{25} 1.5703, occurs in many essential oils, often together with anethole. It is a colorless to slightly yellowish liquid with a sweet, mimosa, hawthorn odor. *p*-Anisaldehyde can be hydrogenated to anise alcohol and readily oxidizes to anisic acid when exposed to air. Synthetic routes to anisaldehyde usually involve the oxidation of *p*-cresyl methyl ether. Manganese dioxide and sulfuric acid are usually used for oxidation. In a Russian process, *p*-cresyl methyl ether is oxidized with alkali peroxysulfates in the presence of silver salts [150].

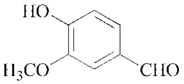


p-Anisaldehyde

Other industrial processes are the liquid-phase oxidation in the presence of cobalt catalysts [151] and the electrochemical oxidation in the presence of lower aliphatic alcohols via the corresponding anisaldehyde dialkyl acetal [152].

p-Anisaldehyde is frequently used in sweet blossom compositions (e.g., in lilac and hawthorn types) as well as in flavor compositions for confectioneries and beverages. *p*-Anisaldehyde is an intermediate in many industrial processes. Its hydrogensulfite derivative is used as a brightener for metals in galvanic baths.

Vanillin [*121-33-5*], 4-hydroxy-3-methoxybenzaldehyde, $C_8H_8O_3$, M_r 152.15, *bp* (1.3 kPa) 155 °C, *mp* 82 – 83 °C, d_4^{20} 1.056, is found in many essential oils and foods, but is often not essential for their odor or aroma. However, it does determine the odor of essential oils and extracts from *Vanilla planifolia* and *V. tahitensis* pods, in which it is formed during ripening by enzymatic cleavage of glycosides.



Annually about 12 000 t vanillin are produced synthetically and about 20 t originate from natural sources [153].

Properties. Vanillin is a colorless crystalline solid with a typical vanilla odor. Because it possesses aldehyde and hydroxyl substituents, it undergoes many reactions. Additional reactions are possible due to the reactivity of the aromatic nucleus. Vanillyl alcohol and 2-methoxy-4-methylphenol are obtained by catalytic hydrogenation; vanillic acid derivatives are formed after oxidation and protection of the phenolic hydroxyl group. Since vanillin is a phenol aldehyde, it is stable to autoxidation and does not undergo the Cannizzaro reaction. Numerous derivatives can be prepared by etherification or esterification of the hydroxyl group and by aldol condensation at the aldehyde group. For example, several of these derivatives are intermediates in the synthesis of pharmaceuticals.

Production. Most commercial vanillin is obtained by processing waste sulfite liquors; the remainder is synthesized from guaiacol. Preparation by oxidation of isoeugenol is of historical interest only.

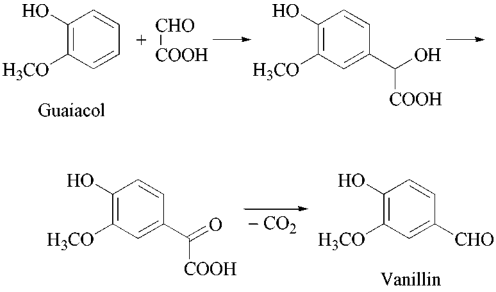
Preparation from Waste Sulfite Liquors:
The starting material for vanillin production is the lignin present in sulfite wastes from the cellulose industry (→ Lignin). The concentrated mother liquors are treated with alkali at elevated temperature and pressure in the presence of oxidants. The vanillin formed is separated from the byproducts, particularly acetovanillone (4-hydroxy-3-methoxyacetophenone), by extraction, distillation, and crystallization.

A large number of patents describe various procedures for the (mainly) continuous hydrolysis and oxidation processes, as well as for the purification steps required to obtain high-grade vanillin [154]. Lignin is degraded either with sodium hydroxide or with calcium hydroxide solution and simultaneously oxidized in air in the presence of catalysts. When the reaction is completed, the solid wastes are removed. Vanillin is extracted from the acidified solution with a solvent (e.g., butanol or benzene) and reextracted with sodium hydrogen sulfite solution. Reacidification with sulfuric acid followed by vacuum distillation yields technical-grade vanillin, which must be recrystallized several times to obtain food-grade vanillin. Water, to which some ethanol may be added, is used as the solvent in the last crystallization step.

Preparation from Guaiacol and Glyoxylic Acid.
Several methods can be used to introduce an aldehyde group into an aromatic ring. Condensation of guaiacol with glyoxylic acid followed by oxidation of the resulting mandelic acid to the corresponding phenylglyoxylic acid and, finally, decarboxylation continues to be a competitive industrial process for vanillin synthesis.

Currently, guaiacol is synthesized from catechol, which is prepared by acid-catalyzed hydroxylation of phenol with hydrogen peroxide. Glyoxylic acid is obtained as a byproduct in the synthesis of glyoxal from acetaldehyde and can also be produced by oxidation of glyoxal with nitric acid. Condensation of guaiacol with glyoxylic acid proceeds smoothly at room temperature and in weakly alkaline media. A slight excess of guaiacol is maintained to avoid formation of disubstituted products; excess guaiacol is recovered. The alkaline solution containing 4-hydroxy-3-methoxymandelic acid is then oxidized in air in the presence of a catalyst until the calculated amount of oxygen is consumed [155]. Crude vanillin is obtained by acidification and simultaneous decarboxylation of the (4-hydroxy-3-methoxyphenyl) glyoxylic acid solution. Commercial grades are obtained by vacuum distillation and subsequent recrystallization as described under method (1).

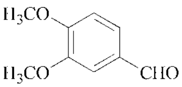
This process has the advantage that, under the reaction conditions, the glyoxyl radical enters the aromatic guaiacol ring almost exclusively para to the phenolic hydroxyl group. Tedious separation procedures are thus avoided.



Uses. The main application of vanillin is the flavoring of foods (e.g., ice cream, chocolate, bakery products, and confectioneries). Small quantities are used in perfumery to round and fix sweet, balsamic fragrances. Vanillin is also used as a brightener in galvanotechnical processes and is an important intermediate in, for example, the production of pharmaceuticals such as L-3,4-dihydroxyphenylalanine (L-DOPA) and methyldopa.

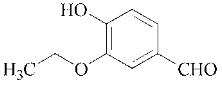
Veratraldehyde [*120-14-9*], 3,4-dimethoxybenzaldehyde, $C_9H_{10}O_3$, M_r 166.18, occurs in a few essential oils and is a crystalline solid (*mp* 44.5 – 45 °C) with a woody, vanilla-like odor.

Veratraldehyde can be prepared by methylation of vanillin. It is used in oriental and warm-woody fragrances, as well as in flavor compositions for vanilla notes. It is an intermediate in, for example, the synthesis of pharmaceuticals.



Ethylvanillin [*121-32-4*], 3-ethoxy-4-hydroxybenzaldehyde, $C_9H_{10}O_3$, M_r 166.18, *mp* 77 – 78 °C, does not occur in nature. Its odor resembles that of vanillin but is approximately three times as strong. Ethylvanillin can be prepared by method (2) as described for vanillin, using guethol instead of guaiacol as the starting material.

Ethylvanillin is used extensively in the chocolate industry. It gives a sweet, balsamic note to flowery and fruity perfume compositions.

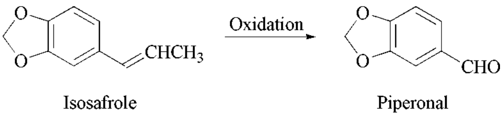


Piperonal [*120-57-0*], heliotropin, 3,4-methylenedioxybenzaldehyde, $C_8H_6O_3$, M_r 150.13, *bp* (1.6 kPa) 139.4 °C, *mp* 37 °C, $d_4^{43.2}$ 1.2792, occurs in a number of essential oils, but never as the main component. It forms white crystals with a sweet-flowery, slightly spicy, heliotrope-like odor.

Production. Piperonal is produced by two main routes:

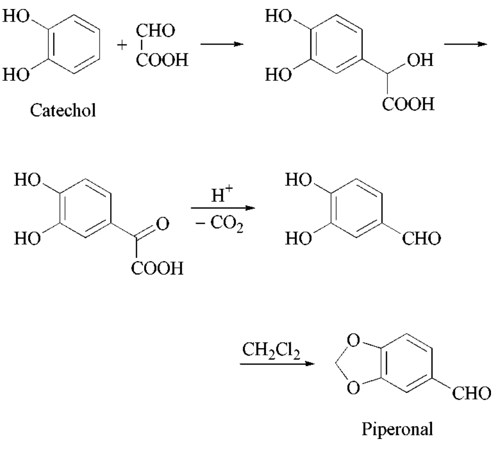
From Isosafrole.

For many years, oxidative cleavage of isosafrole was the only route applicable on an industrial scale. Examples of oxidants that give good yields of piperonal are chromium(VI) salts, oxygen, and ozone.



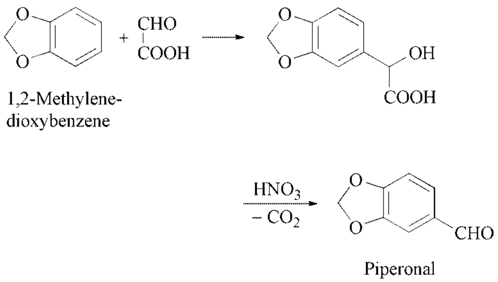
This method is still used currently because safrole (the starting material for isosafrole) can be isolated from essential oils relatively inexpensively and in sufficient quantity.

From Catechol. Several routes have been developed for the synthesis of piperonal from catechol. In one such route, catechol is converted into 3,4-dihydroxymandelic acid with glyoxylic acid in an alkaline medium in the presence of aluminum oxide. 3,4-Dihydroxymandelic acid is oxidized to the corresponding keto acid (e.g., with copper(II) oxide), which is decarboxylated to 3,4-dihydroxybenzaldehyde [156]. The latter product is converted into piperonal, for



example, by reaction with methylene chloride in the presence of quaternary ammonium salts [157].

In another route, catechol is first reacted with methylene chloride and converted into 1,2-methylenedioxybenzene [157]. Reaction with glyoxylic acid in strongly acidic media yields 3,4-methylenedioxymandelic acid [158]. Subsequent oxidation and decarboxylation with nitric acid affords piperonal.

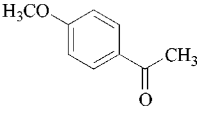


Uses. Piperonal is used in many flowery-spicy fine fragrances and is also an important ingredient of flavor compositions.

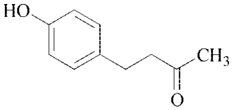
2.6.4. Phenol Ketones

Few of the phenol derivatives that have a keto substituent in their side-chain are of interest as fragrance or flavor substances. A number of phenols and phenyl ethers acetylated in the benzene ring have been identified as volatile components of foods. 4-Methoxyacetophenone is of some interest as a fragrance compound. 4-Hydroxybenzylacetone, a higher mass phenol ketone, has a characteristic raspberry aroma.

4-Methoxyacetophenone [*100-06-1*], acetanisole, $C_9H_{10}O_2$, M_r 150.18, d^{41} 1.0818, n_D^{41} 1.5470, occurs in anise oil. It forms white crystals (*mp* 38 °C) with a sweet odor, reminiscent of hawthorn. 4-Methoxyacetophenone is prepared by Friedel–Crafts acetylation of anisole and is used in soap perfumes.



1-(4-Hydroxyphenyl)-3-butanone [*5471-51-2*], raspberry ketone, $C_{10}H_{12}O_2$, M_r 164.20, *mp* 82 – 83 °C, is a highly characteristic component of raspberry aroma. It forms colorless crystals with a sweet-fruity odor strongly reminiscent of raspberries.



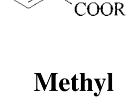
Raspberry ketone is prepared by alkali-catalyzed condensation of the alkali salt of 4-hydroxybenzaldehyde and acetone, followed by selective hydrogenation of the double bond in the resulting 4-hydroxybenzalacetone. Other syntheses start from phenol which is converted into 1-(4-hydroxyphenyl)-3-butanone with methyl vinyl ketone (e.g., in the presence of phosphoric acid) [159] or with 3-oxo-1-butanol in the presence of concentrated sulfuric acid [160].

The ketone is used in fruit flavors, particularly in raspberry compositions.

Trade Names. Frambinon (DRAGOCO), Oxyphenylon (IFF).

2.6.5. Phenol Carboxylates

Alkyl and aralkyl salicylates, as well as methyl 3-methylorsellinate (an oakmoss fragrance) are important phenol carboxylates that are used in flavors and fragrances. The following salicylates are used in perfume and flavor compositions and can be prepared by esterification of salicylic acid.



Methyl salicylate [*119-36-8*], R = CH$_3$, $C_8H_8O_3$, M_r 152.15, *bp* (1.6 kPa) 98 °C, d_4^{25} 1.1782, n_D^{25} 1.5350, is the main component of wintergreen oil and occurs in small quantities in other essential oils and fruit. It is a colorless liquid with a sweet, phenolic odor. Methyl salicylate is used in perfumery as a modifier in blossom fragrances and as a mild antiseptic in oral hygiene products.

Isoamyl salicylate [*87-20-7*], R = $CH_2CH_2CH(CH_3)_2$, $C_{12}H_{16}O_3$, M_r 208.26, *bp* (2 kPa) 151 – 152 °C, d_4^{20} 1.0535, n_D^{20} 1.5065, has been found in a number of fruit aromas. It is a colorless liquid with a sweet, clover-like odor and is used in perfumery for floral and herbal notes, particularly in soap perfumes.

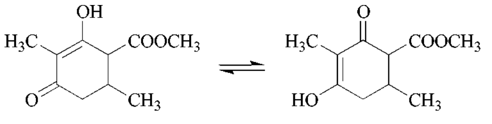
Hexyl salicylate [*6259-76-3*], R = $(CH_2)_5CH_3$, $C_{13}H_{18}O_3$, M_r 222.28, *bp* (1.6 kPa) 167 – 168 °C, d_{25}^{25} 1.035, n_D^{25} 1.5049, has been reported in carnation flower absolute [161]. It is a colorless liquid with a green, flowery-spicy odor, reminiscent of azaleas. It is used for blossom and herbal notes in perfumes, e.g., in soap, personal hygiene products, and detergents.

***cis*-3-Hexenyl salicylate** [*65405-77-8*], R = *cis*-$(CH_2)_2CH{=}CHCH_2CH_3$, $C_{13}H_{16}O_3$, M_r 220.27, *bp* (150 Pa) 125 °C, d_{25}^{25} 1.0589, n_D^{20} 1.5210, has been identified in carnation flower absolute. It is a colorless liquid with a long-lasting, sweet, green balsamic odor. It is used in fine fragrances and for scenting soaps, cosmetics, and detergents.

Benzyl salicylate [*118-58-1*], R = $CH_2C_6H_5$, $C_{14}H_{12}O_3$, M_r 228.25, *bp* (1.3 kPa) 186 – 188 °C, d_4^{20} 1.1799, n_D^{20} 1.5805, which occurs in several essential oils, is a colorless, viscous liquid with a weak, sweet, slightly balsamic odor. Benzyl salicylate is used as a fixative in flowery-spicy perfume compositions and in flavors.

Phenethyl salicylate [*87-22-9*], R = $CH_2CH_2C_6H_5$, $C_{15}H_{14}O_3$, M_r 242.27, *mp* 44 °C, which has not been reported to occur in nature, is a crystalline solid with a weak, long-lasting, balsamic, blossom odor, reminiscent of rose and hyacinth. It is used in perfumery for spicy and balsamic blossom compositions.

Methyl 3-methylorsellinate [*4707-47-5*], methyl 2,4-dihydroxy-3,6-dimethylbenzoate, $C_{10}H_{12}O_4$, M_r 196.20, *mp* 145 °C, is an odor-determining constituent of oakmoss extract and forms colorless crystals with a mossy-earthy odor. It can be prepared from acyclic compounds. In an industrial process, dimethyl malonate is condensed with 4-hexen-3-one (or a mixture of this ketone and 5-chlorohexan-3-one) to give a substituted 3-hydroxy-2-cyclohexenone (**33**). Aromatization, in good yield, is achieved by reaction of the hydroxycyclohexenone with a suitable *N*-haloamide. The intermediate 3-hydroxy-2-cyclohexenone can also be obtained by condensation of methyl 3-oxopentanoate with methyl crotonate [162].



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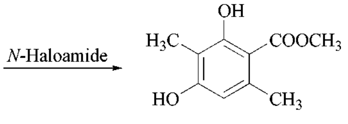
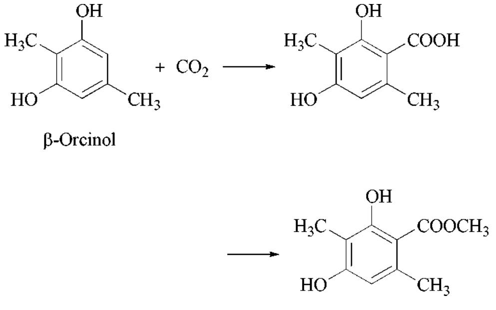


Methyl 3-methyl orsellinate

Another route to methyl 3-methylorsellinate starts from *β*-orcinol, which is converted into a carboxylic acid derivative by reaction with carbon dioxide (Kolbe synthesis). The acid is esterified (e.g., with dimethyl sulfate) [163].



Methyl 3-methylorsellinate is used as a substitute for oakmoss extract in fine fragrances, soaps, and cosmetics.

Trade Name. Evernyl (Givaudan Roure), Veramoss (IFF).

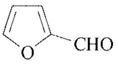
2.7. O- and O, S-Heterocycles

2.7.1. Cyclic Ethers

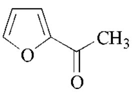
Cyclic ethers used as fragrances include a number of terpenoid compounds. Some of them, such as 1,4-cineole [*470-67-7*] and 1,8-cineole, occur in essential oils in significant quantities. Others are only minor components; examples are rose oxide, nerol oxide [*1786-08-9*], and rose furan [*15186-51-3*], which contribute to the specific fragrance of rose oil, and caryophyllene oxide [*1139-30-6*], which has a woody, slightly ambergris-like odor. α-Cedrene oxide [*11000-57-0*] is another wood-fragrance compound, that can be easily prepared by epoxidation of cedarwood oil hydrocarbons.

Except for some of the above-mentioned compounds, only a few other cyclic ethers are important, for instance, 4,6,6,7,8,8-hexamethyl-1,3,4,6,7,8-hexahydropenta[*g*]benzopyran, a musk fragrance that is used in large amounts.

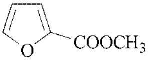
Numerous furan and pyran derivatives, many of which originate from heat treatment of carbohydrates, largely determine the odor of processed foods. Of this group, 2,5-dimethyl-4-hydroxy-2*H*-furan-3-one and maltol are used in fairly large quantities in flavors. The following compounds are used in relatively small amounts in flavor compositions:



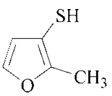
2-Furaldehyde [*98-01-1*], freshyl baked bread odor



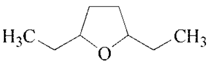
2-Acetylfuran [*1192-62-7*], sweet balsamic odor



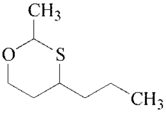
Methyl 2-furoate [*611-13-2*], fruity, mushroom-like odor



2-Methylfuran-3-thiol [*28588-74-1*], roast beef aroma

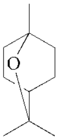


2,5-Diethyltetrahydrofuran [*41239-48-9*], fruity, herbal-minty note



2-Methyl-4-propyl-1,3-oxathiane [*67715-80-4*], typical sulfury note of tropical fruit

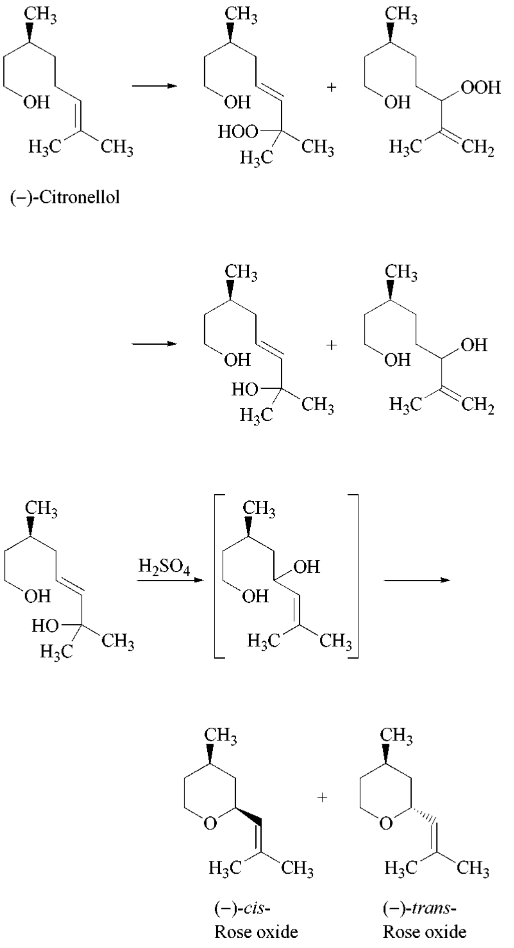
1,8-Cineole [*470-82-6*], 1,8-epoxy-*p*-menthane, eucalyptol, $C_{10}H_{18}O$, M_r 154.25, *bp* (101.8 kPa) 176 – 177 °C, *fp* 1 °C, d_4^{20} 0.9267, n_D^{20} 1.4586, occurs in many terpene-containing essential oils, sometimes as the main component. For example, eucalyptus oils contain up to 85 % 1,8-cineole and laurel leaf oil contains up to 70 %. It is a colorless liquid with a characteristic odor, slightly reminiscent of camphor.



1,8-Cineole is one of the few fragrance materials that is obtained exclusively by isolation from essential oils, especially eucalyptus oils. Technical-grade 1,8-cineole with a purity of 99.6 – 99.8 % is produced in Spain in large quantities by fractional distillation of *Eucalyptus globulus* Labillardière. A product essentially free from other products can be obtained by crystallization of cineole-rich eucalyptus oil fractions.

1,8-Cineole has a fresh odor and is used in large quantities in fragrances as well as in flavors (e.g., in oral hygiene products).

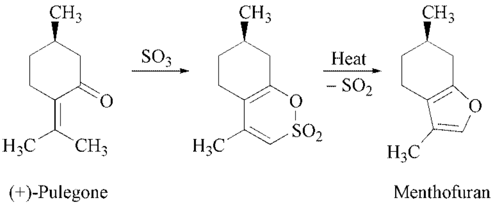
4-Methyl-2-(2-methyl-1-propenyl)tetrahydropyran [*16409-43-1*], rose oxide, $C_{10}H_{18}O$, M_r 154.25, *bp* (1.6 kPa) 70 °C, d_4^{20} 0.875, n_D^{20} 1.4570, $[\alpha]_D$ for the optically pure (−)-*cis* form − 58.1 °, occurs in small quantities, mainly the levorotatory *cis* form, in essential oils (e.g., Bulgarian rose oil and geranium oil). Commercial synthetic products are either optically active or inactive mixtures of the *cis*- and *trans*-isomers. Their physical constants, particularly the optical rotation, depend on the starting material and the method of synthesis. They are colorless liquids with a strong odor reminiscent of geranium oil and carrot leaves. Rose oxide is usually prepared from citronellol (see page 19), which can be converted into a mixture of two allyl hydroperoxides (e.g., by photosensitized oxidation with oxygen). Reduction of the hydroperoxides with sodium sulfite yields the corresponding diols [164]. Treatment with dilute sulfuric acid results in allylic rearrangement and spontaneous cyclization of one of the isomers; a mixture of diastereoisomeric rose oxides is thus formed. The unreacted diol isomer is separated by distillation. (−)-Citronellol as the starting material yields approximately a 1 : 1 mixture of (−)-*cis*- and (−)-*trans*-rose oxide.



Rose oxide is used in rose and geranium perfumes.
*Trade Name.*Rose oxide (DRAGOCO).

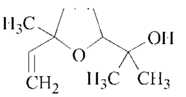
Menthofuran [*494-90-6*], 3,6-dimethyl-4,5,6,7-tetrahydrobenzofuran, $C_{10}H_{14}O$, M_r 150.22, *bp* (1.3 kPa) 78 – 79 °C, d_4^{20} 0.9676, n_D^{20} 1.4855, $[\alpha]_D^{20}$ +94.6 °, occurs mainly as the (+)-isomer, in numerous essential oils (e.g., Mentha oils). It is a colorless liquid with a minty odor.

(+)-Menthofuran [*17957-94-7*] is isolated from Mentha oils or is prepared synthetically, for example, by treatment of (+)-pulegone with fuming sulfuric acid in acetic anhydride and pyrolysis of the resulting sultone.



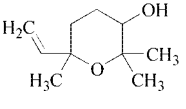
Menthofuran is used mainly in peppermint oil reconstitutions.

Linalool oxide, 2-methyl-2-vinyl-5-(α-hydroxyisopropyl)tetrahydrofuran, $C_{10}H_{18}O_2$, M_r 170.25, *bp* (101.3 kPa) 188 °C, d_4^{20} 0.939 – 0.944, n_D^{20} 1.451 – 1.455, has been identified in essential oils and in fruit aromas. Commercial linalool oxide is a mixture of the *cis* and *trans* forms, [*5989-33-3*] and [*34995-77-2*], respectively. It is a liquid with an earthy-flowery, slightly bergamot-like odor.



Linalool oxide

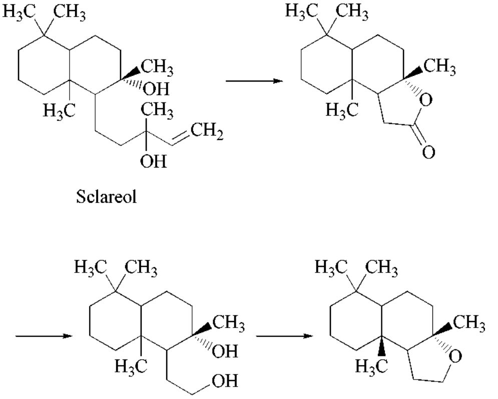
Linalool oxide is prepared by oxidation of linalool (see page 16). The isomeric compound 2,2,6-trimethyl-6-vinyltetrahydro-2*H*-pyran-3-ol [*14049-11-7*], which also occurs in nature, is formed as a byproduct:



Linalool oxide is used in perfumery (e.g., for lavender notes) and for reconstitution of essential oils.

A dehydrated linalool oxide, 2-methyl-2-vinyl-5-isopropenyltetrahydrofuran [*13679-86-2*], occurs naturally; it has a minty eucalyptol odor and is used in perfumery.

3a,6,6,9a-Tetramethyldodecahydronaphtho-[2,1-*b*]furan [*6790-58-5*] (**34**), $C_{16}H_{28}O$, M_r 236.40, *mp* 75 – 76 °C, is a crystalline autoxidation product of ambrein (see Ambergris, page 87) with a typical ambergris odor. It is prepared from sclareol, a diterpene alcohol obtained from plant waste in the production of clary sage oil (see Sage Oils, page 115). Oxidative degradation to a lactone, hydrogenation of the latter to the corresponding diol and dehydration yield (**34**).



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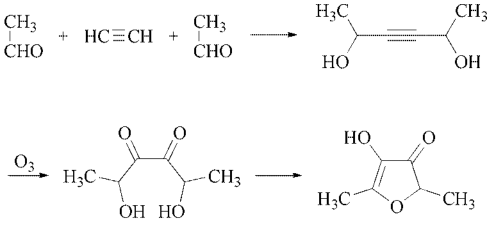
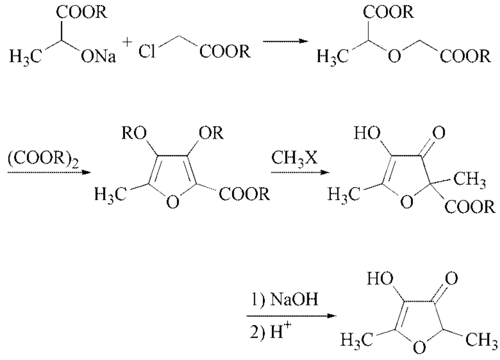
The product is used in perfumery for creating ambergris notes.
Trade Names. Ambrox (Firmenich), Ambroxan (Cognis).

2,5-Dimethyl-4-hydroxy-2*H*-furan-3-one [*3658-77-3*], $C_6H_8O_3$, M_r 128.13, is a constituent of pineapple aroma and is also found in other foods. It forms colorless crystals (*mp* 77 – 79 °C) with a relatively weak, nonspecific odor. Dilute solutions develop a pineapple, strawberry-like odor. It can be prepared by cyclization of hexane-2,5-diol-3,4-dione in the presence of an acidic catalyst [165]. The dione is the ozonization product of 2,5-hexynediol, which is obtained by ethynylation of acetaldehyde.


2,5-Dimethyl-4-hydroxy-2*H*-furan-3-one

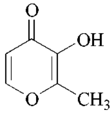
In another process, a dialkyl α-methyldiglycolate (formed from an alkyl lactate and an alkyl monochloroacetate) is reacted with dialkyl oxalate in the presence of a sodium alkoxide and dimethylformamide. The reaction product is cyclized, alkylated, hydrolyzed, and decarboxylated [166].



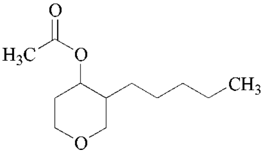
The compound is used in the flavoring of foods.
Trade Name. Furaneol (Firmenich).

Maltol [*118-71-8*], 3-hydroxy-2-methyl-4*H*-pyran-4-one, $C_6H_6O_3$, M_r 126.11, *mp* 162 – 164 °C, occurs in pine needles and the bark of young larch trees. It is produced when cellulose or starch are heated and is a constituent of wood tar oils. It forms crystals with a caramel-like odor, reminiscent of freshly baked cakes.

Although many routes are known for its synthesis, maltol is still isolated mainly from beechwood tar. It is used in aroma compositions with a caramel note and as a taste intensifier, for example, in fruit flavors (particularly in strawberry flavor compositions).



3-Pentyltetrahydro-2*H*-pyran-4-ol acetate [*18871-14-2*], $C_{12}H_{22}O_3$, M_r 214.30, *bp* (0.13 kPa) 102 – 103 °C, d^{25}_{25} 0.974 – 0.978, n^{20}_D 1.448 – 1.451, is a colorless to pale yellow liquid with a sweet-floral, fruity, slightly woody, jasmin-like odor. It is prepared by a Prins reaction of 1-octene with formaldehyde and acetic acid and is used in perfumes for various flower types, especially jasmin.

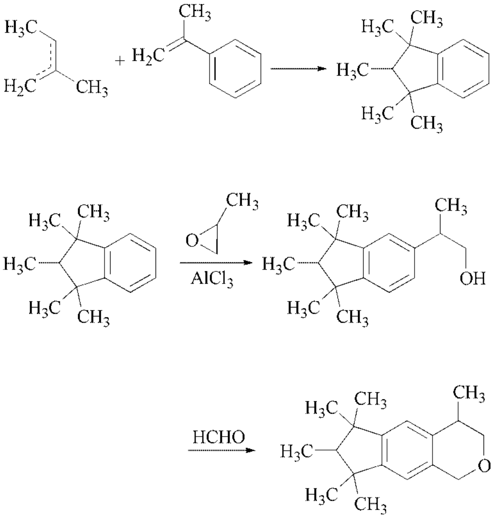


Trade Names. Jasmophyll (Haarmann & Reimer), Jasmopyran (Quest), Jasmal (IFF).

4,6,6,7,8,8-Hexamethyl-1,3,4,6,7,8-hexahydrocyclopenta[*g*]benzopyran [*1222-05-5*] (**35**), $C_{18}H_{26}O$, M_r 258.40, *bp* (1.1 kPa) 129 °C, d^{20}_4 1.0054, n^{20}_D 1.5342, is a viscous liquid with a musklike odor. It is one of the most frequently used synthetic, artificial musk fragrances. The starting material for its synthesis is 1,1,2,3,3-pentamethylindane, which is prepared by cycloaddition of *tert*-amylene to α-methylstyrene. The pentamethylindane is hydroxyalkylated with propylene oxide in a Friedel–Crafts reaction using aluminum chloride as a catalyst (analogous to the synthesis of 2-phenethyl alcohol from benzene and ethylene oxide, see page 51). Ring closure of the resulting 1,1,2,3,3-pentamethyl-5-(β-hydroxyisopropyl)indane to (**35**) is accomplished with paraformaldehyde and a lower aliphatic alcohol via the acetal [167] or with paraformaldehyde and a carboxylic acid anhydride via the acylate [168].

The commercial product is diluted with solvents (e.g., diethyl phthalate, isopropyl myristate, benzyl benzoate) to make it less viscous. It is alkali-stable and does not discolor in light. Therefore, it is a popular ingredient of perfume compositions for soaps, detergents, and cosmetics and is used in large amounts.

Trade Names. Galaxolide (IFF).



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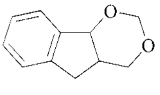
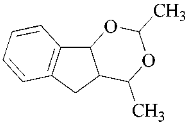
4,4*a*,5,9*b*-Tetrahydroindeno[1,2-*d*]-1,3-dioxane [*18096-62-3*], $C_{11}H_{12}O_2$, M_r 176.21, *bp* (1.3 kPa) 134 °C, *mp* 35 – 36 °C, $d^{15.5}_{15.5}$ 1.159, n^{20}_D 1.559, forms crystals with an indole-like odor. It is prepared by a Prins reaction from indene and formaldehyde in the presence of dilute sulfuric acid [169]. It is used in perfumes for soaps and detergents.



Trade Names. Indoflor (Haarmann & Reimer), Indolarom (IFF).

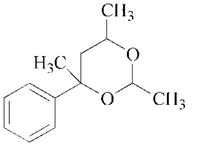
The 2,4-dimethyl homologue [*27606-09-3*] is prepared by using acetaldehyde instead of formaldehyde. Its odor is reminiscent of geranium and magnolia [171].



Trade Name. Magnolan (Haarmann & Reimer).

2,4,6-Trimethyl-4-phenyl-1,3-dioxane [*5182-36-5*], $C_{13}H_{18}O_2$, M_r206.28, *bp* (300 Pa) 100 °C, d^{20}_4 1.159, n^{20}_D1.504, is a colorless to pale yellow liquid. This cyclic acetal has a smell of grapefruit with herbal and fresh aspects.

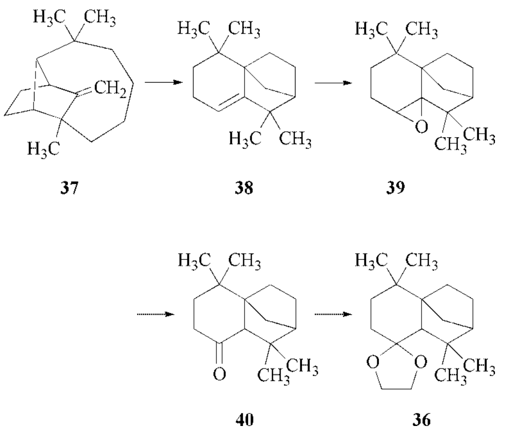
2,4,6-Trimethyl-4-phenyl-1,3-dioxane can be produced by a Prins reaction of methylstyrene with acetaldehyde.



Trade Name. Vertacetal (DRAGOCO), Floropal (Haarmann & Reimer).

Isolongifolanone ethylene glycol acetal [*154171-77-4*], $C_{17}H_{28}O2$, M_r 264.41, *bp* (3 kPa) 142 – 143 °C, d_4^{20} 1.0510, n_D^{20}1.5051 is commercially available as a colorless liquid with strong woody odor with flowery-fresh effects and with a velvety moss/ambra accent. It has an extremely long lasting odor and acts as fixative. Isolongifolanone ethylene glycol acetal is frequently used in soaps, cosmetics, and perfumery compositions.

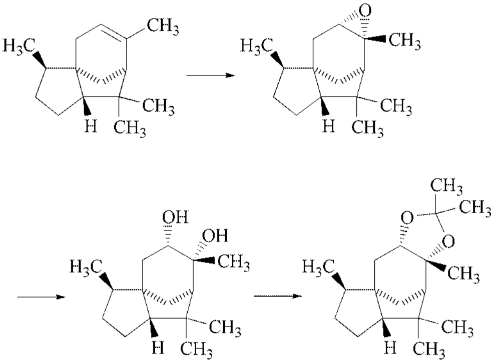
For the production of isolongifolanone acetal (**40**), longifolene (**36**), which is a main component of Indian turpentine oil, is first isomerized to isolongifolene (**37**). The epoxide (**38**), obtained by epoxidation of isolongifolene, is subsequently transformed to isolongifolanone (**39**), which is reacted with ethylene glycol to the cyclic isolongifolanone ethyleneglycolacetal (**40**) [170].



Trade Name. Ysamber-K (DRAGOCO).

5,5,7,9,9,13-Hexamethyl-4,6-dioxatetracyclo[6.5.1.^{1,10}0^{3,7}]tetradecane [*211299-54-6*], cedrene acetonide, $C_{18}H_{30}O_2$, M_r 278.44, *mp* 157 – 158 °C, is a fragrance compound with a powdery-woody, long-lasting amber note. Its industrial synthesis starts with the epoxidation of cedarwood oil fractions that contain sesquiterpene hydrocarbons, mainly α-cedrene. Acid-catalyzed ring opening and acetalization leads to cedrene acetonide [172].

The pure compound is crystalline and is frequently used in soaps, cosmetics and perfumery compositions as a fixative with high substantivity.



Trade Name. Ambrocenide 10 (DRAGOCO).

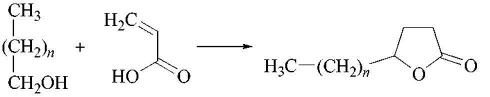
2.7.2. Lactones

Naturally occurring organoleptically important lactones are mainly saturated and unsaturated γ- and δ-lactones, and to a lesser extent macrocyclic lactones. The occurrence of these types of lactones reflects their ready formation from natural acyclic precursors.

The γ- and δ-lactones are the intramolecular esters of the corresponding hydroxy fatty acids. They contribute to the aroma of butter and various fruits. 3,4-Dimethyl-5-pentylidenedihydro-2(5*H*)-furanone [*774-64-1*] is an unsaturated γ-lactone with a distinct nutty flavor. 15-Pentadecanolide is responsible for the musklike odor of angelica root oil. Of the naturally occurring bicyclic lactones, phthalides are responsible for the odor of celery root oil, and coumarin for woodruff.

The macrocyclic esters hold a special position among the industrially produced lactone fragrance compounds. Like the well-known macrocyclic ketones (see Section 2.4), they have outstanding odor properties as musks. However, the lactones can be prepared more easily than the ketones, for example, by depolymerization of the corresponding linear polyesters. Since replacement of a methylene unit by oxygen affects the odor of these compounds very little, oxalactones with 15 – 17-membered rings are commercially produced in addition to 15-pentadecanolide. Several cyclic diesters prepared from long-chain α,ω-dicarboxylic acids and glycols are also valuable musk fragrances.

The γ-lactones described below can be prepared in good yield in a one-step process by radical addition of primary fatty alcohols to acrylic acid, using di-*tert*-butyl peroxide as a catalyst. A patent claims a high yield when the reaction is carried out in the presence of alkali phosphates or alkali sulfates [173].



γ-Lactones

γ-Octalactone [*104-50-7*], ($n = 3$), $C_8H_{14}O_2$, M_r 142.20, *bp* (1.3 kPa) 116 – 117 °C, d_4^{20} 0.977, n_D^{25} 1.4420, occurs as an aroma constituent in many processed and unprocessed foods. It is a pale yellow liquid with a fruity-coconut-like odor and is used both in aroma compositions and in heavy blossom perfumes.

γ-Nonalactone [*104-61-0*], ($n = 4$), "so-called aldehyde C_{18}" $C_9H_{16}O_2$, M_r 156.22, *bp* (1.7 kPa) 136 °C, d_4^{20} 0.9676, n_D^{20} 1.446, occurs in many foods and is a pale yellow liquid with a coconut-like aroma. It has numerous applications, similar to those of γ-octalactone, in aroma compositions and perfumery.
Trade Names. Abricolin (Haarmann & Reimer), Prunolide (Givaudan Roure).

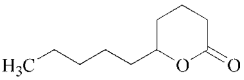
γ-Decalactone [*706-14-9*], ($n = 5$), $C_{10}H_{18}O_2$, M_r 170.25, *bp* (2.3 kPa) 156 °C, d_4^{21} 0.952, $n_D^{19.5}$ 1.4508, is present in a wide variety of foods and is an almost colorless liquid with an intensely fruity odor, reminiscent of peaches. It is used in perfumery for heavy, fruity flower odors and in aroma compositions, particularly peach flavors.

γ-Undecalactone [*104-67-6*], ($n = 6$), "so-called aldehyde C_{14}" $C_{11}H_{20}O_2$, M_r 184.28, *bp* (2.0 kPa) 167 – 169 °C, d_4^{20} 0.944, n_D^{20} 1.4514, occurs in foods and is an almost colorless liquid with a peachlike odor. In addition to preparation by radical addition of 1-octanol to acrylic acid, γ-undecalactone is also prepared by intramolecular cyclization of 10-undecylenic acid with 70 – 80 % sulfuric acid with migration of the double bond.

γ-Undecalactone has many applications in perfume and aroma compositions, similar to those of γ-decalactone.
Trade Name. Pêche pure (Givaudan Roure).

δ-Decalactone [*705-86-2*], $C_{10}H_{18}O_2$, M_r 170.25, *bp* (3 Pa) 117 – 120 °C, $d_4^{27.5}$ 0.9540, n_D^{26} 1.4537, is a flavor constituent of many types of fruit, cheese, and other dairy products. It is a colorless, viscous liquid with a creamy-coconut, peachlike aroma.

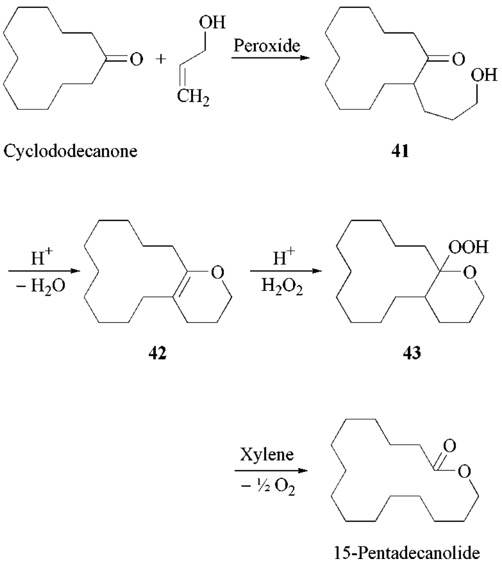
δ-Decalactone can be prepared by peracid oxidation of 2-pentylcyclopentanone. It is used in perfumes and for cream and butter flavorings.



15-Pentadecanolide [*106-02-5*], ω-hydroxypentadecanoic acid lactone, $C_{15}H_{28}O_2$, M_r 240.39, *bp* (1.3 – 1.4 kPa) 169 °C, *mp* 37 – 38 °C, d_4^{40} 0.940, occurs in small quantities in, for example, angelica root oil. It forms colorless crystals with a delicate, musklike odor.

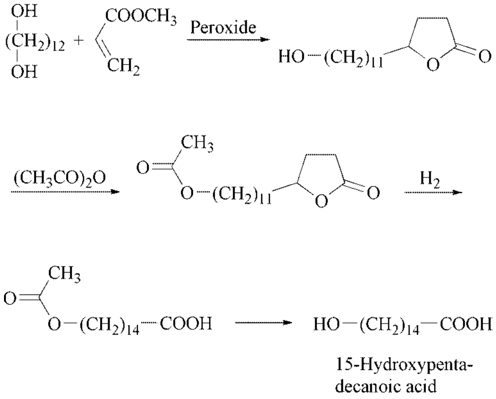
Production. The main industrial syntheses start from cyclododecatriene derivatives (→ Cyclododecatriene, Cyclooctadiene, and 4-Vinylcyclohexene). The 16-membered ring is formed either by expansion of the 12-membered ring or by depolymerization of polyesters of ω-hydroxypentadecanoic acid.

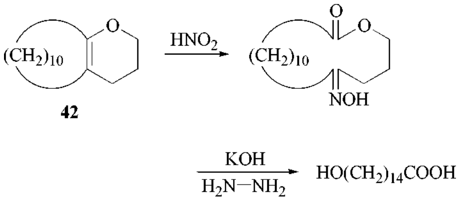
Preparation by Ring Expansion of Cyclododecanone. Radical addition of allyl alcohol to cyclododecanone, for example, with di-*tert*-butyl peroxide as a radical initiator, yields 2-(γ-hydroxypropyl)cyclododecanone (**41**). This is converted into 13-oxabicyclo-[10.4.0]hexadec-1(12)-ene (**42**) by acid-catalyzed dehydration [174]. Addition of hydrogen peroxide, in the presence of sulfuric acid, gives 12-hydroperoxy-13-oxabicyclo[10.4.0]hexadecane (**43**). Cleavage of the peroxide by heating in xylene gives 15-pentadecanolide as well as a small amount of 15-pentadec-11(and 12)-enolide and 11 12-hydroxy-15-pentadecanolide [175].



Preparation from Polyesters of 15-Hydroxypentadecanoic Acid.
In a Japanese process, the required ω-hydroxy acid is prepared from 1,12-dodecanediol in several steps. The diol is added to methyl acrylate in a radical reaction, using di-*tert*-butyl peroxide as a catalyst. The free hydroxyl group in the resulting ω-hydroxy-γ-pentadecalactone is acetylated with acetic anhydride, and the resulting ω-acetoxy-γ-pentadecalactone is converted into 15-hydroxypentadecanoic acid by hydrogenolysis and hydrolysis [176] (see upper one of following figures).

Another route to 15-hydroxypentadecanoic acid starts from 13-oxabicyclo[10.4.0]hexadec-(1,12)-ene (**42**), see (1). Nitrosation to 12-oximino-15-pentadecanolide, followed by a Wolff–Kishner reduction yields 15-hydroxypentadecanoic acid [177]. The reaction can be carried out without isolation of the intermediate oxime.





The polyester of 15-hydroxypentadecanoic acid is prepared by customary methods and is cleaved under high vacuum in the presence of transesterification catalysts.

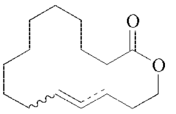
Uses. 15-Pentadecanolide is a highly valuable fragrance material that is used in fairly large amounts in fine fragrances as a fixative with a delicate musk odor.

Trade Names. Cyclopentadecanolid (Haarmann & Reimer), Exaltolid (Firmenich), Pentalide (Soda Aromatic).

Oxacyclohexadec-12/13-en-2-one, (*E*/*Z*) [*34902-57-3*], $C_{15}H_{26}O_2$, M_r 238, *bp* (40 Pa) 88 – 93 °C , d_{20}^{20} 0.961 – 0.971, possesses a musklike, ambrette, and animalic odor.

Production (see production of 15-pentadecanolide page 77). Cleavage of 12-hydroperoxy-13-oxabicyclo[10.4.0]-hexadecane (**43**) in the presence of $Cu(OAc)_2$ and $Fe(SO_4)_2$ gives 43 % of *trans*-pentadec-11-enolide, 26 % *trans*-pentadec-12-enolide, 18 % *cis*-pentadec-11-enolide, 5 % *cis*-pentadec-12-enolide, and 5 % pentadecanolide [178].

Another synthesis uses a pyrolysis of an acetoxy derivative of the lactone [179].

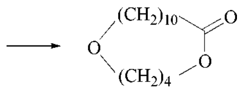


Uses. 15-Pentadec-11/12-enolide is a very powerful musk and combines the strength and tenacity of the aromatic musks with the pleasantness and elegance of the macrocyclic musks.
Trade Names. Habanolide (Firmenich), Globalide (Haarmann & Reimer).

12-Oxa-16-hexadecanolide [*6707-60-4*], 16-hydroxy-12-oxahexadecanoic acid lactone, $C_{15}H_{28}O_3$, M_r 256.38, does not occur in nature. Its odor is comparable to that of 15-pentadecanolide, but less intense. It is prepared by reacting methyl ω-bromoundecanoate with the monosodium salt of 1,4-butanediol. The resulting methyl 16-hydroxy-12-oxapalmitate is condensed to the corresponding polyester, which is subsequently depolymerized.

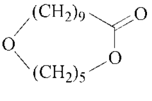
$$HO{-}(CH_2)_4{-}ONa + Br{-}(CH_2)_{10}{-}COOCH_3 \longrightarrow$$

$$HO{-}(CH_2)_4{-}O{-}(CH_2)_{10}{-}COOCH_3 \longrightarrow \text{Polyester}$$



12-Oxa-16-hexa-decanolide

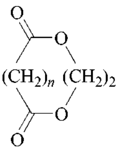
12-Oxa-16-hexadecanolide as well as the stronger smelling 11-oxa isomer [*3391-83-1*], which is obtained in the same way from the corresponding hydroxyoxa acid, are used as substitutes for 15-pentadecanolide in fine fragrances.



11-Oxa-16-hexa-decanolide

Trade Names. 12-Oxa-16-hexadecanolide = Cervolide (Quest), 11-Oxa-16-hexadecanolide = Musk R 1 (Quest).

α,ω-Dodecanedioic acid ethylene ester [*54982-83-1*], (**44**, $n = 10$), $C_{14}H_{24}O_4$, M_r 256.34, *mp* 18 °C, *bp* (2.7 kPa) 139 – 141 °C, d_4^{60} 1.0303, n_D^{40} 1.4588, is a synthetic musk that is prepared by thermal depolymerization of the polyester obtained from 1,12-dodecanedioic acid and ethylene glycol in the presence of a catalyst (e.g., stannous salts of aliphatic monocarboxylic acids) [180].



44

The compound is used in perfumery as a musk fragrance, but is not as long-lasting as the following homologous compound, ethylene brassylate.
Trade Name. Arova 16 (Degussa).

α,ω-Tridecanedioic acid ethylene ester [*105-95-3*], ethylene brassylate (**44** ,$n = 11$), $C_{15}H_{26}O_4$, M_r 270.37, *bp* (1.3 kPa) 140 °C, d_4^{60} 1.0180, n_D^{20} 1.4702, is an artificial fragrance compound, with a sweetish, slightly fatty, musk odor. Like α,ω-dodecanedioic acid ethylene ester, the ester is obtained by depolymerization of the corresponding polyester. Brassylic acid (α,ω-tridecanedioic acid) is prepared by ozonolysis of erucic acid [181]:

$$\underset{\text{Erucic acid}}{H_3C{-}(CH_2)_7{-}CH{=}CH{-}(CH_2)_{11}{-}COOH} \xrightarrow{O_3}$$

$$H_3C{-}(CH_2)_7{-}COOH + \underset{\text{Brassylic acid}}{HOOC{-}(CH_2)_{11}{-}COOH}$$

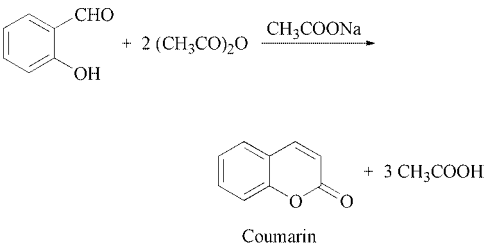
Ethylene brassylate is used in large amounts in perfumery as a fixative and for rounding off sweet-flowery odor notes.
Trade Name. Musk T (Takasago), Ethylene Brassylate (Degussa).

Coumarin [*91-64-5*], 2*H*-1-benzopyran-2-one, $C_9H_6O_2$, M_r 146.15, *bp* (1.33 kPa) 153.9 °C, *mp* 70.6 °C, d_4^{20} 0.935, occurs widely in nature and determines, for example, the odor of woodruff. It forms white crystals with a hay-like, spicy odor. When treated with dilute alkali, coumarin is hydrolyzed to the corresponding coumarinic acid salt (*cis*-2-hydroxycinnamic acid). Heating with concentrated alkali or with sodium ethanolate in ethanol results in the formation of *o*-coumaric acid salts (*trans*-2-hydroxycinnamic acid). 3,4-Dihydrocoumarin is obtained by catalytic hydrogenation, for example, with Raney nickel as a catalyst; octahydrocoumarin is obtained if hydrogenation is carried out at high temperature (200 – 250 °C).

Production. Coumarin is currently produced by Perkin and Raschig syntheses.

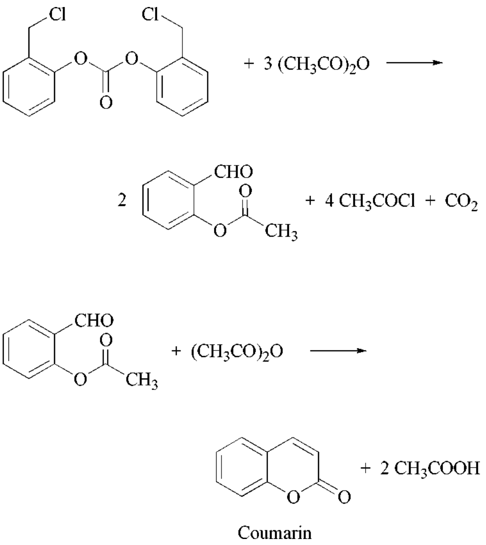
Synthesis from Salicylaldehyde by the Perkin Reaction.

In the presence of sodium acetate, salicylaldehyde reacts with acetic anhydride to produce coumarin and acetic acid. The reaction is carried out in the liquid phase at elevated temperature.



In a special process, the sodium acetate catalyst is retained in the reactor by a built-in filter and is reused [182].

Synthesis from o-Cresol by the Raschig Process.

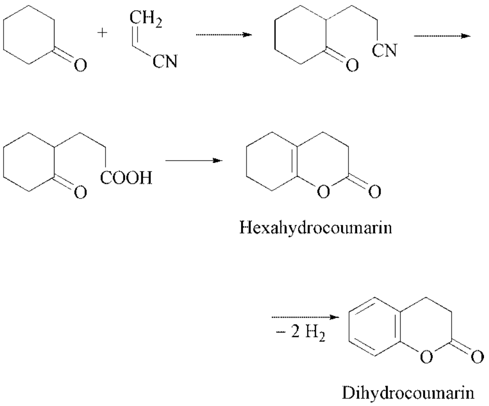


The hydroxyl group of *o*-cresol is protected by a carbonate or phosphate group, and the ester can be converted into the corresponding benzal chloride derivative by chlorination of the methyl group. Reaction of this intermediate with acetic anhydride yields *O*-acetylsalicylaldehyde and acetyl chloride. Ring closure of the aldehyde with acetic anhydride gives coumarin.

Since the odor of coumarin is relatively weak, strong-smelling byproducts (e.g., vinylphenol) must be removed. Many purification methods have been reported and patented.

Uses. Coumarin is one of the most widely used fragrance compounds. It is used in fine fragrances as well as in soap perfumes for spicy green notes. It is also used in galvanization as a brightener.

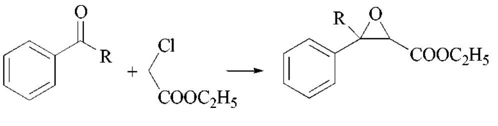
Dihydrocoumarin [*119-84-6*], 3,4-dihydro-2*H*-benzopyran-2-one, $C_9H_8O_2$, M_r 148.16, *bp* (2.3 kPa) 145 °C, *mp* 24 °C, n_D^{25} 1.5528, occurs in a few essential oils and forms colorless crystals with a sweet-herbal odor. Dihydrocoumarin is prepared by hydrogenation of coumarin, for example, in the presence of a Raney nickel catalyst. Another process employs the vapor-phase dehydrogenation of hexahydrocoumarin in the presence of Pd or Pt–Al_2O_3 catalysts [183]. Hexahydrocoumarin is prepared by cyanoethylation of cyclohexanone and hydrolysis of the nitrile group, followed by ring closure to the lactone [184].



Dihydrocoumarin is used in woodruff-type flavor compositions. (Limiting IFRA recommendation)

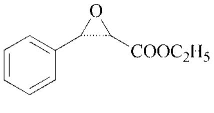
2.7.3. Glycidates

A number of glycidates are important intermediates in the synthesis of fragrance compounds. They are prepared either by epoxidation of the corresponding acrylates or by condensation of aldehydes or ketones with α-chloro substituted fatty acid esters (Darzens reaction).

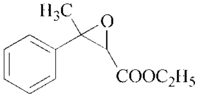


Ethyl 3-phenylglycidate [*121-39-1*], "so-called special aldehyde C_{16}", $C_{11}H_{12}O_3$, M_r 192.21, *bp* (40 Pa) 104 °C, d_4^{20} 1.1023, n_D^{30} 1.5095, is a colorless liquid with a strawberry-like odor; it is not known to occur in nature.

It is prepared by treating ethyl cinnamate with peracetic acid [185] or by condensation of benzaldehyde with ethyl chloroacetate (in the above Darzens reaction, R = H). The glycidate is used as a long-lasting fragrance compound for creating harmonic, fruity notes in household and fine fragrances.



Ethyl 3-methyl-3-phenylglycidate [*77-83-8*], "so-called aldehyde C_{16}", $C_{12}H_{14}O_3$, M_r 206.24, *bp* (2.4 kPa) 153 – 155 °C, d_{25}^{25} 1.506 – 1.513, occurs in two optically active pairs of *cis*- and *trans*-isomers; each isomer has a characteristic odor [186]. The commercial product is a racemic mixture of all four isomers and has a strong, sweetish, strawberry odor. The *cis* : *trans* ratio obtained in the Darzens condensation of acetophenone ($R = CH_3$) and ethyl chloroacetate depends on the base used in the reaction.

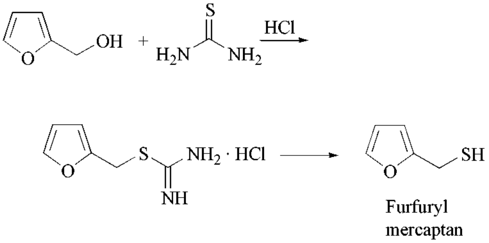


The glycidate is used in household perfumery for fruity notes.

Trade Name. Fraise pure (Givaudan Roure).

2.7.4. Miscellaneous Compounds

2-Furylmethanethiol [*98-02-2*], furfuryl mercaptan, C_5H_6OS, M_r 114.16, *bp* (101.3 kPa) 160 °C, d_4^{20} 1.1319, n_D^{20} 1.5329, is an important constituent of the aroma of roasted coffee. It is a liquid with an unpleasant odor, which becomes like coffee when diluted. Furfuryl mercaptan is prepared from furfuryl alcohol, thiourea, and hydrogen chloride. The resulting *S*-furfurylisothiouronium chloride is cleaved with sodium hydroxide to give furfuryl mercaptan.



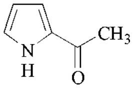
The thiol is used in coffee aromas.

2.8. N- and N, S-Heterocycles

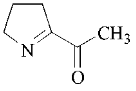
Many nitrogen- and sulfur-containing heterocycles have been identified in the aroma fractions of foods [187]. In roasted products (e.g., coffee) and heat-treated foods (e.g., baked bread or fried meat), these heterocycles are formed from reducing sugars and simple or sulfur-containing amino acids by means of Maillard reactions [188, 189]. Their odor threshold values are often extremely low and even minute amounts may significantly contribute to the aroma quality of many products [190, 191]. Therefore, N- and N, S-heterocyclic fragrance and flavor substances are produced in far smaller quantities than most of the products previously described.

Pyrroles, indoles, pyridines, quinolines, and pyrazines are examples of N-heterocycles that are produced as fragrance and flavor compounds. Thiazoles and dithiazines are examples of nitrogen- and sulfur-containing heterocycles. These heterocyclic compounds are mainly used in aroma compositions, exceptions are indoles and quinolines, which are important fragrance substances.

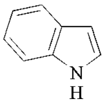
Representatives of the above-mentioned classes are as follows:



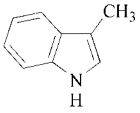
2-Acetylpyrrole [*1072-83-9*], roast odor



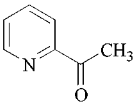
2-Acetyl-3,4-dihydro-5*H*-pyrrole [*85213-22-5*], characteristic odor of white bread crust



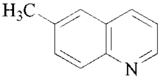
Indole [*120-72-9*], fecal odor, floral in high dissolution



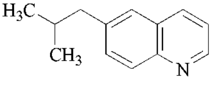
3-Methylindole, skatole [*83-34-1*], indole-like odor



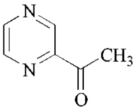
2-Acetylpyridine [*1122-62-9*], roast odor



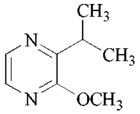
6-Methylquinoline [*91-62-3*], blossom odor, sweet-animalic upon dissolution



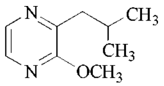
6-Isobutylquinoline [*68141-26-4*], mossy-earthy odor



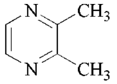
2-Acetylpyrazine [*22047-25-2*], popcorn-like odor



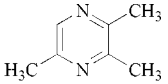
2-Methoxy-3-isopropylpyrazine [*25773-40-4*], green pea odor



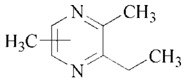
2-Methoxy-3-isobutylpyrazine [*24683-00-9*], green-pepper odor



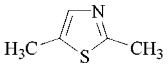
2,3-Dimethylpyrazine [*5910-89-4*], and its 2,5- [*123-32-0*] and 2,6- [*108-50-9*] isomers, roast odor, reminiscent of nuts



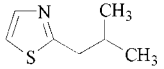
Trimethylpyrazine [*14667-55-1*], roast odor, reminiscent of coffee and cocoa



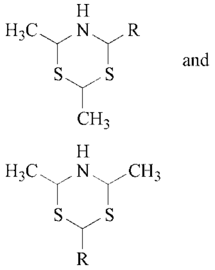
Mixture of 3-ethyl-2,5-dimethylpyrazine [*13360-65-1*] and 2-ethyl-3,5-dimethylpyrazine [*13925-07-0*], roast odor, reminiscent of nuts



2,5-Dimethylthiazole [*4175-66-0*], meat-like odor



2-Isobutylthiazole [*18640-74-9*], tomato odor



R = Methyl, isopropyl, isobutyl, 2-methylbutyl

Alkyldimethyl-1,3,5-dithiazines, roast odor

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 organoleptic 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. Demand for perfumes based on natural materials has increased.

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 and the lavandin plantations in southern France.

The economic importance of the cultivation of aromatic plants has led to the systematic breeding of new varieties. New species 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 $\$ 600 \times 10^6$ [192].

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.

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 organoleptic 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 organoleptic 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 [193].

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 furocoumarins.

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 compounds. 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 sourroundings 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., benzene, toluene, hexane, petroleum ether). On evaporation, the resulting residue contains not only volatile fragrance materials, but also a large proportion of nonvolatile 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. 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 ISO or the Essential Oil Association of the United States (EOA). The physical standards cited according to ISO are taken from the most recent draft, because many standards are already very old but under discussion. The ISO standard number remains the same; so the reader can also check for the older data. EOA specifications were only cited in those cases where no ISO specifications are available. These become more and more the most widely distributed standards. 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., [194], and in ISO specifications, which now include gas chromatograms.

The entire components of the individual products have not been listed for the same reason; further information is available in the literature, e.g., [187, 195]. 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, in [196].

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 [197]. Diallyl disulfide [*2179-57-9*] is an essential odor component of garlic oil:
   $CH_2{=}CHCH_2SSCH_2CH{=}CH_2$
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 [198].
   Aliphatic sulfur compounds, in particular disulfides such as methyl propyl disulfide, dipropyl disulfide, and especially *cis-* and *trans*-propenyl propyl disulfide are mainly responsible for the typical odor of onion oil. Garlic and onion oil are used in seasoning mixtures for the food industry.

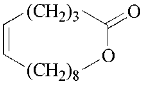
Allspice oil, see Pimento Oils, page 113.

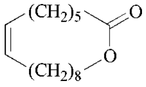
Ambergris (ambra), see Animal Secretions, page 87.

Ambrette seed oil is obtained by steam distillation of the dried, crushed seeds of *Abelmoschus 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-yellow liquid with the strong, musky odor of ambrettolide.

d_{25}^{25} 0.898 – 0.920; n_{D}^{20} 1.4680 – 1.4850; $[\alpha]_{\mathrm{D}}$ – 2°30′ to +3′; acid value: max. 3; saponification value: 140 – 200 [199].

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


5-Tetradecen-14-olide

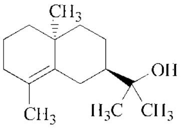

Ambrettolide

Other components are acyclic aliphatic esters and terpenes, such as farnesol and farnesyl acetate. Ambrette seed oil is one of the most expensive essential oils and, thus, is used mainly in fine fragrances.

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. Annual production worldwide is ca. 40 t. It is a pale yellow to amber-yellow, slightly viscous liquid with a mild wood odor.

d_{20}^{20} 0.946 – 0.978; n_{D}^{20} 1.505 – 1.510; $[\alpha]_{\mathrm{D}}^{20}$ + 10 ° to + 60 °; solubility: 1 vol in 1 vol of 90 % ethanol at 20 °C; solutions sometimes become opalescent on dilution; acid value: max. 3.0; ester value (after acetylation): 180 – 198 [200].

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 valerianol [*20489-45-6*], elemol [*639-99-6*], *β*-eudesmol [*473-15-4*], and *epi-γ*-eudesmol [*15051-81-7*] [201].


epi-γ-Eudesmol

Amyris oil is used in perfume compositions, mainly as a fixative.

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. Apiaceae [*Archangelica officinalis* (Moench) Hoffm.], a plant occurring predominantly in Europe. The oil is a pale yellow to deep amber-yellow liquid with a green, herbaceous, peppery, musk-like odor and a bitter-sweet taste.

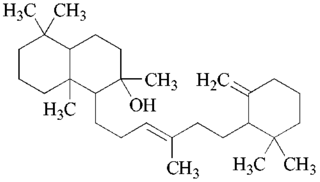
d^{25}_{25} 0.850 – 0.880, occasionally up to 0.930 for oils from stored roots; n^{20}_{D} 1.4735 – 1.4870; $[\alpha]_D$ 0 ° to + 46 °; acid value: max. 7; ester value: 10 – 65; solubility: 1 vol in at least 1 vol of 90 % ethanol, often with turbidity [202]. (Limiting IFRA recommendation)

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^{20}_{D} 1.4800 – 1.4880; $[\alpha]_D$ + 4 ° to + 16 °; acid value: max. 3; ester value: 14 – 32; solubility: 1 vol in at least 4 vol 90 % ethanol, often with considerable turbidity [203].
   Angelica root oil contains ca. 90 % terpenoids and sesquiterpenoids. α-Pinene, 3-carene, limonene, and β-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. The two angelica oils are used mainly in the alcoholic beverage industry.

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 longlasting fragrance complexes. Most of their odoriferous constituents are now produced synthetically and are used for the same purposes.

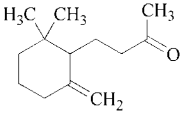
1) *Ambergris* (*ambra*) is a secretion of the sperm whale *Physeter catodon* (*P. macrocephalus* L.), that possibly results from a pathological condition. Ambergris has a lower density than water and washes ashore along the ocean coasts. The major quantity is obtained from killed animals, but only a 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 (up to 85 %) and the odorless triterpene alcohol, ambrein [*473-03-0*].

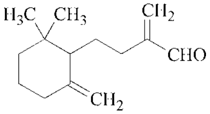


Ambrein

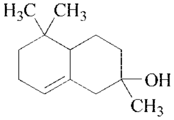
Ambrein is the likely precursor of a number of strongly odoriferous mono-, bi-, and tricyclic compounds that are formed by autoxidation or photooxidation [204]. Examples are as follows:



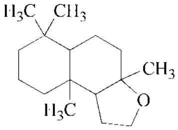
γ-Dihydroionone [*13720-12-2*] (odor: tobacco)



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



α-Ambrinol [*41199-13-3*] (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 is used in fine fragrances.

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.
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 acetone, benzene, or ethanol; yields are 30 – 50 %, 20 – 25 %, and 45 – 80 %, respectively. The resinoids have the following specifications [205]

Acid value	15 – 30	30 – 35	15 – 30
Ester value	145 – 200	145 – 200	145 – 200
Carbonyl value	55 – 70	40 – 60	10 – 20

   The intense, for the Siberian beaver leathery, odor of castoreum is caused largely by phenolic compounds (e.g., 4-alkylphenols and catechol derivatives), which beavers take in with their food and excrete into their abdominal pouch. Castoreum is used mainly in fine fragrances for its characteristic, long-lasting odor, particularly for delicate leather nuances.
4) *Civet* is a glandular secretion produced by both sexes of the civet cat (Viverridae). Two species are known: *Civetticitis civetta* that inhabits Ethiopia, and *Viverra zibetha* that is found in India, Malaya, Indochina, and Indonesia.

   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; *mp* 20 – 25 °C; acid value: 100 – 140; ester value: 20 – 40; carbonyl value: 15 – 25 [206]. Civetone (for formula, see Section 2.4) is the main odoriferous constituent of civet (2.5 – 3.4 %). Civet contains other macrocyclic ketones such as cyclohexa- and cycloheptadecanone and 6-*cis*-cycloheptadecenone. Traces of indole and skatole contribute to the animal note.

   Civet has a distinctly different odor from musk and was formerly a versatile ingredient of fine fragrances.
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 available at extremely high prices.

   (−)-Muscone and related macrocyclic ketones are responsible for the odor of musk [207]. Like other animal secretions, musk is preferentially used as an alcoholic tincture in fine fragrances.

Anise 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^{20}_{D} 1.552 – 1.561; $[\alpha]^{20}_{\mathrm{D}}$ − 2 ° to + 2 °; solubility: 1 vol in 3 vol of 90 % ethanol at 20 °C; *fp* 15 – 19.5 °C [208].

The main component of anise oil is *trans*-anethole, which may be present at a concentration up to 94 % and which determines the melting point of the oil.

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 oil (see page 117), which also contains a high percentage of anethole. Annual worldwide production of both oils is ca. 500 t.

Anise oil is used for flavoring foods, beverages, and oral hygiene products.

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; $[\alpha]_{\mathrm{D}}^{20}$ $-25°$ to $-8°$.

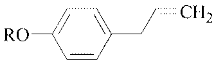
The major components of armoise oil (Marrakesh-type) are the ketones camphor (40 %) and α- and β-thujone (35 % and 5 % respectively). Since *Artemisia herba-alba* exists as various chemotypes, the composition of the oil may vary widely. For example, each of the above-mentioned ketones may occur in a concentration over 50 % or less than 10 %.

Armoise oil is used in fairly large amounts in fine fragrances (e.g., for chypre notes).

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

1) *Réunion basil oil* 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 pale yellow to amber-yellow liquid with a fresh, green, spicy odor characteristic of estragole. d_{20}^{20} 0.948 – 0.970; n_{D}^{20} 1.5100 – 1.5200; $[\alpha]_{\mathrm{D}}^{20}$ $-1°$ to $+2°$; solubility: 1 vol in 7 vol of 80 % ethanol [209].

   The oil typically has a high content of methylchavicol (min. 75 %, max. 85 %).

   R = H_3C, methylchavicol (estragole) [*140-67-0*]
   R = H, chavicol [*501-92-8*]

   Annual production (ca. 200 to 300 t) is used predominantly for seasoning foods.

2) *European basil oil* is produced mainly in France, Italy, the Balkan countries, Egypt, and South Africa. The major components of this oil are linalool (35 – 50 %) and methylchavicol (15 – 25 %). It is used for food flavoring and in perfumery.

Bay oil is obtained by steam distillation of the leaves of *Pimenta racemosa* (Mill.) J. W. 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; $[\alpha]_{\mathrm{D}}^{20}$ close to 0°; phenols content: min. 50 % [210].

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, eugenol, and chavicol. The phenol content is determined largely by the latter two compounds.

Total production of bay oil is ca. 50 t/a. It has antiseptic properties because of its high phenol content and is, therefore, used for perfuming after-shave lotions.

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. (IFRA recommendation)

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 [211].

Benzoe Sumatra resinoid is used in perfumery, mainly as a fixative with a warm, balsamic note. (IFRA recommendation)

Bergamot oil see Citrus Oils, page 94.

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} 1.040 – 1.050; n^{20}_{D} 1.5410 – 1.5460; $[\alpha]_{\mathrm{D}}$ 0 ° to + 0°25′; acid value: max. 8; aldehyde content (calculated as benzaldehyde): min. 95 %; solubility: 1 vol in 2 vol of 70 % ethanol [212].

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

Black currant absolute (Bourgeons de cassis absolute) is obtained by solvent extraction via the concrete obtained from the dormant buds of the black currant bush *Ribes nigrum* L. (Saxifragaceae). The yield is ca. 3 %. Black currant absolute is a dark green paste with the characteristic, powerful, penetrating odor of black currants.

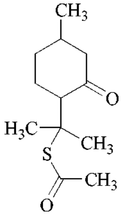
It has been used as a major ingredient in some fine fragrances.

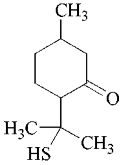
Bois de rose oil, see Rosewood Oil, page 115.

Buchu leaf oils are obtained by steam distillation of *Agathosma betulina* (Bergius) Pillans (syn. *Barosma betulina*) and *A. crenulata (L.)* Pillans (syn. *Barosma crenulata*) (Rutaceae) leaves. The oils are dark yellow to brown liquids with a characteristic minty-fruity odor, reminiscent of black currant.

d^{25}_{25} 0.912 – 0.956, n^{20}_{D} 1.474 – 1.488; $[\alpha]_{\mathrm{D}}$ − 36 ° to − 8 °; acid value: 1 – 5; ester value: 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 black currant odor are *p*-menthane-8-thiol-3-one [*38462-22-5*] and its S-acetate derivative [*57074-34-7*] which are two of the small number of naturally occurring sulfur-containing terpenoids known to date [213,214].



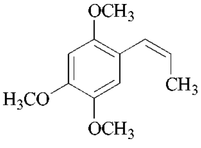


Buchu oil is used as a flavor ingredient (e.g., in fruit aromas) and in perfumery in chypre bases and in certain types of eaux de cologne; only very small amounts are employed because of its intensity.

Calamus 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. (Limiting IFRA recommendation)

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

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



β-Asarone

The following data are typical for European and Indian oils, respectively:

d^{25}_{25} 0.940 – 0.980 and 1.060 – 1.080; n^{20}_{D} 1.5010 – 1.5160 and 1.5500 – 1.5525; $[\alpha]_{\mathrm{D}}$ + 5 ° to + 35 ° and − 2 ° to + 6.5 °; acid value: max. 4; ester value: 3 – 20; solubility: 1 vol in 5 vol of 90 % ethanol; solutions may be turbid [215].

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 β-asarone.

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 cooling and 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^{20}_{D} 1.4670 – 1.4720; $[\alpha]_{\mathrm{D}}$ + 16 ° to + 28 °; solubility: 1 vol in 1 vol of 95 % ethanol; solutions usually become cloudy on further dilution [216].
   In addition to monoterpene hydrocarbons, this oil contains up to 35 % cineole.
   Camphor oils with a higher cineole content can be obtained by further fractionation or by steam distillation of the leaves of other varieties of the camphor tree. They are marketed under the trade name eucalyptus oil 70 – 80 % by Chinese producers, but are not true eucalyptus oils (see Eucalyptus Globulus Oil, page 100).
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^{20}_{D} 1.5100 – 1.5500; $[\alpha]_{\mathrm{D}}$ 0 ° to +3 °; *fp* 6 °C; solubility: 1 vol in 2 vol of 90 % ethanol [217].

The oil contains more than 80 % safrole and, like Brasilian sassafras oil, is therefore used as a raw material for the production of piperonal via isosafrole (see page 69). (IFRA recommendation)

Camphor oils with a high safrole content can also be obtained by steam distillation of the wood of *Cinnamomum parthenoxylon* Nees.

The production of natural camphor and camphor oils was formerly several thousand of tons per year. Nowadays it has declined to 500 t/a 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.

Cananga oil, see Ylang-Ylang and Cananga Oils, page 120.

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

d^{20}_{20} 0.905 – 0.920; n^{20}_{D} 1.4840 – 1.4890; $[\alpha]^{20}_{\mathrm{D}}$ + 67 ° to + 80 °; ketone content (calculated as carvone): 50 – 60 %; solubility: 1 vol in 5 vol of 80 % ethanol; acid value: max. 1 [218].

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 produced mainly in Poland and Hungary. It is used primarily for flavoring foods and alcoholic beverages, but also for the production of (+)-carvone.

Cardamom oil is obtained by steam distillation of the seeds of *Elettaria cardamomum* (L.) Maton var. minuscula Burkill (Zingiberaceae). It is a colorless or very pale yellow liquid with an aromatic, penetrating, slightly camphoraceous odor and a persistent, pungent, strongly aromatic taste.

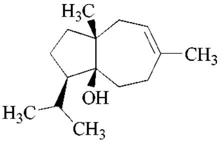
d^{20}_{20} 0.919 – 0.936; n^{20}_{D} 1.4620 – 1.4680; $[\alpha]^{20}_{\mathrm{D}}$ + 22 ° to + 41 °; solubility: 1 vol in 2 to 5 vol of 70 % ethanol, solutions sometimes slightly opalescent [219].

The major components of cardamom oil are 1,8-cineole and α-terpinyl acetate (ca. 30 % each). It is produced from cultivated or wild plants in the mountainous regions of southern India, Sri Lanka, Indonesia, Thailand, southern China, and Guatemala. Cardamom oil is used primarily for seasoning foods and occasionally in perfumery.

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^{20}_{D} 1.4800 – 1.4930; $[\alpha]^{20}_{\mathrm{D}}$ – 30 ° to – 4 °; acid value: min. 5.0; ester value: 9 – 58; ester value (after acetylation): 50 – 95; solubility: 1 vol in 2 vol of 80 % ethanol [220].

The main constituent of carrot seed oil is carotol [*465-28-1*], which may be present in over 50 % concentration and is responsible for the characteristic odor.



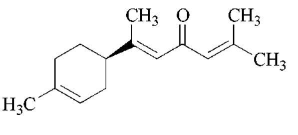
Carotol

Carrot seed oil is used in the alcoholic beverage industry, in food flavors, and in perfume compositions.

Castoreum, see Animal Secretions, page 87.

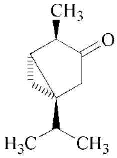
Cedar Oils. Several different conifer species are called cedars and the corresponding oils vary considerably in composition. Worldwide annual production is about 800 t. The following cedar oils are commercially important:

1) *Atlas cedarwood oil* is obtained by steam distillation of wood from *Cedrus atlantica* (Endl.) Manetti ex Carr. (Pinaceae). It is a yellowish to brownish, slightly viscous liquid with a sweet aromatic odor and a lasting, woody undertone.
   d_{25}^{25} 0.925 – 0.940; n_D^{20} 1.5060 – 1.5160; $[\alpha]_D$ + 50 ° to + 77 °; ketone content (calculated as atlantone): min. 20 %; solubility: 1 vol in at least 5 vol of 95 % ethanol [221].
   Atlas cedarwood oil and Himalaya cedarwood oil [from *Cedrus deodara* (D. Don) G. Don] both contain α-atlantone [*32207-08-2*] as their main odoriferous component. They are used mainly in soap perfumes.



E-(+)-α-Atlantone

2) *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 [*546-80-5*].
   d_{25}^{25} 0.910 – 0.920; n_D^{20} 1.4560 – 1.4590; $[\alpha]_D$ – 14 ° to – 10 °; ketone content (calculated as thujone): min. 60 %; solubility: 1 vol in 3 vol of 70 % ethanol at 25 °C [222].

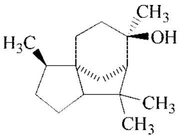


(–)-Thujone

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.

3) *Chinese cedarwood oil* is similar in composition to Texas cedarwood oil (see below). Chinese cedarwood oil is obtained by steam distillation of the wood of *Chamaecyparis funebris* Endl. = *Cupressus funebris* Endl. (Cupressaceae), which is a weeping cypress, indigenous to China [223]. Annual production lies between 850 and 900 t. Chinese cedarwood oil is an almost colorless to light yellow oil with a woody, bitter odor. d_{20}^{20} 0.938 – 0.960; n_D^{20} 1.5000 – 1.5080; $[\alpha]_D^{20}$ – 35 ° to – 20 °; cedrol content : min. 10 %, max. 16 % (by GLC); solubility: 1 vol in 5 vol of 95 % ethanol at 20 °C [224].
4) *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 ° to – 30 °; total alcohol content (calculated as cedrol): 35 – 48 %; cedrol content: min 20 % (by GLC), solubility: 1 vol in 5 vol of 90 % ethanol at 20 °C [225].
   For uses, see Virginia cedarwood oil.
5) *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 an almost colorless to pale yellow, viscous liquid with a characteristic cedarwood odor. The oil sometimes solidifies at room temperature.
   d_{20}^{20} 0.941 – 0.965; n_D^{20} 1.5020 – 1.5100; $[\alpha]_D^{20}$ – 36 ° to – 16 °; solubility: 1 vol in 5 vol of 95 % ethanol; sum of cedrol and widdrol: min. 15 %, max. 30 % (by GLC) [226, 227].

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 (production around 1600 t/a) 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. page 41) and cedryl methyl ether (see p. page 34) are produced from cedrol. The oils contain other sesquiterpenes, particularly α-cedrene and thujopsene, which can be converted to valuable fragrance materials. By acetylation of the mixture cedryl methyl ketone (see page 39) is produced; for production of ambrocenide pure α-cedrene is used (see page 76).

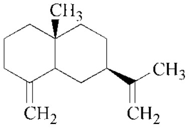


(+)-Cedrol

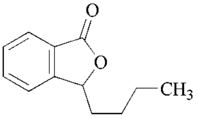
Celery seed oil is obtained by steam distillation of the crushed, ripe seeds of celery, *Apium graveolens* L. (Apiaceae). It is an almost colorless to brownish-yellow liquid with a characteristic, pervasive, spicy, very persistent odor.

d^{20}_{20} 0.867 – 0.908; n^{20}_{D} 1.4780 – 1.4880; $[\alpha]^{20}_{D}$ +65 ° to +78 °; solubility: 1 vol in no more than 6 vol of 90 % ethanol at 20 °C; acid value: max. 6; ester value: 20 – 70 [228].

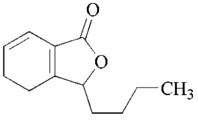
Major mono- and sesquiterpene hydrocarbons in the oil are (+)-limonene (58 to 79 % according to ISO) and β-selinene [*17066-67-0*]. Its typical, long-lasting odor is caused primarily by two lactones, 3-butylphthalide [*6066-49-5*] and sedanenolide [*62006-39-7*] which each occur at a concentration of ca. 1 %.



(+)-β-Selinene



3-Butylphthalide

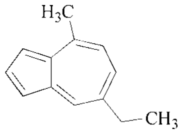


Sedanenolide (3-butyl-4,5-dihydrophthalide)

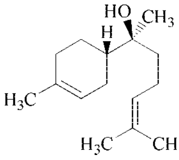
Celery for the production of seed oil is grown mainly in southern France, India, and California. The seed oil is used chiefly for flavoring foods, although small quantities are also used in perfumery.

Chamomile oils are available in three 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. Annual production is ca. 10 t. Blue chamomile oil 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 (−)-α-bisabolol [*23089-26-1*] contribute to the anti-inflammatory properties of blue chamomile oil.



Chamazulene



(−)-α-Bisabolol

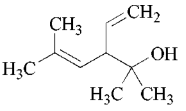
d^{25}_{25} 0.910 – 0.950; acid value: 5 – 50; ester value: 0 – 40; ester value (after acetylation): 65 – 155; solubility: solutions in 95 % ethanol usually remain turbid [229].

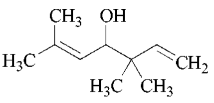
2) *Roman chamomile oil* (English chamomile oil) is produced from the dried flowers of *Chamaemelum nobile* (L.) All. (*Anthemis nobilis* L.), Asteraceae, which are cultivated primarily in Belgium, but also in England, France, and Hungary. The oil is distilled in France and England. It is a light blue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

d^{20}_{20} 0.900 – 0.920; n^{20}_{D} 1.4380 – 1.4460; $[\alpha]^{20}_{D}$ − 2 ° to + 3 °, acid value: max. 8; ester value: 250 – 340; solubility: 1 vol in 0.6 vol of 90 % ethanol (solutions may contain a slight precipitate) [230].

The constituents of Roman chamomile oil include esters of angelic and tiglic acids.

3) *Moroccan chamomile oil* (wild chamomile oil) is produced from *Ormenis* species (e.g., *O. multicaulis, O. mixta*) that grow wild in Morocco. It is a light yellow liquid with a sweet, herbaceous, woody balsamic odor. Its main constituents are irregular monoterpenes, such as santolina alcohol [*35671-15-9*] and artemisia alcohol [*29887-38-5*].


Santolina alcohol


Artemisia alcohol

Cinnamon oils

1) *Cassia oil* (Chinese cinnamon oil) is obtained by steam distillation of the leaves, leaf stalks, and young twigs, of *Cinnamomum aromaticum* Nees (*C. cassia* Bl., Lauraceae). It is a yellow to reddish-brown liquid with a sweet-spicy, cinnamon-like odor, annual production around 300 t.
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 value: max. 15; content of carbonyl compounds (calculated as cinnamaldehyde): min. 80 % [231].
In contrast to cinnamon bark oil, cassia oil contains a considerable amount of 2-methoxycinnamaldehyde (5 to 10 %) in addition to its main constituent, cinnamaldehyde. Cassia oil is used predominantly in flavor compositions. (Limiting IFRA recommendation)
2) *Cinnamon leaf oil* is produced by steam distillation of the leaves of the cinnamon tree, *Cinnamomum zeylanicum* Blume. 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; $[\alpha]_D^{20}$ $-2.5°$ to $+2°$; solubility: 1 vol in 2 vol of 70 % aqueous ethanol at 20 °C; phenol content: 75 – 85 % [232].
The main component of cinnamon leaf oil is eugenol. The oil is used as such or as a source of high-grade eugenol (see page 66).
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.
d_{25}^{25} 1.010 – 1.030; n_D^{20} 1.5730 – 1.5910; $[\alpha]_D$ $-2°$ to $0°$; aldehyde content (calculated as cinnamaldehyde): 55 – 78 %; solubility: 1 vol in at least 3 vol of 70 % ethanol [233]. The oil is used predominantly in flavor compositions. (Limiting IFRA recommendation)

Cistus oil, see Labdanum Oil, page 104.

Citronella oil, see Cymbopogon Oils, page 98.

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). The essential oils and the essence oils have similar compositions.

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, page 109 and Petitgrain Oils, page 112).

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.

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, most citrus peel oils are produced by other methods. For instance, the peel of the whole fruit 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.

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 a larger amount 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 α-terpinene and β-pinene). The important aroma-determining components of citrus oils are functionalized terpenes and aliphatic compounds (predominantly carbonyl compounds and esters), present only in very low concentrations. 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 cold-pressing peels from the unripe fruits of *Citrus aurantium* L. subsp. *bergamia* (Risso et Poit.) Wight et Arn. (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} 1.465 – 1.470; $[\alpha]_{\mathrm{D}}^{20}$ + 15 ° to + 32 °; evaporation residue 4.5 – 6.4 %; solubility: 1 vol in 1 vol of 85 % ethanol at 20 °C; acid value: max. 2.0; ester value: 86 – 129, corresponding to an ester content of 30 – 45 % (calculated as linalyl acetate) [234].
   Bergamot is still grown almost exclusively in the Italian province of Calabria, where the soil and climatic conditions are very favorable for its cultivation. The bergamot is grafted onto bitter orange plants. The quality of the oil is determined by its ester content and varies with the species. Annual production is ca. 90 t.
   Linalyl acetate, linalool (10 %), and citral (1 %) are important components of bergamot oil. Its terpene content (25 – 50 %) is relatively low for a citrus oil.
   Use of the untreated oil in cosmetics is limited by the photosensitizing properties of bergaptene (a furocoumarin) present in the oil, thus an IFRA recommendation exists. Bergamot oil is used in many perfumes and is an important component of eaux de cologne.
2) *Grapefruit oil* is obtained by cold pressing of the outer peels of the fruits of *Citrus paradisi* Macfad. (Rutaceae). It is a yellow to reddish orange liquid, with fresh citrus-like odor characteristic of grapefruit peel.
   d_{20}^{20} 0.852 – 0.860; n_{D}^{20} 1.4740 – 1.4790; $[\alpha]_{\mathrm{D}}^{20}$ + 91 ° to + 96 °; carbonyl value: min. 3.25; evaporation residue: min. 5.0 %, max. 10.0 % [235].
   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 ca. 90 % terpene hydrocarbons (mainly (+)-limonene), 0.5 % alcohols (mainly linalool), 1.8 % aldehydes (mainly octanal and decanal), 0.5 % ketones (mainly nootkatone), 0.3 % esters (mainly octyl and decyl acetate), and 7.5 % nonvolatile components [236,237].
   The sesquiterpene ketone nootkatone (for structure, see page 39) is primarily responsible for the characteristic aroma of grapefruit oil.
   Grapefruit oil is used mainly for flavoring fruit beverages. Annual production is 200 to 220 t. (Limiting IFRA recommendation)
3) *Lemon oil* is obtained by pressing peel from the fruits of *Citrus limon* (L.) Burm. f., (Rutaceae). It is a pale yellow to pale greenish-yellow liquid with a characteristic lemon peel odor. ISO differentiates between American, Mediterranean, and Equatorial type. The American type is subdivided into 'coastal' and 'desert' type. In the following the physical properties of the 'coastal' type are given.
   d_{20}^{20} 0.852 – 0.858; n_{D}^{20} 1.4730 – 1.4760; $[\alpha]_{\mathrm{D}}^{20}$ + 57 ° to + 65.6 °; evaporation residue: 1.75 – 3.6 % [238]; acid value: max. 2 %; content of carbonyl compounds (calculated as citral): 8.0 – 14.0 %.
   The composition of lemon oils depends on the variety of lemon and the country of origin. Their main components are terpenes – (+)-limonene (ca. 65 %), β-pinene, and γ-terpinene (8 – 10 % each) being the most important. 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 is in the coastal type between 1.6% and 2.9 %, in Italian lemon oil between 1.4 and 3.2 % [238].

Annual worldwide production is about 3.7×10^3 t, most of which originates from the United States, Italy, and Argentina.

Lemon oil is used in many food flavors. Because of its fresh odor, relatively large quantities are also employed in eaux de cologne and other perfumery products (see IFRA recommendation).

4) *Lime oil* may be either cold-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 aurantiifolia* (Christm. et Panz.) Swingle and the Persian (Tahiti) lime, *C. latifolia* Tanaka (Rutaceae). 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 organoleptic components than the West Indian lime oils and are thus comparatively mild and flat [239]. Consequently, West Indian lime oils are more popular.

*Pressed lime oils*are obtained by rasping and puncturing (type B). Other methods are also employed for West Indian limes: the whole fruits may be chopped and the oil–juice emulsion subsequently centrifuged (type A) [240,241].

Pressed lime oil (Mexican type, A) is a yellowish green liquid with a strong, characteristic odor, reminiscent of lemon. Limiting IFRA recommendation.

Type A: d^{20}_{20} 0.875 – 0.884, n^{20}_{D} 1.482 – 1.486, $[\alpha]^{20}_{\mathrm{D}}$ + 35 ° to + 42 °; carbonyl value: min. 16, max. 31, corresponding to 4.5 to 8.5 % of carbonyl compounds expressed as citral; evaporation residue: 10.0 – 14.5 % [242].

Cold-pressed lime oils are produced in a quantity of about 300 t/a. The composition and uses of pressed lime oil are similar to those of pressed lemon oil.

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.

Distilled 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^{20}_{D} 1.474 – 1.478; $[\alpha]^{20}_{\mathrm{D}}$ + 34 ° to + 45 °; evaporation residue: max. 2.5 %; content of carbonyl compounds (calculated as citral): max. 1.5 % [243].

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 [*470-67-7*], 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*]).

Annual worldwide production of distilled West Indian lime oil is about 750 t. The oil is used primarily in soft drinks.

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.

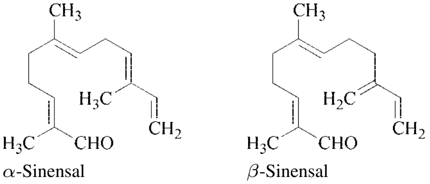
d^{20}_{20} 0.848 – 0.855; n^{20}_{D} 1.474 – 1.478, $[\alpha]^{20}_{\mathrm{D}}$ + 64 ° to + 75 °; evaporation residue: 1.6 – 4.0 %; content of carbonyl compounds (calculated as decanal): 0.4 – 1.2 %; acid value: max. 2.0 [244].

The main components are limonene (ca. 70 %) and γ-terpinene (ca. 20 %). The characteristic feature of mandarin oil is its content of α-sinensal, methyl N-methylanthranilate (which is responsible for fluorescence), and long-chain unsaturated aliphatic aldehydes.

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.

6) *Orange oil bitter* 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} 0.8480 – 0.8600; n_D^{20} 1.4720 – 1.4760; $[\alpha]_D^{20}$ +88 ° to +98 °; evaporation residue: 2 – 5 %; aldehyde content (calculated as decanal): min. 0.5 %, max. 2.9 % [245].
   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.
   Worldwide production of bitter orange oil (ca. 10 t/a) is lower than that of other pressed peel oils. Bitter orange oil is used in eaux de cologne and liqueurs. Limiting IFRA recommendation.
7) *Orange oil sweet* 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). Specifications for the oils depend on the cultivated varieties and the country of origin [246]
   The ISO specification of Orange oil sweet is as follows:
   d_{20}^{20} 0.842 – 0.850; n_D^{20} 1.4700 – 1.4760; $[\alpha]_D^{20}$ +94 ° to +99 °; evaporation residue: 1.0 – 5.0 %; content of carbonyl compounds (calculated as decanal): 0.9 – 3.1 %.
   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 α-sinensal [*17909-77-2*] and β-sinensal [*6066-88-8*], which contribute particularly to the special sweet orange aroma, also occur in other citrus oils, although in lower concentration.
   Worldwide production of cold-pressed orange oil is over 27 000 t/a. Its main uses are the flavoring of beverages and confectioneries and perfuming eaux de cologne, soap, and household products.



Civet, see Animal Secretions, page 87.

Clary sage oil, see Sage Oils, page 115.

Clove oils are produced from the 15 – 20-m high clove tree *Syzygium aromaticum* (L.). Merr. et L. M. Perry, syn: *Eugenia caryophyllus* (Spreng.) Bullock ex S. G. Harrison (Myrtaceae).

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 ° to 0 °; solubility: 1 vol in 2 vol of 70 % ethanol at 20 °C; phenol content: min. 85 %, max. 93 % [247].
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; solubility: 1 vol in 2 vol of 70 % ethanol at 20 °C; phenol content: minimum 82 % [248].
   The main component of all clove oils is eugenol (draft for a GLC specification for leaf oils: 80 to 92 %), which is responsible for their odor and antiseptic properties. Other major constituents are eugenyl acetate and caryophyllene. Clove bud oil has a higher acetate content and a more delicate odor than leaf oil, but is much more expensive than the leaf oil. Leaf oil is produced and used in the largest quantities.
   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 2000 – 2200 t/a, 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 (see page 65).

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; $[\alpha]_{\mathrm{D}}$ – 33 ° to – 7 °; solubility: 1 vol in 5 – 10 vol of 95 % ethanol [249].

The oils consist primarily of sesquiterpene hydrocarbons; their main component is caryophyllene (> 50 %, for formula, see Section 2.3).

Copaiba balsam oils and balsams are used mainly as fixatives in soap perfumes.

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 spicy odor, reminiscent of linalool.

d_{20}^{20} 0.862 – 0.878; n_{D}^{20} 1.4620 – 1.4700; $[\alpha]_{\mathrm{D}}^{20}$ + 7 ° to + 13 °; solubility: 1 vol in 8 vol of 65 % ethanol at 20 °C; acid value: max. 3.0; linalool content by chromatography: min. 68 % [250].

The main component of coriander oil is (+)-linalool (60 – 80 %). Mono- and polyunsaturated fatty aldehydes, although minor components, contribute to the characteristic aroma of the oil because of their powerful odor.

Coriander is mainly cultivated in the CIS, Poland, and Hungary. Worldwide oil production is 50 – 100 t/a. 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.

Cornmint oil, see Mint Oils, page 107.

Cumin oil is obtained by steam distillation of ripe fruits of *Cuminum cyminum* L. (Apiaceae). It is a light yellow to brown liquid with a strong, somewhat fatty and green odor.

d_{20}^{20} 0.905 – 0.930; n_{D}^{20} 1.490 – 1.5060; $[\alpha]_{\mathrm{D}}^{20}$ + 1 ° to + 8 °; solubility: 1 vol in 8 vol of 80 % ethanol at 20 °C; aldehyde content: 45 – 58 % (calculated as cuminaldehyde) [251].

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 parts of the plants that grow above ground. The following oils are of commercial interest:

1) *Citronella oil* is available in two types:
   a) *Ceylon or Sri Lanka citronella oil* is produced by steam distillation of fresh or partly dried leaves and stems of the grass species *Cymbopogon nardus* (L.) W. Watson–"lenabattu"–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; $[\alpha]_{\mathrm{D}}^{20}$ – 25 ° to – 12 °; solubility: 1 vol in 2 vol of 80 % ethanol at 20 °C; ester value (after acetylation): 157 – 200; carbonyl value: 18 – 55, corresponding to 5 – 15 % carbonyl compounds (calculated as citronellal) [252].

      Ceylon oil is less valuable than Java oil and is used almost exclusively for perfuming toilet soaps, washing powders, and household products.
   b) *Java citronella oil* is obtained by steam distillation of fresh or partially dried stems and leaves of *Cymbopogon winterianus* Jowitt syn. *Cymbopogon nardus* W. Watson var. mahapengiri Winter, which is grown in Southeast Asia, India, and Indonesia, as well as in Central and South America. It is a pale yellow to pale yellowish brown liquid with a slightly 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; $[\alpha]_{\mathrm{D}}^{20}$ $-5°$ to $0°$; solubility: 1 vol in 2 vol of 80 % ethanol at 20 °C, opalescence is sometimes observed when ethanol is continuously added; ester value (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 value: min. 127, corresponding to 35 % carbonyl compounds (calculated as citronellal) [253].

Java citronella oil may contain up to 97 % acetylizable compounds and up to 45 % carbonyl compounds, depending on the time of harvesting. Is 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 (see page 22) and the geraniol fraction (see page 15) 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 and geraniol, 11 – 15 % citronellol, 3 – 8 % geranyl acetate, 2 – 4 % citronellyl acetate, and many other minor components.

Annual worldwide production was reported to be $>$ 5000 t in 1971 and is now less than 2000 t. Main producers are Taiwan, China (province of Hainan), and Java [254].

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; $[\alpha]_{\mathrm{D}}^{20}$ $-6°$ to $0°$; content of carbonyl compounds (calculated as citral): min. 75 %; solubility: freshly distilled oil is soluble in 70 % ethanol at 20 °C, but solubility diminishes on storage and the oil may become insoluble in 90 % ethanol. Residues remain after vacuum distillation of oils stored for longer times due to the high molecular mass products formed by polymerization of myrcene. The oil contains up to 20 % myrcene [255].
   b) *Indian lemongrass oil* is obtained from the so-called Indian variety of lemongrass, *Cymbopogon flexuosus* (Nees ex Steud.) Stapf. The oil is produced mainly in India. Its physical constants differ slightly from those of the West Indian type, the main difference being in the density, which is d_{20}^{20} 0.885 – 0.905 [256].

      The two oils were formerly the main source of natural citral, obtained as a ca. 4 : 1 mixture of geranial and neral by distillation (see page 21). However, lemongrass oil has declined in commercial importance due to the competitive synthesis of citral (see page 21) and isolation of natural citral from Litsea cubeba oil (see page 106). Nevertheless, between 300 and 500 t/a are still produced. In addition to being processed into citral, it is used to some extent for perfuming soap and household products.
3) *Palmarosa oil* is obtained by steam distillation of wild or cultivated *Cymbopogon martinii* (Roxb.) W. Watson. var. *motia,* collected when in blossom. It is a pale yellow liquid with a characteristic roselike odor and a grassy note.

   d_{20}^{20} 0.880 – 0.894; n_{D}^{20} 1.4710 – 1.4780; $[\alpha]_{\mathrm{D}}^{20}$ $-1.4°$ to $+3°$; solubility: 1 vol in 2 vol of 70 % ethanol at 20 °C; acid value: max. 1.0; the following data are valid for oil from India, oils of other origin possess slightly different data, ester value: min. 7, max. 36; ester value (after acetylation): 260 – 280, corresponding to a total alcohol content of 88 – 95 %, free alcohol content (calculated as geraniol): 74 – 94 % [257]. High-grade palmarosa oil may contain up to 95 % geraniol and its esters; it is produced in smaller quantities than other oils obtained from aromatic grasses. Annual worldwide production is ca. 150 t. Palmarosa oil is the starting material for geraniol and geranyl esters of high odor quality, but it is also used for perfuming soaps and cosmetics.

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 woodlike odor that has an ambergris note.

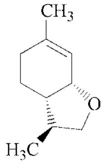
d_{20}^{20} 0.863 – 0.885; n_D^{20} 1.468 – 1.478; $[\alpha]_D^{20}$ + 15 ° to + 30 °; solubility: 1 vol in 8 vol of 90 % ethanol.

This oil is produced exclusively in southern France and Algeria (ca. 10 t/a); its major components are α-pinene and 3-carene. Degradation products of higher terpenoids are responsible for the typical ambergris note [258,259].

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 tealike odor reminiscent of dried fruits. The composition of the oil is very complex; its main components are furanoid sesquiterpenes. It is used predominantly for aroma compositions.

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

1) *Dill weed oil* is prepared from flowering dill by steam distillation. Its main components are α-phellandrene (up to 60 %) and the so-called (+)-dill ether [*74410-10-9*] (up to 30 %). 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 %). This oil has a typical caraway odor and taste in contrast to the weed oil, which contains only a small amount of carvone.

Commercially available dill oils are mixtures of both types, because the plants are harvested not according to the criteria for the special oils, but when the state of ripeness guarantees a maximum yield. They generally contain α-phellandrene (10 – 20 %), limonene (30 – 40 %), dill ether (3 – 10 %), and carvone (30 – 40 %).

The main growing areas are the Balkan states, Hungary, and the United States. Dill oils are used primarily for seasonings in the pickling and canning industries.

Elemi oil, Elemi resinoid are obtained from exuded gum resin of *Canarium luzonicum* (Miq.) (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 oleoresin 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 ° [260].

The major components of elemi oil are limonene, α-phellandrene, and the sesquiterpene alcohol elemol. Both the resinoid and the oil have a fresh, citrus-like, peppery odor and are used predominantly in soap perfumes.

Estragon oil, see Tarragon Oil, page 117.

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, e.g., from *Eucalyptus fruticetorum* F.v. Muell. (*E. polybractea* R. T. Bak.), *E. smithii* R. T. Bak., and *E. leucoxylon* F.v. Muell.

      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 % [261].

      The minor components of this oil differ from those of *E. globulus* oil.

b) *Eucalyptus globulus oil* is produced by steam distillation of the leaves and twigs, recently collected of *Eucalyptus globulus* Labillardière. It is an almost colorless to pale yellow liquid with a fresh odor, characteristic of 1,8-cineole. The crude oil contains ca. 65 % cineole and more than 15 % α-pinene. Commercially available qualities are rectified, and have a cineole content of 70 – 75 % or 80 – 85 %. The respective specifications of these two types are as follows:

d_{20}^{20} 0.904 – 0.920 and 0.906 – 0.920; n_{D}^{20} 1.460 – 1.468 and 1.458 – 1.465; $[\alpha]_{\mathrm{D}}^{20}$ 0 ° to + 10 ° and + 2 ° to + 10 °; solubility 1 vol in 5 vol of 70 % ethanol and 1 vol in 5 vol of 80 % ethanol at 20 °C [262].

The oil is produced mainly in Spain and Portugal, where the wood is used in the cellulose industry, and in China. Worldwide production is between 3500 and 4000 t/a.

Eucalyptus oils with a high cineole content are used for cineole production (see page 72). 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. Distillation fractions of camphor oil (see page 90) are also marketed as eucalyptus oils with a cineole content of 70 – 80 %.

Eucalyptus citriodora oil is obtained by steam distillation of leaves and twigs 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} 1.450 – 1.456; $[\alpha]_{\mathrm{D}}^{20}$ – 1 ° to + 3 °; solubility: 1 vol in 2 vol of 80 % ethanol at 20 °C; carbonyl value (calculated as citronellal): min. 70 % [263].

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

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/a, but considerable quantities are also produced in other countries (e.g., South Africa and India). The annual production worldwide is about 1300 t. *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 (see page 22).

3) *Eucalyptus dives oil* is obtained by steam distillation of fresh leaves of *Eucalyptus dives* var. *Schau, Typus,* grown in New South Wales.

d_{15} 0.889 – 0.910; n_{D}^{20} 1.477 – 1.481; $[\alpha]_{\mathrm{D}}^{20}$ – 75 ° to – 50 °; content of carbonyl compounds (calculated as piperitone): 40 – 50 % [264].

In addition to (–)-piperitone (for formula see page 30), the oil contains 15 – 25 % α- and β-phellandrene. The oil was previously used as a starting material in the manufacture of (–)-menthol, but has lost much of its significance. Annual worldwide production in 2002 has dropped to 50 t.

4) *Eucalyptus staigeriana oil* is produced by steam distillation of the leaves of *Eucalyptus staigeriana* F. v. Muell. It has a fresh, lemon-like odor and contains ca. 30 % citral. Further constituents are geraniol and nerol and their acetates, as well as (–)-limonene. It is used mainly in perfumery [265].

Fennel oil is commercially available in sweet and bitter types that are obtained from two varieties of a subspecies of common fennel, *Foeniculum vulgare* Mill., subsp. *capillaceum* Gilib. (Apiaceae). The sweet oil is obtained from the *dulce* variety and the bitter oil from the variety *vulgare* (Mill.) Thell.

The oils are produced both in the Mediterranean countries and in other continents and are obtained by steam distillation of crushed fennel seeds. They are colorless to pale yellow liquids with a typical fennel odor and a camphoraceous, initially sweet taste that later becomes bitter.

d_{20}^{20} 0.961 – 0.977; n_{D}^{20} 1.5280 – 1.5430; $[\alpha]_{\mathrm{D}}^{20}$ + 11 ° to + 24 °; *fp* 3 – 11.5 °C; solubility: 1 vol in 5 vol of 80 % ethanol.

Both oils are similar in composition; their major components are *trans*-anethole (> 80 % in sweet fennel oil) and fenchone (up to ca. 25 % in bitter fennel oil). Sweet fennel oil is more important because of its higher anethole content. While both oils are used in flavors, small quantities are also employed in perfumery.

Fir needle oils, see Pinaceae Oils, page 113.

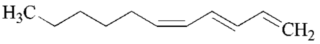
Galbanum oil and galbanum resinoid are produced from the gumlike exudate of *Ferula galbaniflua* Boiss. and Buhse (Apiaceae) growing in northern Iran and *F. rubricaulis* Boiss. growing in southern Iran.

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

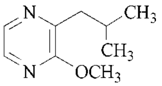
The oil is produced by steam distillation and is a colorless to light yellow liquid with a green, slightly spicy odor.

d_{20}^{20} 0.8670 – 0.8900; n_D^{20} 1.4780 – 1.4850; $[\alpha]_D^{20}$ + 7 ° to + 17 °; acid value: max. 2; solubility: 1 vol in at least 6 vol of 90 % ethanol [266].

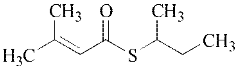
In addition to 75 % monoterpene hydrocarbons and ca. 10 % sesquiterpene hydrocarbons, galbanum oil contains a fairly large number of terpene and sesquiterpene alcohols and their acetates. Minor components, with entirely different structures and low odor threshold values, contribute strongly to the chacteristic odor. Examples are as follows:



(*E,Z*)-1,3,5-Undecatriene [*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.

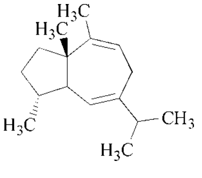
Geranium oil is obtained by steam distillation of the flowering herb *Pelargonium graveolens* l'Heritier ex Aiton, *P. roseum* Willdenow, and other nondefined hybrids that have developed into different ecotypes in different geographical regions. The oil is an amber to greenish-yellow liquid with the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

The main cultivation areas are Réunion and Madagascar (Bourbon type), Morocco and Egypt (North African type), and China. The Bourbon quality is more valuable and thus more expensive. Annual worldwide production is ca. 300 t. Specifications of geranium oils [267] are given in Table 3.

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*-γ-eudesmol [*15051-81-7*] (for structure see page 86). The Chinese type also contains (−)-6,9-guaiadiene, however a smaller amount of menthone/isomenthone and a higher amount of (−)-citronellol than the Bourbon type.

Table 3. Specifications of geranium oils

Parameter	Type of geranium oil			
	Bourbon	Egyptian	Moroccan	Chinese
d_{20}^{20}	0.884 – 0.892	0.887 – 0.892	0.883 – 0.900	0.882 – 0.8
n_D^{20}	1.4620 – 1.4680	1.4660 – 1.4700	1.4640 – 1.4720	1.4600 – 1
$[\alpha]_D^{20}$	− 14 ° to − 8 °	− 12 ° to − 8 °	− 13 ° to − 8 °	− 14 ° to − 8 °
Solubility in 70 % ethanol (20 °C), vol : vol	1 : 3	1 : 2.2	1 : 3	1 : 5
Acid value (max.)	10	6	10	10
Ester value	52 – 78	42 – 58	35 – 80	55 – 75
Ester value (after acetylation)	205 – 230	210 – 222	192 – 230	215 – 232
Content of carbonyl compounds (as isomenthone), %	max. 16	max. 16	max. 16	max. 10
Alcohol content (as citronellol), %	42 – 55	40 – 58	35 – 58	



(−)-6,9-Guaiadiene

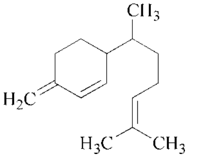
Geranium oil is one of the most important natural raw materials in the fragrance industry. It is used for creating rosy notes, especially in soap.

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

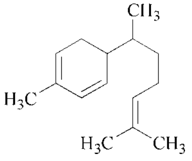
Ginger oil is produced by steam distillation of dried, ground rhizomes. It is a light yellow to yellow liquid with the aromatic, persistent odor of ginger, but lacking the pungency usually associated with ginger. The citrus note of ginger oil is due to traces of citral.

d_{25}^{25} 0.871 – 0.882; n_D^{20} 1.4880 – 1.4940; $[\alpha]_D$ − 45 ° to − 28 °; saponification value: max. 20; soluble in ethanol, solutions are usually turbid [268].

The major components of the oil are β-sesquiphellandrene [*20307-83-9*] (about 15 %) and zingiberene [*495-60-3*] (30 to 40 %).

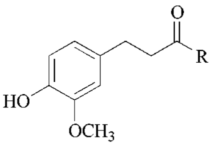


β-Sesquiphellandrene

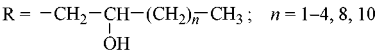


Zingiberene

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:



$$R = -CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-(CH_2)_n-CH_3\ ; \quad n = 1\text{–}4, 8, 10$$

Shogaols: $R = -CH{=}CH-(CH_2)_n-CH_3$; $n = 2, 4, 6, 8$

Main cultivation areas for ginger are India, Malaysia, Taiwan, 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.

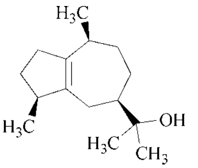
Grapefruitoil, see Citrus Oils, page 94.

Green cognac oil, see Lie de Vin Oil, page 106.

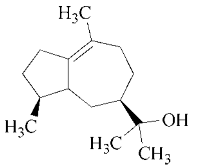
Guaiac wood oil is obtained by steam distillation of ground wood and sawdust from the tree *Bulnesia sarmienti* Lorentz (Zygophyllaceae), which is up to 20 m high and grows wild in the Gran Chaco region of Paraguay and in Argentina. The annual production is ca. 150 t. The oil is a dark yellowish, viscous 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} 0.960 – 0.975; n_D^{20} 1.5020 – 1.5070; $[\alpha]_D$ − 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 % [269].

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



Guaiol



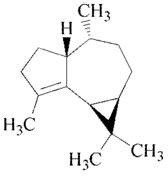
Bulnesol

Guaiac wood oil is used extensively in perfume compositions for its excellent fixative properties. Also the acetates of the sesquiterpene alcohols of this oil are used in perfumery.

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} 0.918 – 0.930; n_D^{20} 1.5010 – 1.5050; $[\alpha]_D$ – 130 ° to – 35 °; solubility: 1 vol in 10 vol of ethanol.

It consists almost entirely of sesquiterpene hydrocarbons, and its main component (> 60 %) is α-gurjunene [*489-40-7*].



α-Gurjunene

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.

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.

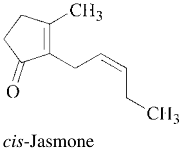
mp 48 – 51 °C; ester value: 70 – 125.

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

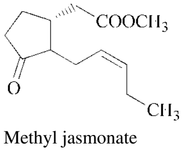
n_D^{20} 1.4780 – 1.4920; acid value: 8 – 14; ester value: 120 – 220.

One ton of jasmin blossoms yields ca. 2.5 – 3 kg of concrete when it is extracted two or three times with hexane or benzene. 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*-jasmone [*488-10-8*], and methyl jasmonate [*1211-29-6*] contribute strongly to the typical jasmin fragrance.



cis-Jasmone



Methyl jasmonate

The absolute is one of the most valuable blossom fragrances used in fine fragrances.

Juniper berry oil is obtained by steam distillation of berries 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 ° to 0 °; solubility: 1 vol in 10 vol of 95 % ethanol, solutions usually turbid; acid value: max. 2; ester value: min. 12 [270].

The slightly turpentine-like odor and the relatively low solubility of the oil are caused by its high content of α-pinene and other monoterpene hydrocarbons. The main oxygen-containing component is 1-terpinen-4-ol.

Most juniper berries are obtained from bushes growing in European countries, such as Italy, Czech Republic, Slovakia, Hungary, and former Yugoslavia.

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.

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; $[\alpha]_D$ + 0° 15′ to + 7 °, 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 value: 18 – 86; ester value: 31 – 86 [271].

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 resinoids and absolutes are excellent natural fixatives.

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; $[\alpha]_{\mathrm{D}}$ – 19 ° to – 10 °; solubility: 1 vol in at least 1 vol of 80 % ethanol; acid value: max. 3; saponification value: 15 – 45; saponification value (after acetylation): 36 – 85 [272].

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

Laurel leaf oil is used extensively in the food industry, e.g., for seasoning meat products and soups.

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 liquid with a fresh, sweet, floral, herbaceous odor on a woody balsamic base. The following physical constants are valid for spontaneous lavender from France.

   d_{20}^{20} 0.880 – 0.890; n_{D}^{20} 1.458 – 1.464; $[\alpha]_{\mathrm{D}}^{20}$ – 11.5 ° to – 7 °; solubility: 1 vol in 2 vol of 75 % ethanol at 20 °C; acid value: max. 1.0; ester value: 102.5 – 165, corresponding to an ester content of 35.8 – 58 % (calculated as linalyl acetate) [273].

   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 ("spontaneous" or "population" lavender). Lavender oil is produced in a yield of 10 – 25 kg/ha; total production is ca. 100 t/a. It has the following typical composition (%): *cis*-β-ocimene (4 – 10), *trans*-β-ocimene (1.5 – 6), cineole (< 1), camphor (< 0.5), linalool (25 – 38), linalyl acetate (25 – 45), 1-terpinen-4-ol (2 – 6), and lavandulyl acetate (> 2).

   Cloned varieties of lavender (e.g., *Maillette* and *Matherone*) yield more oil per hectare and can be grown at lower altitudes; however, they produce a poorer quality oil. Bulgarian lavender oil is similar in composition to that obtained from French population lavender, but is of poorer quality: about 50 to 70 t are produced per year.

   Lavender oils of a special quality are also produced in several other areas throughout the world (e.g., Tasmania).

2) *Spanish spike lavender oil* is produced by steam distillation of flowering tops of spike, *Lavandula latifolia* Medik. (Lamiaceae). It is an almost colorless to light orange 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; $[\alpha]_{\mathrm{D}}^{20}$ – 7 ° to + 2 °; solubility: 1 vol in 3 vol of 70 % ethanol; solutions may become opalescent on dilution; acid value: max. 1.0; ester value: 3 – 14; ester value (after acetylation): 130 – 200 [274].

   The main components of Spanish spike lavender oil are linalool (34 – 50 %), cineole (16 – 39 %), and camphor (8 – 16 %).

   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. At present, annual worldwide production is ca. 150 – 200 t.

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

   Data for lavandin oil abrialis:d_{20}^{20} 0.887 – 0.897; n_{D}^{20} 1.4560 – 1.4660; $[\alpha]_{\mathrm{D}}^{20}$ – 5 ° to – 2 °; solubility: 1 vol in 4 vol of 70 % ethanol at 20 °C; acid value: max. 1.0; ester value: 77 – 108, corresponding to an ester content of 27 – 38 % (calculated as linalyl acetate) [276].

   Data for *lavandin oil grosso* (a specific clone of lavandin, cultivated in the South of France: d_{20}^{20} 0.891 – 0.899; n_{D}^{20} 1.4580 – 1.4620; $[\alpha]_{\mathrm{D}}^{20}$ – 7 ° to – 3.5 °; solubility:

1 vol in 3 vol of 70 % ethanol at 20 °C; acid value: max. 1; ester value: 100 – 137, corresponding to an ester content of 35 – 48 % (calculated as linalyl acetate) [262].

Lavandin plants are sterile and can be propagated only by using cuttings. The oils from the most important varieties, *abrialis* and *grosso,* contain linalool and linalyl acetate as major constituents as well as 6 – 11 % cineole and 7 – 11 % camphor for abrialis, and 4 – 7 % cineole and 6 – 8 % camphor for grosso. A third variety is called *super* because its oil contains a high concentration of linalyl acetate, 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. Former Yugoslavia is another lavandin-producing country. Worldwide annual production is up to 1100 t.

All three oils are used primarily in soap perfumes; considerable quantities are also employed in eaux de cologne and in bath products.

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 pastelike concretes with ethanol, followed by evaporation, yields absolutes. These extracts differ from the essential oils in being more soluble and in having a dark green color and a longer-lasting odor with a haylike, spicy note. They are also used in eaux de cologne and fine fragrances, sometimes after decoloration (removal of chlorophyll with activated charcoal).

Lemon oil, see Citrus Oils, page 94.

Lemongrass oil, see Cymbopogon Oils, page 98.

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; $[\alpha]_{\mathrm{D}}$ – 1 ° to + 2 °; acid value: 32 – 70; ester value: 200 – 245; solubility: 1 vol in at least 2 vol of 80 % ethanol [277].

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

Lime oil, see Citrus Oils, page 94.

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 to dark yellow liquid with a fresh odor, reminiscent of citral.

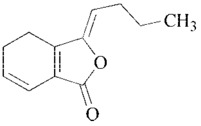
d_{20}^{20} 0.880 – 0.892; n_{D}^{20} 1.4800 – 1.4870; $[\alpha]_{\mathrm{D}}^{20}$ + 3 ° to + 12 °; carbonyl content (calculated as citral): min. 74 %; solubility: 1 vol in 3 vol of 70 % ethanol at 20 °C [278].

The oil is used mainly for the production of citral; smaller quantities are employed for perfuming household products. The main producer is China. The worldwide annual production is about 1000 t.

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 reminiscent of celery and angelica.

d_{25}^{25} 0.960 – 0.985 (leaf oil); d_{20}^{20} 1.010 – 1.090 (root oil); n_{D}^{20} 1.5350 – 1.5580; $[\alpha]_{\mathrm{D}}^{20}$ – 1 ° to + 5 °; acid value: 2 – 16; ester value: 170 – 260; solubility: 1 vol in 1.5 vol of 85 % ethanol at 20 °C [279].

The main constituent of the leaf oil is α-terpinyl acetate, while the main constituent and odor-determining component of the root oil is ligustilide [*4431-01-0*]. A few percent ligustilide are also present in the leaf oil.



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.

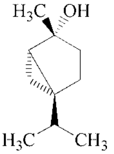
Mace oil, see Nutmeg Oil, page 109.

Mandarin oil, see Citrus Oils, page 94.

Marjoram oil (sweet marjoram oil) is obtained by steam distillation of the herb *Origanum majorana* L. (*Majorana hortensis* Moench, Lamiaceae). The plants are cultivated in France, Hungary, Egypt, and Tunisia. The oil 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; $[\alpha]_{\mathrm{D}}$ + 14 ° to + 24 °; acid value: max. 2.5; saponification value: 23 – 40; saponification value (after acetylation): 68 – 86; solubility: 1 vol in 2 vol of 80 % ethanol [280].

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.



(+)-*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.

Spanish marjoram oil is obtained by steam distillation of the flowering tops of *Thymus mastichina* L. (Lamiaceae), a wild plant growing in Spain. The oil is a slightly yellow liquid with a fresh camphoraceous, spicy odor.

d_{20}^{20} 0.890 – 0.920; n_{D}^{20} 1.460 – 1.470; $[\alpha]_{\mathrm{D}}^{20}$ – 4 to + 6 °; 1,8-cineole content: min. 30 %, max. 68 %; solubility: 1 vol in 3 vol of 70 % ethanol [281].

Mentha citrata oil, see Mint Oils.

Mimosa absolute is obtained from the blossoms of the mimosa tree *Acacia dealbata* Link (Mimosaceae), which grows in the forests of southern France and in Morocco.

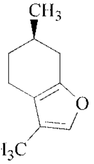
The absolute is a yellowish brown liquid with a slightly green, flowery odor and extremely high tenacity.

Annual production in France (Grasse) is ca. 3 – 6 t [282]. Mimosa absolute is used mainly in fine fragrances as a flowery fixative.

Mint oils are listed in order of the quantities produced.

1) *Cornmint oil* is produced by steam distillation of the flowering herb *Mentha arvensis* L. var. *piperascens* Malinv. and var. *glabrata* Holmes (Lamiaceae). The crude oil, containing ca. 70 % (−)-menthol, is then partially dementholized by freezing and centrifuging. The dementholized oil is an almost colorless to amber-yellow liquid with a characteristic minty odor; typical specifications for oils of Chinese and Indian origin are as follows:
   d_{20}^{20} 0.890 – 0.910; n_{D}^{20} 1.4570 – 1.4650; $[\alpha]_{\mathrm{D}}^{20}$ – 24 ° to – 13 °; ester content (calculated as menthyl acetate): 3 – 9 %; total alcohol content (calculated as menthol): 40 – 60 %; ketone content (calculated as menthone): 25 – 45 %; solubility: 1 vol in 4 vol of 70 % ethanol [283].
   Dementholized oil still contains ca. 45 % (−)-menthol; (−)-menthone and (−)-menthyl acetate are other major components. Dementholized *Mentha arvensis* oil was formerly produced primarily in Brazil. Currently, cornmint oil is produced mainly in China; smaller amounts are produced in India and Paraguay. The world production of the oil is estimated to be 17 000 to 18 000 t/a. 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 (see page 30).
2) *Peppermint oil* is produced by steam distillation of the aerial plant *Mentha* x *piperita* L. var. *piperita*. 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} 1.4590 – 1.4650; $[\alpha]_D^{20}$ – 30 ° to – 14 °; solubility: 1 vol in 5 vol of 70 % ethanol at 20 °C; ester value: 12 – 30; ester value (after acetylation): 135 – 200; carbonyl value: 54 – 115 [284].
As in cornmint oil, the main component of peppermint oil is (–)-menthol; it also contains (–)-menthone (ca. 20 %) and (–)-menthyl acetate (up to 8 %). However, peppermint oil, unlike cornmint oil, has a high content of (+)-menthofuran [*17957-94-7*] (1 – 8 %, according to GLC).



(+)-Menthofuran

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 ca. 3600 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.

3) *Spearmint oil* is obtained by steam distillation of the flowering tops of *Mentha spicata* L. (native spearmint) and *Mentha* x *cardiaca* Ger. (Scotch spearmint). It is an almost colorless to yellow-green liquid with a fresh, caraway-minty odor.
d_{20}^{20} 0.920 – 0.937; n_D^{20} 1.485 – 1.491; $[\alpha]_D^{20}$ – 60 ° to – 45 °; solubility: 1 vol in 1 vol of 80 % ethanol at 20 °C; carbonyl value: min. 200, corresponding to a carvone content of 55 % [285].
The compositions of Scotch and native spearmint oils differ as shown in Table 4 [286]. 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 ca. 1750 t, 55 % being of the native type and 45 % of the Scotch type.

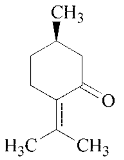
Table 4. Characteristic components of Scotch and native spearmint oils

Compound	Content of compound in spearmint oil, %	
	Scotch	Native
Limonene	15	9
3-Octanol	2	1
Menthone	1	< 0.1
Dihydrocarvone	1	2.5
Sabinene hydrate	0.1	1.5
Dihydrocarvyl acetate	< 0.1	0.6
cis-Carvyl acetate	0.1	0.6

By far the most spearmint oil is used for flavoring toothpaste and chewing gum. Smaller quantities are used in other oral hygiene products and in pharmaceutical preparations.

4) *Mentha citrata oil* is distilled from the herb *Mentha citrata* Ehrh. It has a lavender-like odor and contains linalool and linalyl acetate as major components (together ca. 70 %). Recently, hybrids of the plant have been developed in the United States and other countries that yield oils with a total linalool content of over 80 % [287]. Currently, the main cultivation area is Eastern Asia. *Mentha citrata* oils are used mainly for perfuming soap and cosmetics.

5) *Pennyroyal oil* is obtained by steam distillation of the flowering tops of *Mentha pulegium* L. It is an almost colorless to amber-yellow liquid with a herbaceous, minty odor.
d_{20}^{20} 0.930 – 0.944; n_D^{20} 1.4800 – 1.4900; $[\alpha]_D^{20}$ + 15 ° to + 24 °; solubility: 1 vol in 3 vol of 70 % ethanol; content of carbonyl compounds (calculated as pulegone) min. 80 % [288].
The main component of pennyroyal oil is (+)-pulegone [*89-82-7*] (ca. 80 %). About 50 t of the oil are produced per year, mainly in southern Spain and Tunisia.



(+)-Pulegone

An oil of similar composition, also called pennyroyal oil, is obtained in North America from *Hedeoma pulegioides* L. Pennyroyal oil has lost its significance as a starting material for the production of (−)-menthol. However, it is still used in perfume compositions for soap and oral hygiene products.

Musk, see Animal Secretions, page 87.

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.

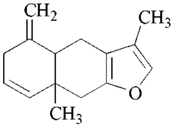
Myrrh resinoids are obtained in 20 – 45 % yield by extracting the gum with suitable solvents (e.g., benzene, hexane). They are waxlike, brown-yellow to red-brown masses with a balsamic odor and an aromatic bitter taste.

Acid value: 20 – 35; ester value: 165 – 200; carbonyl value: 20 – 75 [289].

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; $[\alpha]_{\mathrm{D}}$ − 83 ° to − 60 °; acid value: 2 – 13; saponification value: 9 – 35; solubility: 1 vol in 7 – 10 vol of 90 % ethanol; solutions are occasionally opalescent or turbid [290].

Typical aroma-determining compounds of the myrrh plant are furanosesquiterpenoids such as lindestrene [*2221-88-7*] [291].



Lindestrene

Neroli oil and orange flower absolute are obtained from the blossoms of the bitter orange tree, *Citrus aurantium* L. subsp. *aurantium,* syn. *Citrus aurantium* L. subsp. *amara var. pumilia*, (Rutaceae), which is grown in France, Italy, and North Africa. *Neroli oil* is produced by steam distillation (about 4 t/a) 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; $[\alpha]_{\mathrm{D}}^{20}$ + 2 ° to + 11 °; solubility: 1 vol in 3.5 vol of 85 % ethanol at 20 °C; acid value: max. 2.0; ester value: 26 – 60 [292].

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. Their typical flavor is created by a number of nitrogen-containing trace constituents, such as indole and derivatives of anthranilic acid.

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 eaux de cologne.

Nutmeg (mace) oil is obtained by steam distillation of the dried and crushed nuts and/or the coverings (mace) of nutmeg, which are the fruits of *Myristica fragrans* Houtt. (Myristicaceae). The tree grows in Indonesia and in the West Indies and becomes 15 – 20 m high. Nutmeg oil is a colorless to pale yellow liquid with a pleasant spicy odor. Its physical constants and odor vary with the place of origin. Specifications of Indonesian and (in parentheses) West Indian nutmeg oil are as follows:

d_{20}^{20} 0.885 – 0.907 (0.862 – 0.882); n_{D}^{20} 1.4750 – 1.4850 (1.4720 – 1.4760); $[\alpha]_{\mathrm{D}}^{20}$ + 6 ° to + 18 ° (+ 25 ° to + 40 °); solubility (both oils): 1 vol in 5 vol of 90 % ethanol at 20 °C (solutions sometimes opalescent), for freshly distilled oils, 1 vol in 3 – 4 vol [293].

Indonesian oils contain a higher percentage of higher boiling components than do West Indian oils (produced mainly in Grenada).

The oils contain ca. 90 % terpene hydrocarbons, mainly sabinene and α- and β-pinene. Major oxygen-containing constituents are 1-terpinen-4-ol and phenol ether derivatives (mainly myristicin).

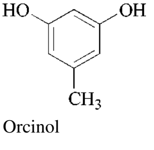
Nutmeg oil is used mainly in food flavorings and to a lesser extent in perfumery. Worldwide annual production is 400 to 450 t, more than 120 t/a is produced in Indonesia alone.

Oakmoss absolute and tree moss absolute are obtained from tree lichens. *Oakmoss absolute* is derived from *Evernia prunastri* (L.) Arch. (Usneaceae), 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.

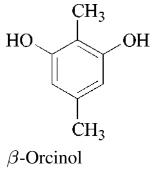
The concretes are green to brown waxy pastes; the absolutes are more or less viscous liquids with an earthy, mossy, woody odor and a slight phenolic, leather note.

Resorcinol derivatives, e.g., orcinol [*504-15-4*], β-orcinol [*488-87-9*], their monomethyl ethers, and methyl 3-methylorsellinate [*4707-47-5*] are mainly responsible for the characteristic earthy-moss-like odor of the oakmoss products.

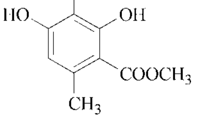
Tree moss concretes and absolutes are prepared from *Pseudevernia furfuracea*, a lichen growing on conifer bark. Their odors are different from those of the corresponding oakmoss products.



Orcinol



β-Orcinol



Methyl 3-methylorsellinate

Large quantities of oakmoss (mousse de chêne) and tree moss (mousse d'arbre) are collected annually in former Yugoslavia, France, and Morocco [294]. In 1997 1900 t of Pseudevernia furfuracea and 700 t of Evernia prunastri were processed, mainly in Grasse [295].

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. (IFRA recommendation).

Olibanum oil and olibanum resinoid are obtained from frankincense, which is a gum resin collected from the bark of the tree *Boswellia carteri* Birdw. (syn. *B. sacra* Flueck.) or *B. frereana* Birdw. (Burseraceae) growing in Yemen 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; $[\alpha]_D$ – 15 ° to + 35 °; solubility: 1 vol in 6 vol of 90 % ethanol, solutions occasionally opalescent; acid value: max. 4.0; ester value: 4 – 40 [296].

Various qualities are commercially available. Their compositions may vary considerably because they are prepared from the resins of different *Boswellia* species [297].

Olibanum oil and resinoid are used in oriental type perfumes for their odor and their good fixative properties.

Opopanax oil and opopanax resinoid (also: Opoponax) 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; $[\alpha]_D$ – 32 ° to – 9 °; acid value: max. 4; saponification value: 4 – 20; solubility: 1 vol in 10 vol of 90 % ethanol; solutions are occasionally turbid [298].

Opopanax oil and resinoid are used in perfume compositions with oriental characteristics. (IFRA recommendation).

Orange flower absolute, see Neroli Oil, page 109.

Orange oils, see Citrus Oils, page 94.

Origanum oils are produced from several species of the flowering herb *Origanum* (Lamiaceae). Spanish origanum oil is derived from *Coridothymus capitatus* Rchb. and is often called white thyme oil. The oils differ mainly in their content of carvacrol and thymol, which are major constituents. Oil with a high carvacrol content [*499-75-2*] (for formula, see page 116) 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_{25}^{25} 0.935 – 0.960; n_D^{20} 1.5020 – 1.5080; $[\alpha]_D$ − 2 ° to + 3 °; phenol content: 60 – 75 %; solubility: 1 vol in 2 vol of 70 % ethanol; solutions may become turbid when further diluted [299].

According to ISO the Spanish origanum oil is derived from *Thymbra capitata* (L.) Cav. It is a yellowish to dark brown, almost black oil with an aromatic, phenolic, and spicy odor; d_{20}^{20} 0.930 – 0.955; n_D^{20}1.5000 – 1.5130; $[\alpha]_D^{20}$ − 5 ° to + 2 °; solubility: 1 vol in 4 vol of 70 % ethanol at 20 °C; carvacrol content by GLC: 60 to 75 % [300]. (Both botanical names – *Coridothymus* and *Thymbra* – are not mentioned in the Zander dictionary [196].)

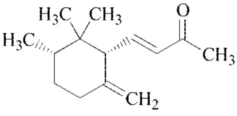
Origanum oils are used in perfume compositions and in seasoning mixtures.

Orris root oil is obtained by steam distillation of the rhizomes of the two species of iris, *Iris pallida* Lam. or *Iris germancia* L. (Iridaceae). Prior to distillation the rhizomes are stored for about two years in order to develop the aroma 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.

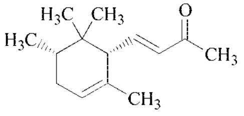
Acid value: 175 – 235, corresponding to an acid content of 71 – 95 % (calculated as myristic acid); ester value: 4 – 35; ketone content (calculated as irone): 9 – 20 %; soluble with ethanol in all proportions at 50 °C [301].

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.*

The main constituents of the oil are (−)-*cis*-γ-irone [*89888-04-0*] and (−)-*cis*-α-irone [*89888-03-9*], which are responsible for its odor [302].



(−)-*cis*-γ-Irone



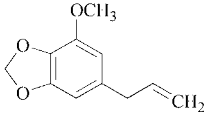
(−)-*cis*-α-Irone

The oil, respectively the butter, is very expensive and is used in perfumery and in flavor compositions.

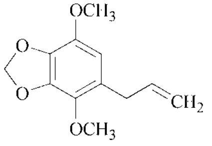
Palmarosa oil, see Cymbopogon Oils, page 98.

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

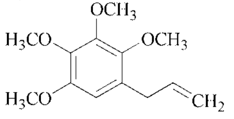
1) *Parsley leaf oil* is produced by steam distillation of the aerial parts of the plant, including the immature seeds. It is a yellow to light-brown liquid with the typical odor of the herb. d_{25}^{25} 0.908 – 0.940; n_D^{20} 1.5030 – 1.5300; $[\alpha]_D$ − 9 ° to + 1 °; acid value: max. 2; soluble in 95 % ethanol; solutions may be opalescent [303].
   The oil consists mainly of monoterpene hydrocarbons. Its main constituent is 1,3,8-menthatriene [*18368-95-1*], which – together with two pyrazines and (*Z*)-dec-6-enal – is important for the aroma of parsley leaves [304].
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 ° to − 4 °; acid value: max. 6; ester value: min. 1, max. 10; solubility: 1 vol in 6 vol of 85 % ethanol, solutions are sometimes slightly turbid [306].
   Characteristic components of parsley seed oil are myristicin [*607-91-0*], apiol [*523-80-8*], and 2,3,4,5-tetramethoxyallylbenzene [*15361-99-6*] [305].



Myristicin



Apiol



2,3,4,5-Tetramethoxyallylbenzene

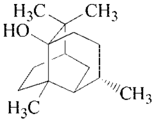
Parsley oils are used in the food industry in seasonings, for example, for meat and sauces.

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

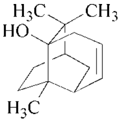
d_{20}^{20} 0.952 – 0.975; n_{D}^{20} 1.5050 – 1.5150; $[\alpha]_{\mathrm{D}}^{20}$ – 60 ° to – 40 ° (in exceptional cases to – 32 °); solubility: 1 vol in 10 vol of 90 % ethanol at 20 °C; acid value: max. 4.0; ester value: max. 10 [307].

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 norpatchoulenol [*41429-52-1*] present only at a concentration of 0.2 – 1 % [308].



Patchoulol



Norpatchoulenol

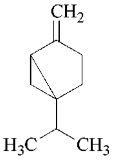
Worldwide production lies between 900 and 1000 t/a. Patchouli oil is very tenacious and is used in perfumery for oriental and fougère notes.

Pennyroyal oil, see Mint Oils, page 107.

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 broken unripe 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.

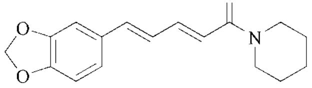
d_{20}^{20} 0.870 – 0.890; n_{D}^{20} 1.480 – 1.492; $[\alpha]_{\mathrm{D}}^{20}$ – 16 ° to + 4 °; solubility: 1 vol in 3 vol of 95 % ethanol; ester value: max. 11 [309].

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



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.

Peppermint oil, see Mint Oils, page 107.

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

d_{25}^{25} 1.095 – 1.110; n_{D}^{20} 1.5670 – 1.5790; $[\alpha]_{\mathrm{D}}$ – 1 ° to + 2 °; acid value: 30 – 60; ester value: 200 – 225; solubility: 1 vol in at least 0.5 vol of 90 % ethanol [310].

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.

The oil is used for its excellent fixative properties in perfumes for soap and cosmetics. Use of Peru balsam itself is now banned because it is allergenic. (IFRA recommendation)

Petitgrain oils are obtained by steam distillation of the leaves of citrus trees (Rutaceae family). The oils derived from the bitter orange tree are the most important. Other petitgrain oils (mandarinier, citronnier, and bergamotier) are less important. Petitgrain oil mandarinier is a source of natural methyl *N*-methylanthranilate, which is present at a concentration of more than 50 %. Petitgrain oils are essential constituents of eaux 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. Leaves and twigs are steam distilled. Petitgrain oil Paraguay is a colorless to 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; $[\alpha]_{\mathrm{D}}^{20}$ – 6 ° to – 1 °; solubility: 1 vol in 4 vol of 70 % ethanol at 20 °C; acid value: max. 1; ester value: 127 – 184, corresponding to an ester content of 45 – 65 % (calculated as linalyl acetate) [311].

Annual production is ca. 250 – 280 t.

Petitgrain oil bigarade is obtained by steam distillation of the leaves, twigs, and small green fruits of the bitter orange tree *Citrus aurantium* L. subsp. *aurantium,* grown in France, Italy, and North Africa. It is a pale yellow to amber yellow liquid, with a slight blue fluorescence and with a characteristic ethereal and pleasant odor.

d_{20}^{20} 0.886 – 0.898; n_{D}^{20} 1.4560 – 1.4720; $[\alpha]_{\mathrm{D}}^{20}$ – 6 ° to + 1 °; solubility: 1 vol in 5 vol of 70 % ethanol at 20 °C; acid value: max. 2; ester value: 140 – 217, corresponding to an ester content of 50 – 77 % (calculated as linalyl acetate) [312].

Annual production is ca. 3 to 5 t.

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 Jamaica. 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; $[\alpha]_{\mathrm{D}}^{20}$ – 5 ° to 0 °; solubility: 1 vol in 2 vol of 70 % ethanol at 20 °C; phenol content: min. 65 % [313].

The major components of pimento berry oil are eugenol (up to 75 %), 1,8-cineole, and caryophyllene. 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.

Pinaceae needle oils from Pinaceae species contain (−)-bornyl acetate as their main odoriferous component. Other main constituents are monoterpene hydrocarbons such as α- and β-pinene, limonene, 3-carene, and α- and β-phellandrene. 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; $[\alpha]_{\mathrm{D}}$ – 67 ° to – 34 °; solubility: 1 vol in 7 vol of 90 % ethanol; ester content (calculated as bornyl acetate): 4 – 10 % [314].
   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} 0.898 – 0.912; n_{D}^{20} 1.4685 – 1.4730; $[\alpha]_{\mathrm{D}}$ – 45 ° to – 33 °; solubility: 1 vol in 1 vol of 90 % ethanol, solutions may become hazy when further diluted; ester content (calculated as bornyl acetate): 32 – 44 % [315].
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; $[\alpha]_{\mathrm{D}}$ – 24 ° to – 19 °; solubility: 1 vol in 4 vol of 90 % ethanol (turbidity may occur), ester content (calculated as bornyl acetate): 8 – 16 % [316].
4) *Pine needle oil* is produced primarily in Austria (Tyrol), former Yugoslavia, and the CIS by steam distillation of the needles of the

Norwegian or Scotch pine, *Pinus sylvestris* L. 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; $[\alpha]_{\mathrm{D}}$ $-4°$ to $+10°$; solubility: 1 vol in 6 vol of 90 % ethanol, sometimes slightly opalescent; ester content (calculated as bornyl acetate): 1.5 – 5 % [317].

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* Zenari 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; $[\alpha]_{\mathrm{D}}^{25}$ $-16°$ to $-3°$; solubility: 1 vol in 10 vol of 90 % ethanol; bornyl acetate content is similar to that of pine needle oil.

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.) Carrière (Eastern Hemlock), 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; $[\alpha]_{\mathrm{D}}$ $-25°$ to $-10°$; 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 % [318].

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* x *damascena* Mill. (Rosaceae) that is mainly cultivated in Turkey, Bulgaria (Kazanlik rose), and Morocco. 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 to greenish-yellow liquid with the characteristic odor of rose blossoms and distinct tea and honey notes.

   d_{20}^{20} 0.848 – 0.880; n_{D}^{25} 1.4520 – 1.4700; $[\alpha]_{\mathrm{D}}^{20}$ $-5°$ to $-1.8°$; *fp* between 16 and 23.5 °C; ester value: min. 7, max. 24. Due to the presence of paraffin hydrocarbons (stearoptenes) the determination of the physical constants at 20 °C can be difficult or impossible because of a low freezing-point [319].

   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, Bulgarian rose oil also contains a number of components which, although present in low concentrations, contribute to the characteristic fragrance. Among these are β-damascenone (see page 39) and rose oxide (see page 72) [320].

   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 limited and is only about 30 t per year.

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

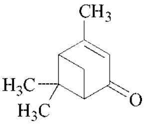
   The absolute is a reddish liquid with a typical rose odor. The phenethyl alcohol content of its volatile fraction is 60 – 75 % [321].

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 or yellow-greenish liquid with a characteristic, refreshing, pleasant odor.

For oils type *Spain*: d_{20}^{20} 0.892 – 0.910; n_{D}^{20} 1.4640 – 1.4760; $[\alpha]_{\mathrm{D}}^{20}$ $-5°$ to $+8°$; ester content (calculated as bornyl acetate): 2 – 5 %; acid value: 1.0; solubility: 1 vol in 3 vol of 90 % ethanol.

For oils type *Tunisia and Morocco*: d_{20}^{20} 0.907 – 0.920; n_{D}^{20} 1.4640 – 1.470; $[\alpha]_{\mathrm{D}}^{20}$ $-2°$ to $+5°$; ester content (calculated as bornyl acetate): 2 – 5 %; acid value: 1.0; solubility: 1 vol in 2 vol of 80 % ethanol [322]

Major components are 1,8-cineole, α-pinene, and camphor, which comprise up to 55 %, 30 % and 22 %, respectively of commercial oils. The composition of the oil varies with its origin. North African oils (e.g., from Tunisia) are comparatively high in cineole. Spanish oils have a lower cineole content, but a higher camphor (up to 22 %) and monoterpene hydrocarbon content (30 – 40 %). Verbenone [*18309-32-5*] is also important for the odor; it may occur in traces or as a major component; its content in the Spanish oils is higher than in the North African ones [323].



Verbone

The main producers of rosemary oil are in Tunisia and Spain. About 100 to 150 t are produced annually. Rosemary is used widely in perfumery and in large amounts for perfuming bath foams, shampoos, and hair tonics.

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

d_{20}^{20} 0.870 – 0.887; n_D^{20} 1.4620 – 1.4690; $[\alpha]_D^{20}$ $-2\,°50'$ to $+4\,°$; solubility: 1 vol in 9 vol of 60 % ethanol at 20 °C; acid value: max. 1; ester value: max. 5; ester value (after acetylation): 247 – 280, corresponding to an alcohol content of 82 – 96 % (calculated as linalool) [324].

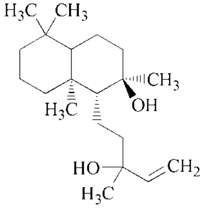
Brazilian rosewood oil is no longer competitive as a raw material for linalool. Increasing production costs, as well as the development of large-scale processes for fully synthetic linalool (for production of vitamin A), have led to a sharp decline in production (annual production ca. 20 – 30 t). Currently, rosewood oil is only used in small amounts in perfumes, e.g., for soaps.

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). The quality *Broyée en vert* is obtained after cutting the fresh material and immediate distillation. Another quality named *Traditionelle* exists, which is obtained by steam distillation after drying of the tops and foliage on the field. Both qualities are pale yellow to yellow liquids with a herbaceous odor and a winelike bouquet.

   Physical constants for the quality *Broyée en vert*: d_{20}^{20} 0.890 – 0.902; n_D^{20} 1.4560 – 1.4660; $[\alpha]_D^{20}$ $-20\,°$ to $-10\,°$; solubility: 1 vol in 3 vol of 80 % ethanol; solutions become opalescent on dilution; acid value: max. 1; ester content (calculated as linalyl acetate): 63 – 75 % [325].

   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*]. Sclareol is the main component in the concrete, obtained by solvent extraction of *S. sclarea* L. leaves.



   Sclareol

   Sclareol is used as a starting material for a number of ambergris fragrances. Major cultivation areas for *S. sclarea* L. are the CIS, the Mediterranean and Balkan countries, and more recently the United States. The annual production is between 50 and 150 t.

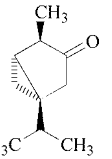
   Clary sage oil is used extensively in fine fragrances.

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

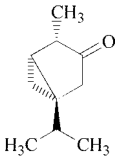
   d_{20}^{20} 0.910 – 0.930; n_D^{20} 1.4580 – 1.4740; $[\alpha]_D$ $+2\,°$ to $+30\,°$; saponification value: 6 – 20; ketone content (calculated as thujone): 28 – 78 %; solubility: 1 vol in 2 vol of 80 % ethanol at 20 °C [326].

   The major components of *S. officinalis* oil are camphor and α-thujone [*546-80-5*]. β-

thujone [*471-15-8*] is present in ca. 5 % concentration.



α-Thujone [(−)-thujone]



β-Thujone [(+)-isothujone]

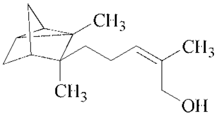
The oil is used in pharmaceutical preparations and in perfumery to create dry, spicy-herbaceous notes.

3) *Spanish sage oil* is produced by steam distillation of leaves and twigs of *Salvia lavandulifolia* Vahl (Lamiaceae) growing in Spain in the provinces Granada, Murcia, Almeria, and Jaén. The oil is an almost colorless to pale yellow liquid with the characteristic camphoraceous odor of the leaves.
d_{20}^{20} 0.907 – 0.930; n_D^{20} 1.465 – 1.472; $[\alpha]_D^{20}$ − 12 ° to + 17 °; solubility: 1 vol in 2 vol of 80 % ethanol at 20 °C; acid value: max. 2.0; ester value: min. 15, max. 55 [327].
Unlike Dalmatian sage oil, Spanish sage oil contains no or only traces of α- or β-thujone; camphor and 1,8-cineole are the major components and are responsible for the odor of the oil, which is used primarily in pharmaceutical preparations.
Altogether about 50 t of Spanish and Dalmatian oils are produced annually.

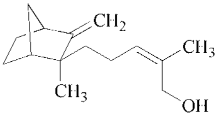
Sandalwood oil, East Indian is obtained by steam distillation of the heartwood of *Santalum album* L. (Santalaceae). It is a slightly viscous, almost colorless to golden yellow liquid with a characteristic, sweet, woody, long-lasting odor.

d_{20}^{20} 0.968 – 0.983; n_D^{20} 1.5030 – 1.5080; $[\alpha]_D^{20}$ − 21 ° to − 12 °; solubility: 1 vol in 5 vol of 70 % ethanol at 20 °C; ester value: min. 10; free alcohol content (calculated as santalol): min. 90 %.

East Indian sandalwood oil consists almost exclusively of closely related sesquiterpenoids; the alcohols *cis*-α-santalol [*115-71-9*] (45 – 55 %) and *cis*-β-santalol [*77-42-9*] (18 – 24 %) are mainly responsible for its odor [328].



α-Santalol



β-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 %. Indian production is ca. 60 t/a. Smaller quantities are produced in neighboring countries.

East Indian sandalwood oils are used extensively in perfumery as very valuable, stable fixatives.

Sassafras oil, Brazilian is obtained by steam distillation of the roots, trunks, and branches of *Ocotea pretiosa* (Nees) Mez (Lauraceae). 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} 1.082 – 1.094; n_D^{20} 1.5330 – 1.5370; $[\alpha]_D^{20}$ − 0.5 ° to + 3.0 °; solubility: 1 vol in 2 vol of 90 % ethanol; *fp* + 7.5 to + 9.5 °C [329].

The main component of the oil is safrole, which may make up more than 90 % of the oil and determines its freezing point. (IFRA recommendation)

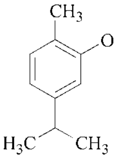
Production from trees that grow wild in Brazil, Paraguay, and Columbia exceeds that of North American sassafras oil, which is similar in composition. The main use of the oil is for the production of safrole and products derived from it (e.g., isosafrole and piperonal, see page 69).

Chinese sassafras oils (annual production about 950 t) are fractions, rich in safrole, that are obtained from oils of different species of the camphor tree (see Camphor Oils, page 90).

Savory oil is obtained by steam distillation of the whole dried herb *Satureja hortensis* L. (Summer savory) or *S. montana* L. (Lamiaceae) (Winter savory). 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; $[\alpha]_D$ − 5 ° to + 4 °; phenol content: 20 – 59 %; saponification value: max. 6; solubility: 1 vol in 2 vol of 80 % ethanol at 25 °C; solutions in 10 vol of ethanol may be slightly hazy [330].

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*].



Carvacrol

Savory oil is used mainly in the food industry, e.g., for flavoring sauces and soups.

Spearmint oil, see Mint Oils, page 107.

Spike oil, see Lavandula Products, page 105

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 ° to + 2 °; solubility: 1 vol in 3 vol of 90 % ethanol; *fp* min. 15 °C [331].

The main component of star anise oil, as in anise oil, is *trans*-anethole (86 – 93 %, determined by GLC). Pure anethole can be obtained by rectification (see page 64). 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 toothpaste.

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 grasslike 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. Styrax oil has a sweet-balsamic odor with a styrene-like top note. It is used in perfumery in flowery compositions. (IFRA recommendation).

Tagetes oil (Marigold oil) is produced by steam distillation of the flowering plants *Tagetes minuta* L. (*T. glandulifera* Schrank., Asteraceae). The main producers are in France, 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.

It is used in accentuated flowery fragrances and in aroma compositions to achieve fruity effects. (IFRA recommendation)

Tarragon oil (estragon oil) is produced by steam distillation of leaves, stems, and flowers of *Artemisia dracunculus* L. (Asteraceae). It is a colorless to pale yellow liquid with a characteristic, spicy, delicate estragon odor reminiscent of liquorice and sweet basil.

d_{20}^{20} 0.918 – 0.943; n_D^{20} 1.5080 – 1.5180; $[\alpha]_D^{20}$ + 2 ° to + 6 °; acid value: max. 1; ester value: max. 18; solubility: 1 vol in 4 vol of 90 % ethanol [332].

The main component of tarragon oil is estragole (methylchavicol, see page 89), which may make up > 60 % of the oil.

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.

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

d_{20}^{20} 0.888 – 0.906; n_D^{20} 1.4750 – 1.4800; $[\alpha]_D^{20}$ + 5 ° to + 15 °; cineole content: max. 15 % (by GLC); terpinen-4-ol content: min. 30 % (by GLC); solubility: 1 vol in 2 vol of 85 % ethanol [333].

Tea tree oil is used in perfumery for creating certain nuances and for earthy notes. In addition there is an increasing interest for using this oil in aroma therapy. Annual production is ca. 150 t.

Thuja oil, see Cedar Leaf Oil, page 92.

Thyme oil is obtained by steam distillation of flowering plants of *Thymus zygis* L. var. *gracilis* Boissier (Lamiaceae). Thyme oil is not to be confused with white thyme oil; see under Origanum Oil. 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 $-1°$; total phenol content: min. 38 %, max. 56 %; solubility: 1 vol in 3 vol of 80 % ethanol [334].

The main constituents of thyme oil are thymol and carvacrol (up to 60 %); for structures of these compounds, see p. page 63, page 116. Other chemotypes of *T. vulgaris* are limited to specific areas and yield, e.g., oils that contain geraniol, linalool, α-terpineol, and cineole; these oils are of minor importance.

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.

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.

Both the resinoid and the balsam are used in perfumery, mainly for their fixative properties.

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. In perfumery tonka bean absolute is used as a fixative and produces a dry sweetness in men's fragrances.

Tree moss absolute, see Oakmoss Absolute, page 110.

Tuberose absolute is obtained by solvent extraction, via the concrete, from the blossoms of *Polianthes tuberosa* L. (Agavaceae). The plants are cultivated in Morocco, 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.

Turpentine oils (→ Turpentines) are used in large quantities by the fragrance industry as starting materials for the manufacture of single fragrance and flavor compounds. 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, page 113). Nevertheless, they are used either as such or indirectly as fragrant solvents for perfuming household products. IFRA recommends that these oils should only be used when the level of peroxides is kept to the lowest practical level.

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.

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 5 [335].

Worldwide production of turpentine oils is ca. 300 000 t/a, of which approximately one third is produced in the United States and Canada as sulfate turpentine oil. Other major producers are the CIS, Scandinavia, and China.

The main components of all turpentine oils are terpene hydrocarbons. The balsam and sulfate turpentine oils produced in the South-

Table 5. 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 *bp* 170 °C, %	90	90	90	60
Evaporation residue, %	2.5	2.5	2.5	2.5
Acid value	1	1	1	1

east of the United States contain mainly α- and β-pinene (60 – 70 % and 20 – 25 %, respectively); *Pinus palustris* Mill. (long leaf pine) gives the (+)-enantiomers and *Pinus caribaea* 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 compounds. European turpentine oils originate mainly from Portugal, where distillation of *Pinus pinaster* Aiton resin or wood gives a turpentine oil that consists of 70 – 85 % (−)-α-pinene and 10 – 20 % (−)-β-pinene [336].

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; $[\alpha]_D$ − 28 ° to − 2 °; acid value: 5 – 50; saponification value: 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 [337].

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.

Valerian is cultivated in Belgium, northern France, east Germany, Poland, Hungary, and southern Russia. The so-called Kesso roots obtained from *Valeriana officinalis* L. var. *angustifolia* Miq., cultivated in Japan, give a much larger yield of oil.

Valerian oil is produced in limited quantities and is used in flavor and fragrance compositions and, to a small extent, in pharmaceutical preparations.

Vanilla extract (an oleoresin) is produced by extraction of the pods of *Vanilla planifolia* Andrews or *V. tahitensis* J. W. 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.

Vanillin and phenol derivatives are primarily responsible for its aroma. The main producers of *V. planifolia* pods are Madagascar, the Comoro Islands, and Réunion (Bourbon); *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.

Verbena oil is produced by steam distillation of the leaves of *Aloysia triphylla* (L'Hér.) Britton [*Lippia citriodora*(Lam) Humb., Bonpl. et Kunth, *L. triphylla* (L'Hér.) Kuntze, (Verbenaceae)]. It is a light yellow liquid with a delicate lemon odor.

d_{20}^{20} 0.890 – 0.920; n_D^{20} 1.4820 – 1.4880; $[\alpha]_D$ − 18 ° to − 10 °; content of carbonyl compounds (calculated as citral): 32 – 38 %; solubility: 1 vol in 1 vol of 90 % ethanol.

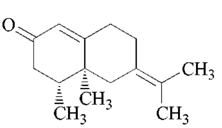
The major components of "true" verbena oil are citral (ca. 40 %), geraniol, and nerol (ca. 5 % each).

The verbena plant, originates in South America, but is cultivated mainly in southern France. The oil is used in fine fragrances. IFRA recommendation.

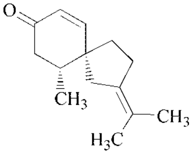
Vetiver oil is produced by steam distillation of the roots of the grass *Vetiveria zizanioides* (L.) Nash (Poaceae), which grows wild or is cultivated in many tropical and subtropical countries. The oil is a brown to reddish-brown, viscous liquid with a characteristic precious-wood- and rootlike, long-lasting odor. The following specifications are for oil produced in Haiti:

d_{20}^{20} 0.980 – 1.001; n_D^{20} 1.5160 – 1.5270; $[\alpha]_D^{20}$ +22 ° to +46 °; acid value: min. 1, max. 14; ester value: 5 – 35; carbonyl value: 23 – 59; solubility: 1 vol in 2 vol of 80 % ethanol at 20 °C.

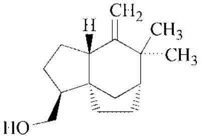
The tenacity of the highly complex vetiver oil is attributed to its high sesquiterpene content. The ketones α-vetivone [*15764-04-2*] and β-vetivone [*18444-79-6*], which form up to 10 % of the oil, as well as khusimol [*16223-63-5*] (up to 15 %) and its derivatives, contribute significantly to its odor [338].



α-Vetivone



β-Vetivone



Khusimol

The oil contains a considerable number of bi- and tricyclic primary, secondary, and tertiary sesquiterpene alcohols, called vetiverols or vetivenols. 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 producers are Indonesia, China, and Haiti (ca. 300 t/a).

Vetiver oil is used in fine fragrances for long-lasting precious-wood notes. It is also used as starting material for vetiveryl acetate (see page 41).

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).

Violet leaf absolute is used frequently in perfume compositions, but only in very low concentration because of its intense odor.

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* (Lam.) Hook. f. et Thomson (Annonaceae). These cananga trees normally grow to a height of 20 m but are pruned to a height of 2.10 – 3.00 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". 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 value. Specifications of fractions obtained from Comoro Island oils are given in Table 6 [339, 340].
   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 odoriferous constituents such as *p*-cresyl methyl ether (about 8 %), methyl benzoate (about 5 %), (−)-linalool (about 11 %), benzyl acetate (about 30 %), and geranyl acetate (about 4 %). The other fractions contain increasing amounts of sesquiterpene hydrocarbons (mainly caryophyllene and germacrene D), which can reach 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.
   Ylang-ylang Extra and I are used mostly in fine fragrances; ylang-ylang II and III are employed in soap perfumes.
2) *Cananga oil* is produced by steam distillation of the flowers of *Cananga odorata* (DC) Hook. f. et Thomson subsp. *macro-*

Table 6. Specification of ylang-ylang oils from the Comoro Islands

Parameter	Ylang-ylang fractions			
	Extra	I	II	III
d_{20}^{20}	0.955 – 0.976	0.938 – 0.960	0.925 – 0.945	0.906 – 0.925
n_{D}^{20}	1.498 – 1.506	1.501 – 1.509	1.502 – 1.511	1.503 – 1.513
$[\alpha]_{\mathrm{D}}^{20}$	$-40°$ to $-20°$	$-46°$ to $-25°$	$-60°$ to $-35°$	$-72°$ to $-45°$
Acid value	< 2	< 2	< 2	< 2
Ester value	140 – 185	100 – 160	75 – 115	45 – 75

phylla (Annonaceae). 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; $[\alpha]_{\mathrm{D}}^{20}$ $-30°$ to $-15°$; solubility: 1 vol in 1 vol of 95 % ethanol at 20 °C (solution may be turbid); acid value: max. 2; ester value: 13 – 35 [341].

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

Cananga oil originates almost exclusively in Java, where the flowers are collected throughout the year; annual production is 30 – 50 t. The oil is used mainly in soap perfumes.

4. Quality Control

Quality control of fragrance and flavor substances, as well as the products derived from them, comprises the comparison of sensory, analytical, and if necessary, microbiological data with standards and specifications. To a large extent these have been established in official specification collections (Pharmacopoeias, ISO, Association Française de Normalisation (AFNOR), Essential Oil Association, Merck Index).

In the past few decades, a precise analytical methodology has been developed for sensory evaluation and has proved to give reliable results [342]. Analytical determination of identity and purity aids greatly in establishing the acceptability of fragrance and flavor materials.

Single fragrance and flavor compounds are characterized by generally accepted physical constants, such as density, refractive index, optical rotation, and melting point. The advantages of these parameters are their speed of measurement and the possibility of comparison with other laboratories; therefore, they will continue to be indispensable. In addition, these measurements can be done more and more by robots controlled by computers.

Determinations of content by chemical parameters, such as ester and carbonyl values, are being increasingly supplemented by chromatographic procedures such as GC and HPLC and by spectroscopic techniques (UV, IR, NIR, and NMR).

Standardization of specifications for complex fragrance and flavor materials, such as essential oils and animal secretions, is far more difficult than for single compounds. In addition to organoleptic and physical properties, the content of certain typical components is determined. Problems concerning the natural, botanical, and geographical origins of these products are solved by using modern chromatographic and spectroscopic analytical techniques (and combinations such as GC – MS). Furthermore the determination of chiral properties of the molecules by enantioselective capillary GC has become a routine method. Isotope ratio mass spectrometry (IRMS) reveals the stable isotope ratios of the bioelements C, H, O, N, and S and the positional isotope analysis can be performed by Site-specific Natural Isotope Fractionation – NMR (SNIF – NMR) [343]. These methods have become very effective tools for authenticity control.

The analysis of trace components (halogens, heavy metals, and pesticides) in flavors and fragrances that are used in foods and cosmetics is becoming increasingly important. Radioactivity values in materials of natural origin are also monitored.

5. Economic Aspects

The flavor and fragrance industry has grown from an artisanal development into an industrial business. The total market for these product categories is estimated to about \$ 16×10^9, Europe and North America being the leading markets with shares of about \$ 5.4 and 4.1×10^9, respectively. Total annual growth rates till 2005 are forecasted to reach about 4.5 %, growth in Europe and North America will be below 3 %. In general it is predicted that sales of flavors will grow by about 5.5 % and fragrances on a whole by about 3 %.

The flavor and fragrance industry has undergone a great degree of consolidation since the mid-1990s. The top ten flavor and fragrance producers have combined sales in excess of \$ 9×10^9, corresponding to about 55 % of the total value. The remaining 45 % of the market are shared by more than 1000 other companies, many of them serving only one to three customers. Out of the top ten companies, four have annual sales in excess of \$ 1×10^9, namely Givaudan and Firmenich of Switzerland, IFF of the USA and Quest, which is affiliated with ICI. Takasago of Japan also reports sales in excess of \$ 1×10^9, however its sales in the flavors and fragrances field are less than that. The remaining top ten companies, in addition to the aforementioned, are Dragoco and Haarmann and Reimer, both in Germany, Universal Flavors in the USA, and Hasegawa in Japan. The last one of this group, BBA of the USA, has recently been taken over by IFF. In conclusion, it can be foreseen that further consolidation will increase the market shares of these top ten companies over the next five years.

6. Toxicology and Environmental Aspects

The addition of flavor and fragrance compounds to foods, cosmetics and toiletries, and other consumer products is intended to improve the quality of those products. So these chemicals must not have adverse effects on health or well-being. To avoid any problems caused by perfumed consumer products, the fragrance industry decided to build up a self-regulatory system.

Already in 1966 in the USA the Research Institute for Fragrance Materials, Inc. (RIFM, Two University Plaza, Suite 406, Hackensack, N.J. 07601) was established for the sole purpose of fragrance safety. As an independent nonprofit organization, RIFM has a continuing program, testing fragrance materials of good commercial quality. All judgements in matters pertaining to the evaluation of safety are made exclusively, and independently by an international expert panel of toxicologists, pharmacologists, and dermatologists drawn from the academic world. Those results are published as 'RIFM monographs' in the journal 'Food and Chemical Toxicology' [344] and in the Internet under www.rifm.org/data/start.cfm. These monographs contain specifications and data on biological activity (e.g., acute, short-term, and long-term toxicity, toxicokinetics, and metabolism).

In 1973 national associations of fragrance manufacturers have formed the International Fragrance Association (IFRA, 8, Rue Charles Humbert, CH-1205 Genève, Switzerland), an international organization with scientific aims concerned with all aspects of safety evaluation and regulation of the fragrance industry. IFRA represents over 100 fragrance manufacturers in 15 countries and edits guidelines advising against the use of fragrance materials under conditions that might provoke irritation and sensitization reactions or phototoxic effects (see Section 1.5.2). The activities of RIFM and IFRA are harmonized by a Joint Advisory Committee. Similarly to IFRA, the International Organization of the Flavor Industry (IOFI, same adress as IFRA) publishes lists of naturally occurring and nature-identical flavor components, which may be used up to given concentrations, and of artificial flavor substances that are considered to be nontoxic.

For more than 40 years the Flavor and Extract Manufacturers' Association's (FEMA) Expert Panel Food Additives conducts a comprehensive program of safety evaluation of flavoring substances under the authority of Section 201(s) of the Federal Food, Drug, and Cosmetic Act. FEMA publishes compendiums with flavor components commonly known as GRAS.

In the 1980s and especially in the 1990s a growing awareness developed that flavor and fragrance chemicals can also affect the environment. So the Material Safety Data Sheets of flavors and fragrances (MSDS, see EEC Directive 91/155/EEC) now contain in addition to the toxicological information also ecological information, mainly: biodegradability and aquatic toxicity. In most countries, the use of flavor and fragrance materials in consumer products is extensively regulated.

Recent Discussions. In 2002 *nitromusks* were identified in surface water, fish, and human fat and milk samples. Due to their low biodegradability these substances – having been used for 100 years – accumulate in the environment. In addition a relatively high log (partition coefficient octanol – water) ($\log P_{\mathrm{ow}} > 5$) shows that these substances are lipophilic and therefore accumulate also in fat tissue. RIFM has initiated the execution of various studies: acute and subchronic toxicity, irritation, sensitization and photosensitization potential, genotoxicity, carcinogenicity bioassay; studies on dermal absorption and pharmacokinetic.

Reports of *polycyclic musks* in the environment have also prompted a review of the safety of these important fragrance ingredients and similar studies as for nitromusks were conducted. For both groups the following summary is valid: Margins of safety based on the no-adverse-effect levels from subchronic studies are sufficient to conclude that direct exposure from use of these materials in fragrances or indirect exposure from their presence in the environment pose no significant risks to human health. Their environmental risk assessment is the subject of separate reviews.

The discussions on the nitro and polycyclic musks have given increased evidence of the importance of knowing as much as possible about properties of fragrance materials such as biodegradability and partition coefficient octanol – water.

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