

2 Single Fragrance and Flavor Materials

Fragrance and flavor materials of commercial interest are arranged according to the Beilstein system of functional groups, not according to their sensory 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). Materials that are only produced in small quantities, but which are important due to their high odor intensity, are mentioned but not described in detail.

When available, trade names are given for individual fragrance and flavor materials. The names of the suppliers are given as follows:

Agan	= Agan Aroma Chemicals Ltd., Israel
Aromor	= Aromor Flavors & Fragrances Ltd., Israel
BASF	= BASF AG, Germany
BBA	= Bush Boake Allen, Ltd., UK
Calchauvet	= Calchauvet, France
Charabot	= Charabot S.A., France
Cognis	= Cognis Deutschland GmbH, Germany
Degussa.	= Degussa., Germany
Dragoco	= DRAGOCO Gerberding & Co. AG, Germany
DRT	= Les Derives Resiniques et Terpeniques, France
Firmenich	= Firmenich S.A., Switzerland
Giv.-Roure	= Givaudan-Roure (International) S.A., Switzerland
H&R	= Haarmann & Reimer GmbH, Germany
IFF	= International Flavors & Fragrances, USA

Kao	= Kao Corp., Japan
Kuraray	= Kuraray Co. Ltd., Japan
Millenium	= Millenium Specialty Chemicals, USA
NZ	= Nippon Zeon Co., Ltd., Japan
PFW	= PFW Aroma Chemicals B.V., Netherlands
Quest	= Quest International, UK
Rhodia	= Rhodia, France
Soda Aromatic	= Soda Aromatic Co., Ltd., Japan
Takasago	= Takasago Perfumery Co., Japan
Treatt	= R.C. Treatt & Co., Ltd., UK
Vioryl	= Vioryl S.A., Greece

Monographs on fragrance materials and essential oils which have been published by the Research Institute for Fragrance Materials (RIFM) in 'Food and Chemical Toxicology' are cited below the individual compounds as 'FCT' with year, volume and page of publication.

2.1 Aliphatic Compounds

The acyclic terpenes are discussed separately in Section 2.2. Some of the cycloaliphatic fragrance and flavor materials 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 [10].

2.1.2 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 C₄–C₁₀ alcohols, isoamyl alcohol). Unsaturated alcohols are most important (e.g., leaf alcohol with its intensely green odor) and may impart characteristic notes to compositions.

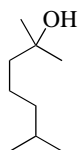
Naturally occurring fatty alcohols used in the fragrance industry are produced principally by reduction of the methyl esters of the corresponding carboxylic acids, which are obtained by transesterification of natural fats and oils with methanol. Industrial reduction processes include catalytic hydrogenation in the presence of copper–chromium oxide catalysts (Adkins catalysts) and reduction with sodium (Bouveault–Blanc reduction). Unsaturated alcohols can also be prepared by the latter method. Numerous alcohols used in flavor compositions are, meantime, produced by biotechnological processes [11]. Alcohols are starting materials for aldehydes and esters.

3-Octanol [589-98-0]

$\text{CH}_3(\text{CH}_2)_4\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$, $\text{C}_8\text{H}_{18}\text{O}$, M_r 130.23, $bp_{97.6\text{kPa}}$ 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.

FCT 1979 (17) p. 881.

2,6-Dimethyl-2-heptanol [13254-34-7]



$\text{C}_9\text{H}_{20}\text{O}$, M_r 144.26, $bp_{101.3\text{kPa}}$ 170–172 °C, d_{20}^{20} 0.8186, n_D^{20} 1.4248, which has not yet been found in nature, is a colorless liquid with a delicate, flowery odor reminiscent of fresas. It is synthesized from 6-methyl-5-hepten-2-one and methylmagnesium chloride by a Grignard reaction, followed by hydrogenation, and is used in flowery perfume compositions.

FCT 1992 (30) p. 30.

Trade Names. Dimetol (Giv.-Roure), Freesiol (H&R), Lolitol (IFF).

trans-2-Hexen-1-ol [928-95-0]

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{CHCH}_2\text{OH}$, $\text{C}_6\text{H}_{12}\text{O}$, M_r 100.16, $bp_{101.3\text{kPa}}$ 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.

FCT 1974 (12) p. 911.

cis-3-Hexen-1-ol [928-96-1], leaf alcohol

$\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_2\text{OH}$, $\text{C}_6\text{H}_{12}\text{O}$, M_r 100.16, $bp_{101.3\text{kPa}}$ 156–157 °C, d_4^{20} 0.8459, 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. Biotechnological processes have been developed for its synthesis as a natural flavor compound, e.g., [12].

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.

FCT 1974 (12) p. 909.

1-Octen-3-ol [3391-86-4]

$\text{CH}_3(\text{CH}_2)_4\text{CH}(\text{OH})\text{CH}=\text{CH}_2$, $\text{C}_8\text{H}_{16}\text{O}$, M_r 128.21, $bp_{94.6\text{kPa}}$ 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-earthly odor that can be prepared by a Grignard reaction from vinylmagnesium bromide and hexanal. It is used in lavender compositions and in mushroom aromas.

FCT 1976 (14) p. 681.

Trade Names. Matsutake alcohol (Takasago), Morillol (BSAF).

9-Decen-1-ol [13019-22-2]

$\text{CH}_2=\text{CH}(\text{CH}_2)_7\text{CH}_2\text{OH}$, $\text{C}_{10}\text{H}_{20}\text{O}$, M_r 157.27, $bp_{0.27\text{kPa}}$ 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.

FCT 1974 (12) p. 405.

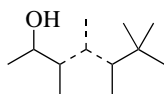
Trade Names. Rosalva (IFF), Trepanol (Takasago).

10-Undecen-1-ol [112-43-6]

$\text{CH}_2=\text{CH}(\text{CH}_2)_8\text{CH}_2\text{OH}$, $\text{C}_{11}\text{H}_{22}\text{O}$, M_r 170.29, $bp_{2.1\text{kPa}}$ 133 °C, d_4^{15} 0.8495, n_D^{20} 1.4500, was tentatively identified, e.g., in the wax gourd (*Benincasa hispida*, Cogn.) [13], 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.

FCT 1973 (11) p. 107.

3,4,5,6,6-Pentamethyl-3(or -4)-hepten-2-ol [81787-06-6] and [81787-07-7] and 3,5,6,6-Tetramethyl-4-methyleneheptan-2-ol [81787-05-5] (mixture)



$C_{12}H_{24}O$ M_r 184.32, is a mixture of isomers where one of the dashed lines represents a carbon–carbon double bond, the others a single bond. None of the compounds occur in nature. It is a colorless to slightly yellow liquid, d_4^{20} 0.864–0.872, n_D^{20} 1.454–1.460, with a fine woody, ambra, dry odor with a clean vetiver character. Synthesis starts from 2-methyl-2-butene (isoamylene) which is dimerized and the product acetylated to give the corresponding hepten-2-ones (see p. 17). The hepten-2-ols are obtained by reduction with $NaBH_4$ [14]. The mixture is used in perfume compositions, for example, for detergents.

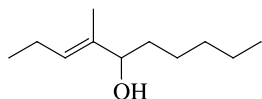
Trade Name. Kohinool (IFF).

2-*trans*-6-*cis*-Nonadien-1-ol [28069-72-9], violet leaf alcohol

$CH_3CH_2CH=CHCH_2CH_2CH=CHCH_2OH$, $C_9H_{16}O$, M_r 140.22, $bp_{1.5kPa}$ 96–100 °C, d_4^{25} 0.8622, n_D^{25} 1.4631, 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. FCT 1982 (20) p. 771.

4-Methyl-3-decen-5-ol [81782-77-6]



$C_{11}H_{22}O$, M_r 170.30, d_4^{20} 0.8420–0.8480, n_D^{20} 1.449–1.454, a colorless to pale yellow liquid with a powerful rich fresh, green, floral, violet-leaf-like odor. It is used in modern perfume oils as a substitute for the methyl alkynoates (see p. 22) and is found in perfume oils for nearly all applications.

4-Methyl-3-decen-5-ol is prepared by Grignard reaction of pentyl magnesium bromide and 2-methyl-2-pental [14a].

Trade Name. Undecavertol (Giv.-Roure).

2.1.3 Aldehydes and Acetals

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 C₈–C₁₃, 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 > C₁₃ 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. 2-*trans*,4-*trans*-Decadienal [25152-84-5] with its specifically fatty odor character is indispensable in chicken meat flavor compositions.

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. 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, aldehyde C₆

CH₃(CH₂)₄CHO, C₆H₁₂O, *M_r* 100.16, *bp*_{101.3 kPa} 128 °C, *d*₄²⁰ 0.8139, *n*_D²⁰ 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.

FCT 1973 (11) p. 111.

Octanal [124-13-0], caprylaldehyde, aldehyde C₈

CH₃(CH₂)₆CHO, C₈H₁₆O, *M_r* 128.21, *bp*_{101.3 kPa} 171 °C, *d*₄²⁰ 0.8211, *n*_D²⁰ 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 eau de cologne, and in artificial citrus oils.

FCT 1973 (11) p. 113.

Nonanal [124-19-6], pelargonaldehyde, aldehyde C₉

CH₃(CH₂)₇CHO, C₉H₁₈O, *M_r* 142.24, *bp*_{101.3 kPa} 190–192 °C, *d*₄²⁰ 0.8264, *n*_D²⁰ 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. FCT 1973 (11) p. 115.

Decanal [112-31-2], **caprinaldehyde, aldehyde C₁₀**

$\text{CH}_3(\text{CH}_2)_8\text{CHO}$, $\text{C}_{10}\text{H}_{20}\text{O}$, M_r 156.27, $bp_{101.3\text{kPa}}$ 208–209 °C, d_4^{15} 0.830, 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.

FCT 1973 (11) p. 477.

Undecanal [112-44-7], **aldehyde C₁₁**

$\text{CH}_3(\text{CH}_2)_9\text{CHO}$, $\text{C}_{11}\text{H}_{22}\text{O}$, M_r 170.29, $bp_{2.4\text{kPa}}$ 117 °C, d_4^{23} 0.8251, 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.’

FCT 1973 (11) p. 481.

Dodecanal [112-54-9], **lauraldehyde, lauric aldehyde, aldehyde C₁₂**

$\text{CH}_3(\text{CH}_2)_{10}\text{CHO}$, $\text{C}_{12}\text{H}_{24}\text{O}$, M_r 184.32, $bp_{13.3\text{kPa}}$ 185 °C, d_4^{15} 0.8352, 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.

FCT 1973 (11) p. 483.

Tridecanal [10486-19-8]

$\text{CH}_3(\text{CH}_2)_{11}\text{CHO}$, $\text{C}_{13}\text{H}_{26}\text{O}$, M_r 198.34, $bp_{1.3\text{kPa}}$ 128 °C, d_4^{18} 0.8356, 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, aldehyde MOA**

$\text{CH}_3(\text{CH}_2)_7\text{CH}(\text{CH}_3)\text{CHO}$, $\text{C}_{11}\text{H}_{22}\text{O}$, M_r 170.29, $bp_{98.8\text{kPa}}$ 119–120 °C, d_4^{23} 0.8948, 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 by-product in the manufacture of 2-methylundecanal by hydroformylation of 1-decene (see 2-methylundecanal). It is used in perfumery to refresh green and citrus nuances.

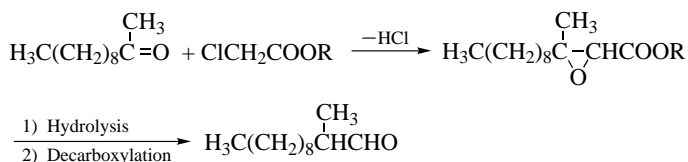
FCT 1976 (14) p. 609.

2-Methylundecanal [110-41-8], methylnonylacetaldehyde, aldehyde MNA

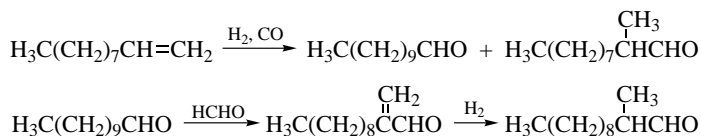
$\text{CH}_3(\text{CH}_2)_8\text{CH}(\text{CH}_3)\text{CHO}$, $\text{C}_{12}\text{H}_{24}\text{O}$, M_r 184.32, $b_{p_{1.3\text{kPa}}}$ 114 °C, d_4^{15} 0.830, n_D^{20} 1.4321, is reported as being found in nature. It is a colorless liquid, with an odor markedly different from that of the isomeric dodecanal. It has a fatty odor with incense and ambergris notes.

2-Methylundecanal is produced by two routes:

1. 2-Undecanone 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 [15]. 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 by-products by fractional distillation [16].



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.

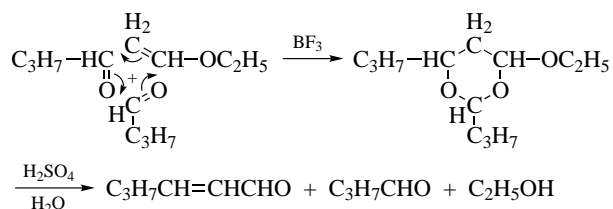
FCT 1973 (11) p. 485.

***trans*-2-Hexenal [6728-26-3], leaf aldehyde**

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{CHCHO}$, $\text{C}_6\text{H}_{10}\text{O}$, M_r 98.14, $b_{p_{101.3\text{kPa}}}$ 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 [17].



Biosynthetic ways for its production as natural flavor material have been developed [18].

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.

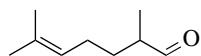
FCT 1975 (13) p. 453.

cis-4-Heptenal [6728-31-0]

$\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_2\text{CHO}$, $\text{C}_7\text{H}_{12}\text{O}$, M_r 112.17, $bp_{1.33\text{ kPa}}$ 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-butyne) 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 [19].

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

2,6-Dimethyl-5-hepten-1-al [106-72-9]



$\text{C}_9\text{H}_{16}\text{O}$, M_r 140.23, $bp_{2\text{ kPa}}$ 79–80 °C, d_4^{28} 0.848, n_D^{20} 1.4492 was identified in ginger. It is a yellow liquid with a powerful, green, cucumber-like and melon odor. It can be prepared by Darzens reaction of 6-methyl-5-hepten-2-one with ethyl chloroacetate. The intermediate glycidate is saponified and decarboxylated to yield the title compound.

It is used in many fragrance types and is invaluable in the creation of melon and cucumber notes.

Trade Name. Melonal (Giv.-Roure).

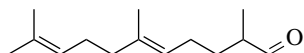
10-Undecenal [112-45-8]

$\text{CH}_2=\text{CH}(\text{CH}_2)_8\text{CHO}$, $\text{C}_{11}\text{H}_{20}\text{O}$, M_r 168.28, $bp_{0.4\text{ kPa}}$ 103 °C, d_4^{21} 0.8496, n_D^{21} 1.4464, was identified, e.g., in coriander leaf extract [20]. 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.’

FCT 1973 (11) p. 479.

2,6,10-Trimethyl-5,9-undecadienal [24048-13-3] and [54082-68-7]

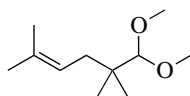


$C_{14}H_{24}O$, M_r 208.35, d_4^{20} 0.870–0.877, n_D^{20} 1.468–1.473, not found in nature, is a clear, colorless to pale yellowish liquid. It has an aldehydic-floral odor reminiscent of nerolidol, with fruity nuances. It can be prepared from geranylacetone (see p. 42) by Darzens reaction with ethyl chloroacetate through the corresponding glycidic ester which is hydrolyzed and decarboxylated.

2,6,10-Trimethyl-5,9-undecadienal is used to modify perfume compositions for soap, detergents and household products.

Trade Names. Oncidal (Dragoco), Profarnesal (H&R).

1,1-Dimethoxy-2,2,5-trimethyl-4-hexene [67674-46-8]



$C_{11}H_{22}O_2$, M_r 186.30, $bp_{1.6\text{kPa}}$ 82 °C, n_D^{20} 1.441, is a colorless to pale yellow liquid with a fresh fruity citrus grapefruit-peel-like odor. It has not been found in nature. It is prepared by reaction of 2,2,5-trimethyl-4-hexenal (from isobutyraldehyde and prenyl chloride) with methanol in the presence of calcium chloride [21].

Due to its alkali stability it is used in citrus compositions for soaps and detergents.

Trade Names. Methyl Pamplemousse (Giv.-Roure), Amarocit (H&R).

2.1.4 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 foodstuffs, 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.

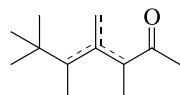
3-Hydroxy-2-butanone [52217-02-4], acetoin

$\text{CH}_3\text{COCH}(\text{OH})\text{CH}_3$, $\text{C}_4\text{H}_8\text{O}_2$, M_r 88.11, $bp_{101.3\text{ kPa}}$ 148 °C, d_{20}^{20} 1.0062, 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 by-product in the fermentation of molasses. It is used for flavoring margarine. FCT 1979 (17) p. 509.

2,3-Butanedione [431-03-8], diacetyl

$\text{CH}_3\text{COCOCH}_3$, $\text{C}_4\text{H}_6\text{O}_2$, M_r 86.09, bp 88 °C, d_4^{20} 0.9831, $n_D^{18.5}$ 1.3933, 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 [22]. Biotechnological production on an industrial scale is referred [23]. It is used mainly in aromas for butter and roast notes. Large quantities are used for flavoring margarine; small amounts are used in perfumes. FCT 1979 (17) p. 765.

3,4,5,6,6-Pentamethyl-3-hepten-2-one [81786-73-4], also contains other double bond isomers [81786-74-5], [81786-75-6], [81786-76-7], [81786-77-8]



$\text{C}_{12}\text{H}_{22}\text{O}$, M_r 182.30, d_{25}^{25} 0.861–0.870, n_D^{20} 1.453–1.461, a colorless to slightly yellow liquid with a complex wood floral note with amber and violet nuances. It is used in perfume oils for a wide range of applications, especially in perfume oils for soaps, shower gels and shampoos.

The material is prepared by acetylation of diisoamylene with acetic anhydride or acetyl chloride under boron trifluoride etherate catalysis [23a].

Trade Name. Koavone (IFF).

2.1.5 Acids and Esters

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.

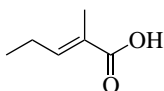
Although the odor of aliphatic esters with a small number of carbon atoms is strictly fruity, it changes to fatty-soapy and even metallic as the number of carbon atoms increases.

Esters are usually prepared by esterification of carboxylic acids with alcohols. Industrial procedures depend on the physical properties of the esters concerned. Biosynthetic methods may be applied to produce natural esters for flavor purposes [24].

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 C₆ are used principally for fruity notes, whereas the acetates of C₈, C₁₀, and C₁₂ 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.

2-Methyl-2-pentenoic acid [3142-72-1]



C₆H₁₀O₂, M_r 114.15, was detected to occur, e.g., in capers. It is a yellow liquid, d_4^{20} 0.979–0.987, n_D^{20} 1.457–1.462, with a dry acid note, found in the odor of strawberries. The acid can be prepared from the corresponding saturated one by α -bromination followed by dehydrobromination.

It is used in fragrances to enhance fruity notes and in strawberry flavors. FCT 2000 (38, suppl. 3) p. S151.

Trade Name. Strawberriff (IFF).

Ethyl formate [109-94-4]

HCOOCH₂CH₃, C₃H₆O₂, M_r 74.08, $bp_{101.3\text{ kPa}}$ 54.5 °C, d^{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.

FCT 1978 (16) p. 737.

cis-3-Hexenyl formate [33467-73-1]

$\text{HCOO}(\text{CH}_2)_2\text{CH}=\text{CHCH}_2\text{CH}_3$, $\text{C}_7\text{H}_{12}\text{O}_2$, M_r 128.17, $bp_{101.3\text{kPa}}$ 155 °C, d_{25}^{25} 0.908, 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. FCT 1979 (17) p. 797.

Ethyl acetate [141-78-6]

$\text{CH}_3\text{COOCH}_2\text{CH}_3$, $\text{C}_4\text{H}_8\text{O}_2$, M_r 88.11, $bp_{101.3\text{kPa}}$ 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. FCT 1974 (12) p. 711.

Butyl acetate [123-86-4]

$\text{CH}_3\text{COO}(\text{CH}_2)_3\text{CH}_3$, $\text{C}_6\text{H}_{12}\text{O}_2$, M_r 116.16, $bp_{101.3\text{kPa}}$ 126.5 °C, d^{20} 0.882, 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. FCT 1979 (17) p. 515.

Isoamyl acetate [123-92-2]

$\text{CH}_3\text{COO}(\text{CH}_2)_2\text{CH}(\text{CH}_3)_2$, $\text{C}_7\text{H}_{14}\text{O}_2$, M_r 130.19, $bp_{101.3\text{kPa}}$ 142.5 °C, d_{25}^{25} 0.868–878, n_D^{18} 1.4017, 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. FCT 1975 (13) p. 551.

Hexyl acetate [142-92-7]

$\text{CH}_3\text{COO}(\text{CH}_2)_5\text{CH}_3$, $\text{C}_8\text{H}_{16}\text{O}_2$, M_r 144.21, $bp_{101.3\text{kPa}}$ 171.5 °C, d_4^{15} 0.8779, 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. FCT 1974 (12) p. 913.

3,5,5-Trimethylhexyl acetate [58430-94-7], **isononyl acetate**

$\text{CH}_3\text{COO}(\text{CH}_2)_2\text{CH}(\text{CH}_3)\text{CH}_2\text{C}(\text{CH}_3)_3$, $\text{C}_{11}\text{H}_{22}\text{O}_2$, M_r 186.29, does not occur in nature. Commercial isononyl acetate contains small amounts of by-products. 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. FCT 1974 (12) p. 1009.

Trade Names. Inonyl acetate (Quest), Isononyl acetate (H&R), Vanoris (IFF).

trans-2-Hexenyl acetate [2497-18-9]

$\text{CH}_3\text{COOCH}_2\text{CH}=\text{CH}(\text{CH}_2)_2\text{CH}_3$, $\text{C}_8\text{H}_{14}\text{O}_2$, M_r 142.20, $bp_{2.1\text{kPa}}$ 67–68 °C, d^{20} 0.8980, 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. FCT 1979 (17) p. 793.

cis-3-Hexenyl acetate [3681-71-8]

$\text{CH}_3\text{COO}(\text{CH}_2)_2\text{CH}=\text{CHCH}_2\text{CH}_3$, $\text{C}_8\text{H}_{14}\text{O}_2$, M_r 142.20, $bp_{1.6\text{kPa}}$ 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.

FCT 1975 (13) p. 454.

Ethyl propionate [105-37-3]

$\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3$, $\text{C}_5\text{H}_{10}\text{O}_2$, M_r 102.13, $bp_{101.3\text{kPa}}$ 99 °C, d_4^{20} 0.8917, 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.

FCT 1978 (16) p. 749.

Ethyl butyrate [105-54-4]

$\text{CH}_3(\text{CH}_2)_2\text{COOCH}_2\text{CH}_3$, $\text{C}_6\text{H}_{12}\text{O}_2$, M_r 116.16, $bp_{101.3\text{kPa}}$ 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.

FCT 1974 (12) p. 719.

Butyl butyrate [109-21-7]

$\text{CH}_3(\text{CH}_2)_2\text{COOCH}_2(\text{CH}_2)_2\text{CH}_3$, $\text{C}_8\text{H}_{16}\text{O}_2$, M_r 144.21, $bp_{101.3\text{kPa}}$ 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.

FCT 1979 (17) p. 521.

Isoamyl butyrate [106-27-4]

$\text{CH}_3(\text{CH}_2)_2\text{COO}(\text{CH}_2)_2\text{CH}(\text{CH}_3)_2$, $\text{C}_9\text{H}_{18}\text{O}_2$, M_r 158.23, $bp_{101.3\text{kPa}}$ 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.

FCT 1979 (17) p. 823.

Hexyl butyrate [2639-63-6]

$\text{CH}_3(\text{CH}_2)_2\text{COO}(\text{CH}_2)_5\text{CH}_3$, $\text{C}_{10}\text{H}_{20}\text{O}_2$, M_r 172.27, $bp_{101.3\text{kPa}}$ 208 °C, d_4^{20} 0.8652, n_D^{15} 1.4160, 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.

FCT 1979 (17) p. 815.

cis-3-Hexenyl isobutyrate [41519-23-7]

$(\text{CH}_3)_2\text{CHCOO}(\text{CH}_2)_2\text{CH}=\text{CHCH}_2\text{CH}_3$, $\text{C}_{10}\text{H}_{18}\text{O}_2$, M_r 170.25, is found in spearmint oil. It smells fruity-green and is used in perfumery to create freshness in blossom compositions.

FCT 1979 (17) p. 799.

Ethyl isovalerate [108-64-5]

$(\text{CH}_3)_2\text{CHCH}_2\text{COOCH}_2\text{CH}_3$, $\text{C}_7\text{H}_{14}\text{O}_2$, M_r 130.19, $bp_{101.3\text{kPa}}$ 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.

FCT 1978 (16) p. 743.

Ethyl 2-methylbutyrate [7452-79-1]

$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{COOCH}_2\text{CH}_3$, $\text{C}_7\text{H}_{14}\text{O}_2$, M_r 130.19, $bp_{101.3\text{kPa}}$ 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**

$\text{CH}_3(\text{CH}_2)_4\text{COOCH}_2\text{CH}_3$, $\text{C}_8\text{H}_{16}\text{O}_2$, M_r 144.21, $bp_{101.3\text{kPa}}$ 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.

FCT 1976 (14) p. 761.

Ethyl 2-methylpentanoate [39255-32-8]

$\text{C}_8\text{H}_{16}\text{O}_2$, M_r 144.22, d_{20}^{20} 0.860–0.870, n_D^{20} 1.401–1.407, a colorless liquid with a fruity-apple odor. It is used to create fruity top notes in perfumes for many purposes, e.g., for shampoos, fabric conditioners, detergents, air fresheners, and soaps.

Trade Name. Manzanate (Quest).

2-Propenyl hexanoate [123-68-2], **allyl caproate**

$\text{CH}_3(\text{CH}_2)_4\text{COOCH}_2\text{CH}=\text{CH}_2$, $\text{C}_9\text{H}_{16}\text{O}_2$, M_r 156.22, $bp_{2\text{kPa}}$ 75–76 °C, d^{20} 0.8869, n_D^{20} 1.4243, has been shown to occur in pineapple. It has a typical pineapple odor and is used in, for example, pineapple flavors.

FCT 1973 (11) p. 489.

Ethyl heptanoate [106-30-9], **ethyl enanthate**

$\text{CH}_3(\text{CH}_2)_5\text{COOCH}_2\text{CH}_3$, $\text{C}_9\text{H}_{18}\text{O}_2$, M_r 158.24, $bp_{101.3\text{kPa}}$ 187–188 °C, d_4^{15} 0.8714, n_D^{15} 1.4144, 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.

FCT 1981 (19) p. 247.

2-Propenyl heptanoate [142-19-8], **allyl enanthate**

$\text{CH}_3(\text{CH}_2)_5\text{COOCH}_2\text{CH}=\text{CH}_2$, $\text{C}_{10}\text{H}_{18}\text{O}_2$, M_r 170.25, $bp_{101.3\text{kPa}}$ 210 °C, $d^{15.5}$ 0.890, n_D^{20} 1.4290, has been found in, e.g., wild edible mushrooms. It is used in perfume compositions for apple-like (pineapple) notes.

FCT 1977 (15) p. 619.

Ethyl octanoate [106-32-1], ethyl caprylate

$\text{CH}_3(\text{CH}_2)_6\text{COOCH}_2\text{CH}_3$, $\text{C}_{10}\text{H}_{20}\text{O}_2$, M_r 172.27, $bp_{101.3\text{kPa}}$ 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.

FCT 1976 (14) p. 763.

Ethyl 2-trans-4-cis-decadienoate [3025-30-7]

$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}=\text{CHCOOCH}_2\text{CH}_3$, $\text{C}_{12}\text{H}_{20}\text{O}_2$, M_r 196.29, $bp_{6\text{Pa}}$ 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]. A biotechnological process for its preparation has been developed [26].

FCT 1988 (26) p. 317.

Methyl 2-octynoate [111-12-6]

$\text{CH}_3(\text{CH}_2)_4\text{C}\equiv\text{CCOOCH}_3$, $\text{C}_9\text{H}_{14}\text{O}_2$, M_r 154.21, $bp_{1.3\text{kPa}}$ 94 °C, d^{20} 0.926, n_D^{20} 1.4464.

FCT 1979 (17) p. 375.

Trade Name. Folione (Giv-Roure).

Methyl 2-nonynoate [111-80-8]

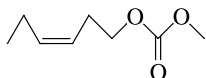
$\text{CH}_3(\text{CH}_2)_5\text{C}\equiv\text{CCOOCH}_3$, $\text{C}_{10}\text{H}_{16}\text{O}_2$, M_r 168.24, $bp_{2.7\text{kPa}}$ 121 °C, d^{20} 0.916–0.918, n_D^{25} 1.4470. Both methyl 2-nonynoate and methyl 2-octynoate have a triple bond and are liquids with a fatty, violet-leaf-like odor. They are used in perfume compositions.

FCT 1975 (13) p. 871.

Ethyl 3-oxobutanoate, ethyl acetoacetate [141-97-9]

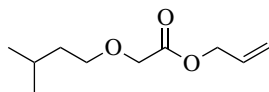
$\text{C}_6\text{H}_{10}\text{O}_3$, M_r 130.14, d_{25}^{25} 1.024–1.029, n_D^{20} 1.417–1.422, is a colorless liquid with a fruity-ethereal, sweet odor reminiscent of green apples. It is used to create fresh fruity top notes in feminine fine fragrances. Ethyl acetoacetate occurs in flavors of natural materials like coffee, strawberries and yellow passion fruits [26a].

FCT 1974 (12), p. 713.

(Z)-3-Hexenyl methyl carbonate [67633-96-9]

$\text{C}_8\text{H}_{14}\text{O}_3$, M_r 158.20, d_{25}^{25} 0.964–0.972, n_D^{20} 1.423–1.429, a colorless liquid with a very natural green, fruity-floral, violet-leaf-like odor. It is used to create green top notes in fine fragrance perfume oils.

Trade Name. Liffarome (IFF).

Pentylxyacetic acid allyl ester [67634-00-8], allyl amyglycolate

$C_{10}H_{18}O_3$, M_r 186.25, d_4^{20} 0.936–0.944, n_D^{20} 1.428–1.433, is a colorless liquid of strong fruity galbanum odor with pineapple modification. It can be prepared by reaction of chloroacetic acid with isoamyl alcohol in the presence of sodium hydroxide and a phase-transfer catalyst, then treating the resulting sodium amyglycolate with allyl alcohol [27]. Allyl amyglycolate is used in fragrance compositions, e.g., for detergents.

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 the following:

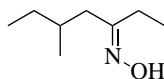
1. 3-mercaptohexanol [51755-83-0], a tropical fruit aroma component,
2. 3-methylthiohexanol [51755-66-9], a volatile constituent of passion fruits,
3. 3-mercapto-2-butanone [40789-98-8], a meat aroma constituent, and
4. 4-mercapto-4-methyl-2-pentanone [19872-52-7], the so-called ‘catty compound’ found in blackcurrant flavor and the wine variety ‘scheurebe’.

Allyl isothiocyanate, however, is an exception in that it is produced in large quantities. A heptanone oxime and the 2-tridecenenitrile have become important as fragrance materials.

Allyl isothiocyanate [57-06-7], allyl mustard oil

$CH_2 = CHCH_2N = C = S$, C_4H_5NS , M_r 99.14, $bp_{101.3\text{kPa}}$ 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 rhodanides [28].

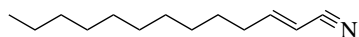
FCT 1984 (22) p. 623.

5-Methyl-3-heptanone oxime [22457-23-4]

$C_8H_{17}NO$, M_r 143.23, $bp_{0.1\text{kPa}}$ 70 °C, n_D^{20} 1.4519, is not reported as being found in nature. It is a colorless to pale yellow liquid with a powerful, green, leafy odor. 5-Methyl-3-heptanone oxime is prepared by oximation of the corresponding ketone. It imparts natural and fresh nuances to fragrance notes and is used in fine perfumery as well as in cosmetics, soaps, and detergents. FCT 1992 (30) p. 87S.

Trade Name. Stemone (Giv.-Roure).

2-Tridecenitrile [22629-49-8]



$C_{13}H_{23}N$, M_r 193.34, d_4^{20} 0.833–0.839, n_D^{20} 1.450–1.455, is a clear, colorless to pale yellowish liquid with a very strong, citrus odor reminiscent of nuances in orange and mandarine oil. It can be prepared by Knoevenagel condensation of undecanal with cyano acetic acid and subsequent decarboxylation.

It is used in compositions with agrumen notes for perfuming, e.g., cosmetics, soaps, and detergents.

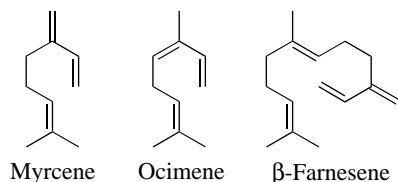
Trade Names. Ozonil (H&R), 'Tridecen-2-nitril' (Dragoco), 'Tridecene-2-nitrile' (Quest).

2.2 Acyclic 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

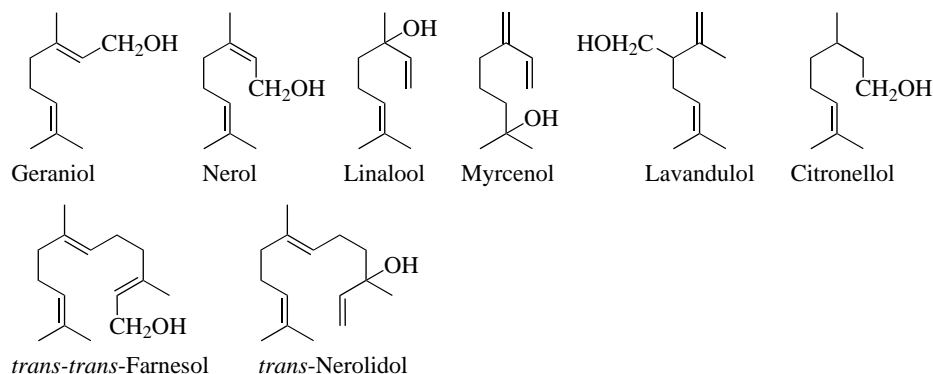
Ocimene

 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 is not separated from small amounts of compounds with similar physical properties but different odor quality.

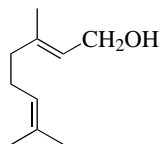


The acyclic terpene alcohols geraniol, linalool, and citronellol are the most important terpene alcohols used as fragrance and flavor substances. Geraniol and linalool are, in addition to nerol and lavandulol, primary products in terpene biosynthesis. The fully saturated alcohols tetrahydrogeraniol and tetrahydrolinalool are also used in large quantities in fragrance compositions. The fragrance materials myrcenol, and its dihydro and tetrahydro derivatives, belong structurally to the terpenes. The sesquiterpene alcohols farnesol and nerolidol are popular materials for perfume compositions.

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, $bp_{101.3\text{ kPa}}$ 230 °C, d^{20} 0.8894, 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.

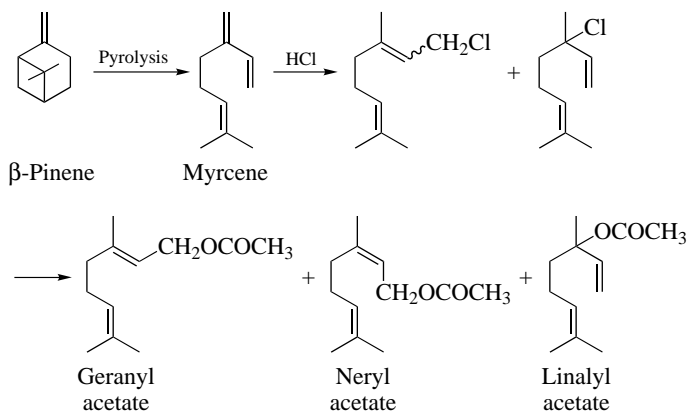
Since geraniol is an acyclic, doubly unsaturated alcohol, it can undergo a number of reactions, such as rearrangement and cyclization. Rearrangement in the presence of copper catalysts yields citronellal. In the presence of mineral acids, it cyclizes to form monocyclic terpene hydrocarbons, cyclogeraniol 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 [29]. 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 [30].



After saponification and fractional distillation of the resulting alcohols, a fraction is obtained that contains ca. 98% geraniol.

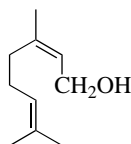
3. *Synthesis from Linalool.* A 96% pure synthetic geraniol prepared by isomerization of linalool has become commercially available. Orthovanadates are used as catalysts, to give a >90% yield of a geraniol–nerol mixture [31]. Geraniol of high purity is finally obtained by fractional distillation.

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 [32].

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.

FCT 1974 (12) p. 881.

Nerol [106-25-2], 3,7-dimethyl-*cis*-2,6-octadien-1-ol



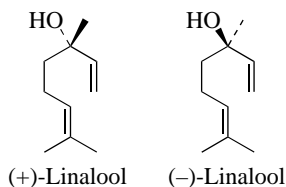
$C_{10}H_{18}O$, M_r 154.25, $bp_{99.3\text{kPa}}$ 224–225 °C, d_4^{20} 0.8796, n_D^{20} 1.4744, occurs in small quantities in many essential oils where it is always accompanied by geraniol; its name originates from its occurrence in neroli oil. Nerol is a colorless liquid with a pleasant roselike odor 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. 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 bouqueting citrus flavors. Technical-grade nerol, often in a mixture with geraniol, is used as an intermediate in the production of citronellol and citral.

FCT 1976 (14) p. 623.

Linalool [78-70-6], **3,7-dimethyl-1,6-octadien-3-ol**

$C_{10}H_{18}O$ M_r 154.25, $bp_{101.3\text{kPa}}$ 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 Ho oils from *Cinnamomum camphora*; rosewood oil contains ca. 80%. (+)-Linalool [126-91-0] makes up 60–70% of coriander oil.

Properties. (\pm)-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 [33]. Together with its esters, linalool is one of the most frequently used fragrance substances and is produced in large quantities.

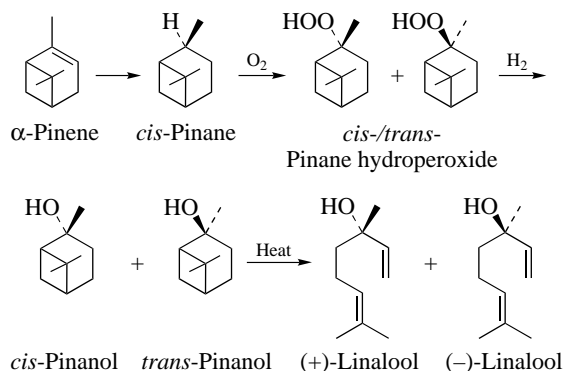
In the presence of acids, linalool isomerizes readily to geraniol, nerol, and α -terpineol. It is oxidized to citral by chromic acid. Oxidation with peracetic acid yields linalool oxides, which occur in small amounts in essential oils and are also used in perfumery. Hydrogenation of linalool gives tetrahydrolinalool, a stable fragrance material. 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 [34].

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.

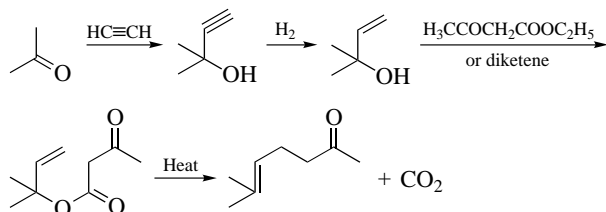
Since linalool is an important intermediate in the manufacture of vitamin E, several large-scale processes have been developed for its production. Preferred starting materials and/or intermediates are the pinenes and 6-methyl-5-hepten-2-one. Most perfumery-grade linalool is synthetic.

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 [35], 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

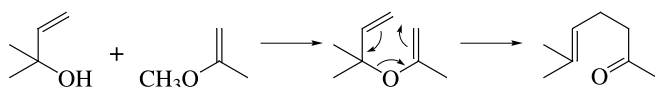
fractional distillation and are pyrolyzed to linalool: (–)- α -pinene yields *cis*-pinanol and (+)-linalool, whereas (–)-linalool is obtained from *trans*-pinanol [36].



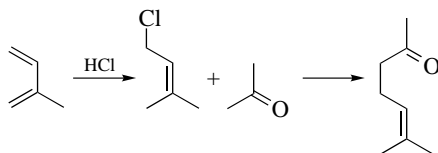
3. *Synthesis from β -Pinene.* For a description of this route, see under Geraniol. Addition of hydrogen chloride to myrcene (obtained from β -pinene) results in a mixture of geranyl, neryl, and linalyl chlorides. Reaction of this mixture with acetic acid–sodium acetate in the presence of copper(I) chloride gives linalyl acetate in 75–80% yield [37]. Linalool is obtained after saponification.
4. *Synthesis from 6-Methyl-5-hepten-2-one.* The total synthesis of linalool starts with 6-methyl-5-hepten-2-one; several large-scale processes have been developed for synthesizing this compound:
 - (a) Addition of acetylene to acetone results in the formation of 2-methyl-3-butyne-2-ol, which is hydrogenated to 2-methyl-3-buten-2-ol in the presence of a palladium catalyst. This product is converted into its acetoacetate derivative with diketene [38] or with ethyl acetoacetate [39]. The acetoacetate undergoes rearrangement when heated (Carroll reaction) to give 6-methyl-5-hepten-2-one:



- (b) In another process, 6-methyl-5-hepten-2-one is obtained by reaction of 2-methyl-3-buten-2-ol with isopropenyl methyl ether followed by a Claisen rearrangement [40]:

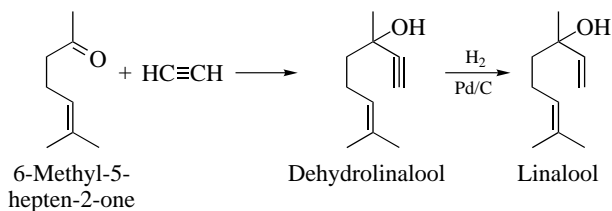


- (c) A third synthesis starts from isoprene, which is converted into 3-methyl-2-butenyl chloride by addition of hydrogen chloride. Reaction of the chloride with acetone in the presence of a catalytic amount of an organic base [41] leads to 6-methyl-5-hepten-2-one:



- (d) In another process, 6-methyl-5-hepten-2-one is obtained by isomerization of 6-methyl-6-hepten-2-one [42]. The latter can be prepared in two steps from isobutylene and formaldehyde. 3-Methyl-3-buten-1-ol is formed in the first step [43] and is converted into 6-methyl-6-hepten-2-one by reaction with acetone [44].

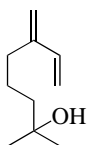
6-Methyl-5-hepten-2-one is converted into linalool in excellent yield by base-catalyzed ethynylation with acetylene to dehydrolinalool [45]. This is followed by selective hydrogenation of the triple bond to a double bond in the presence of a palladium carbon catalyst.



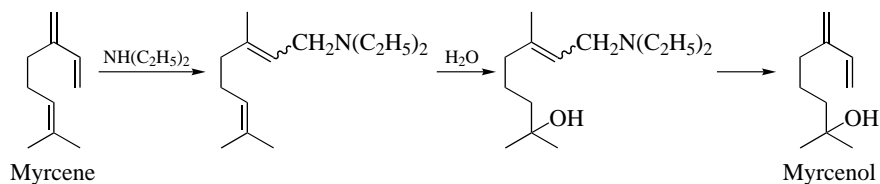
Uses. Linalool is used frequently in perfumery for fruity notes and for many flowery fragrance compositions (lily of the valley, lavender, and neroli). Because of its relatively high volatility, it imparts naturalness to top notes. Since linalool is stable in alkali, it can be used in soaps and detergents.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

FCT 1975 (13) p. 827.

Myrcenol [543-39-5], 2-methyl-6-methylene-7-octen-2-ol



$C_{10}H_{18}O$, M_r 154.25, $bp_{6.7\text{kPa}}$ 78 °C, d_{20}^{20} 0.8711, n_D^{20} 1.4731, is an isomer of geraniol and linalool. It has been identified in Chinese lavender oil [46] 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).

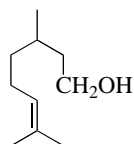


Myrcenol can be prepared by treating myrcene with diethylamine to give a mixture of geranyl- and neryldiethylamine. These compounds are hydrated with a dilute acid to the corresponding hydroxydiethylamines. Deamination to myrcenol is effected by using a palladium-phosphine-cation complex as a catalyst [47].

Myrcenol is used in perfumery to obtain a lifting top note in citrus and lavender compositions. It is mainly important in the production of 4-(4-hydroxy-4-methylpentyl)-3-cyclohexenecarboxaldehyde (see p. 83).

FCT 1976 (14) p. 617.

Citronellol [26489-01-0], 3,7-dimethyl-6-octen-1-ol



$C_{10}H_{20}O$, M_r 156.27, $bp_{101.3\text{kPa}}$ 224.4 °C, d_{20}^{20} 0.8590, 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.

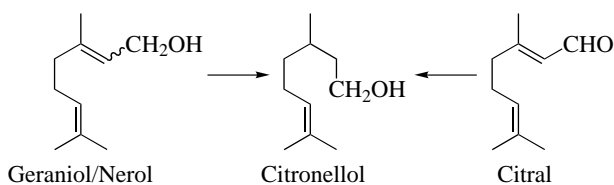
In many natural products citronellol occurs as a mixture of its two enantiomers; the pure (+) or (–) form is seldom found. (+)-Citronellol dominates in oils from *Boronia citriodora* (total citronellol content ca. 80%) and *Eucalyptus citriodora* (citronellol content 15–20%). (–)-Citronellol is the predominant 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. 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 [48].
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 [49].

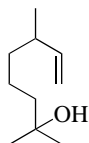


4. *Preparation of (–)-Citronellol from Optically Active Pinenes.* (+)-*cis*-Pinane is readily synthesized by hydrogenation of (+)- α -pinene or (+)- β -pinene, and is then pyrolyzed to give (+)-3,7-dimethyl-1,6-octadiene. This compound is converted into (–)-citronellol (97% purity) by reaction with triisobutylaluminum or diisobutylaluminum hydride, followed by air oxidation and hydrolysis of the resulting aluminum alcoholate [50].

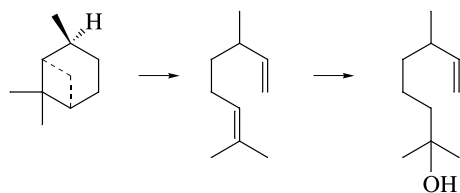
Uses. Citronellol is one of the most widely used fragrance materials, particularly for rose notes and for floral compositions in general. As flavor material, citronellol is added for bouqueting purposes to citrus compositions. It is the starting material for numerous citronellyl esters and for hydroxydihydrocitronellol,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

FCT 1975 (13) p. 757.

Dihydromyrcenol [18479-58-8], 2,6-dimethyl-7-octen-2-ol



$C_{10}H_{20}O$, M_r 156.27, $bp_{1.3\text{kPa}}$ 77–79 °C, d_4^{20} 0.841, is a colorless liquid with a fresh citrus-like odor and a lavender note. It is obtained from 3,7-dimethyl-1,6-octadiene (citronellene), the pyrolysis product of *cis*-pinane [51] and can be prepared by three different processes: (a) by addition of hydrogen chloride and subsequent hydrolysis of the resulting 2,6-dimethyl-2-chloro-7-octene [52]; or (b) by addition of formic acid and subsequent saponification of the resulting dihydromyrcenyl formate [52a]; or (c) by direct hydroxylation with 60–80% sulfuric acid [52b].



cis-Pinane

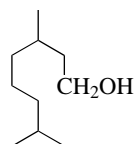
Citronellene

Dihydromyrcenol

Dihydromyrcenol is used in fine fragrances as well as in soap and detergent perfumes for fresh lime and citrusy-floral notes.

FCT 1974 (12) p. 525.

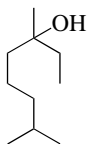
Tetrahydrogeraniol [106-21-8], 3,7-dimethyloctan-1-ol



$C_{10}H_{22}O$, M_r 158.28, $bp_{101.3\text{kPa}}$ 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. FCT 1974 (12) p. 535.

Tetrahydrolinalool [78-69-3], 3,7-dimethyloctan-3-ol



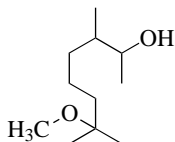
$C_{10}H_{22}O$, M_r 158.28, $bp_{1.3\text{kPa}}$ 78–79 °C, d_4^{20} 0.8294, n_D^{20} 1.4335, is a constituent of honey aroma. It is a colorless liquid with a linalool-like odor that is slightly fresher but distinctly weaker than that of linalool. Tetrahydrolinalool is prepared by catalytic hydrogenation of linalool and is used as a substitute for the less stable linalool in perfuming aggressive media. FCT 1979 (17) p. 909.

2,6-Dimethyl-2-octanol [18479-57-7], tetrahydromyrcenol

$C_{10}H_{22}O$, M_r 158.28, d_{25}^{25} 0.821–0.829, n_D^{20} 1.432–1.437, a colorless liquid with a fresh, citrus, lime-like floral odor. It may be used for all fragrance purposes, due to its high stability especially for perfuming household products like bleach cleaners. It is prepared by hydrogenation of dihydromyrcenol (see p. 33).

Trade Name. Tetralol (Millenium).

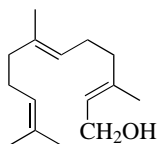
3,7-Dimethyl-7-methoxyoctan-2-ol [41890-92-0]



$C_{11}H_{24}O_2$, M_r 188.31, d_4^{20} 0.898–0.900, n_D^{20} 1.446–1.448, is a clear, almost colorless liquid with sandalwood odor, which has a flowery, woody note. It is not known to have been found in nature.

3,7-Dimethyl-7-methoxyoctan-2-ol is prepared by hydrochlorination of dihydromyrcene, methoxylation of the resulting 2-chloro-2,6-dimethyl-7-octene and epoxidation. The alcohol is obtained by hydrogenation of the epoxide in the presence of Raney nickel and triethylamine [53]. It is used in perfumery as a top note in high quality sandalwood compositions for cosmetics, toiletries, and soaps.

Trade Name. Osyrol (BBA).

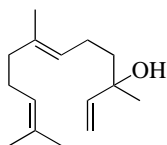
Farnesol [4602-84-0], 3,7,11-trimethyl-2,6,10-dodecatrien-1-ol*trans-trans*-
Farnesol

$C_{15}H_{26}O$, M_r 222.37, $bp_{1.6\text{kPa}}$ 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.

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 and deodorizing properties.

Nerolidol [7212-44-4], 3,7,11-trimethyl-1,6,10-dodecatrien-3-ol

$C_{15}H_{26}O$, M_r 222.37, $bp_{1.6\text{kPa}}$ 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 asymmetric.

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.

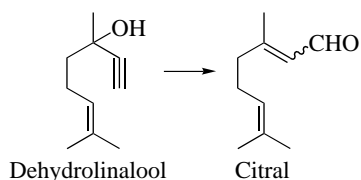
Industrial synthesis of nerolidol starts with linalool, which is converted into geranylacetone by using diketene, ethyl acetoacetate, or isopropenyl methyl ether, analogous to the synthesis of 6-methyl-5-hepten-2-one from 2-methyl-3-buten-2-ol. Addition of acetylene and partial hydrogenation of the resultant dehydronerolidol produces a mixture of *cis*- and *trans*-nerolidol racemates.

many other essential oils. The citrals are colorless to slightly yellowish liquids, with an odor reminiscent of lemon.

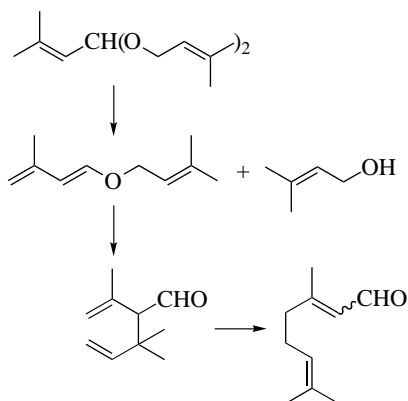
Since citral is an α,β -unsaturated aldehyde with an additional double bond, it is highly reactive and may undergo reactions such as cyclization and polymerization. Geraniol, citronellol, and 3,7-dimethyloctan-1-ol can be obtained from citral by stepwise hydrogenation. Citral can be converted into a 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 and from *Litsea cubeba* oil. 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 [54].
3. *Synthesis from Dehydrolinalool.* Dehydrolinalool is produced on a large scale from 6-methyl-5-hepten-2-one and acetylene and can be isomerized to citral in high yield by a number of catalysts. Preferred catalysts include organic orthovanadates [55], organic trisilyl oxyvanadates [56], and vanadium catalysts with silanols added to the reaction system [57].

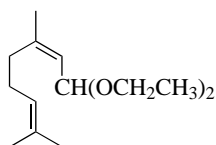


4. *Synthesis from Isobutene and Formaldehyde.* 3-Methyl-3-buten-1-ol, obtained from isobutene and formaldehyde [43], isomerizes to form 3-methyl-2-buten-1-ol [58]. However, it is also converted into 3-methyl-2-butenal by dehydrogenation and subsequent isomerization [59], [60]. Under azeotropic conditions in the presence of nitric acid, 3-methyl-2-buten-1-ol and 3-methyl-2-butenal form an acetal (shown below) [61], 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 [62]:



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. 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. FCT 1979 (17) p. 259.

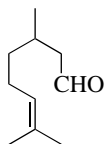
Citral diethyl acetal [7492-66-2], 1,1-diethoxy-3,7-dimethyl-2,6-octadiene



$C_{14}H_{26}O_2$, M_r 226.36, $bp_{2\text{kPa}}$ 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.

FCT 1983 (21) p. 667.

Citronellal [106-23-0], 3,7-dimethyl-6-octen-1-al



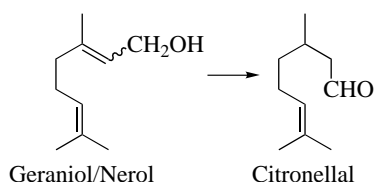
$C_{10}H_{18}O$, M_r 154.25, $bp_{101.3\text{kPa}}$ 207–208 °C, d_4^{20} 0.851, n_D^{20} 1.4477, $[\alpha]_D^{18} + 13.09^\circ$, $[\alpha]_D^{20} - 13.1^\circ$, occurs in essential oils in its (+) and (–) forms, often together with the racemate. (+)-Citronellal [2385-77-5] occurs in citronella oil at 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). Acid-catalyzed cyclization to isopulegol is an important step in the synthesis of (–)-menthol.

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

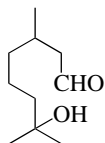
1. *Isolation from Essential Oils.* (+)-Citronellal is obtained from citronella oils by fractional distillation. (±)-Citronellal is isolated from *Eucalyptus citriodora* oil; when necessary, it is purified by using an addition compound, e.g., the bisulfite derivative.
2. *Synthesis from Geraniol or Nerol.* (±)-Citronellal can be obtained by vapor-phase rearrangement of geraniol or nerol in the presence of, e.g., a barium-containing copper–chromium oxide catalyst [63].



3. *Synthesis from Citronellol.* (±)-Citronellal can also be obtained by dehydrogenation of citronellol under reduced pressure with a copper chromite catalyst [64].
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 [65].

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.

FCT 1975 (13) p. 755.

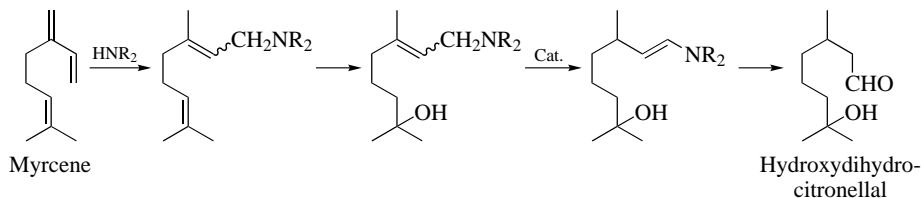
**7-Hydroxydihydrocitronellal [107-75-5], ‘hydroxycitronellal,’
3,7-dimethyl-7-hydroxyoctan-1-al**

$C_{10}H_{20}O_2$ M_r 172.27, $bp_{0.13\text{ kPa}}$ 85–87 °C, d_4^{20} 0.9220, n_D^{20} 1.4488, has been reported to occur in essential oils [66]. 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. Hydroxydihydrocitronellal prepared from (+)-citronellal, for example, has a specific rotation $[\alpha]_D^{20} + 9$ to $+10^\circ$.

Hydroxydihydrocitronellal 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 hydroxydihydrocitronellal 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 [67].
2. *Synthesis from Citronellol.* Citronellol 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 [68]; at atmospheric pressure noble metal catalysts can also be used [69].
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-hydroxyaldehyde enamine in the presence of a palladium(II)–phosphine complex as catalyst. Hydrolysis of the enamine gives 7-hydroxydihydrocitronellal [70].

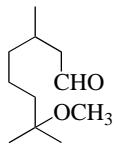


Uses. Because of its fine, flowery odor, hydroxydihydrocitronellal is used in large quantities in many perfume compositions for creating linden blossom and lily of the valley notes. It is also used in other blossom fragrances such as honeysuckle, lily, and cyclamen.

FCT 1974 (12) p. 921.

Trade Name. Laurinal (Takasago).

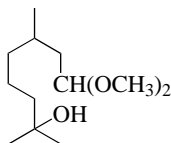
Methoxydihydrocitronellal [3613-30-7], **3,7-dimethyl-7-methoxyoctan-1-al**



$C_{11}H_{22}O_2$, M_r 186.29, $bp_{0.06\text{ kPa}}$ 60 °C, n_D^{25} 1.4380, is a colorless liquid with a fresh, green, blossom odor and is used in perfumery in floral compositions for fresh-green nuances.

FCT 1976 (14) p. 807.

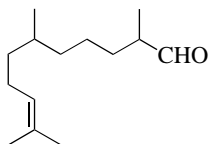
Hydroxydihydrocitronellal dimethyl acetal [141-92-4],
8,8-dimethoxy-2,6-dimethyloctan-2-ol



$C_{12}H_{26}O_3$, M_r 218.34, $bp_{1.6\text{ kPa}}$ 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.

FCT 1975 (13) p. 548.

2,6,10-Trimethyl-9-undecenal [141-13-9]



$C_{14}H_{26}O$, M_r 210.36, $bp_{1.2\text{ kPa}}$ 133–135 °C, d_{25}^{25} 0.840–0.853, 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 a hydrogenated pseudoionone (primarily the

tetrahydro compound) and an alkyl chloroacetate by means of a glycidic ester condensation; this is followed by hydrolysis and decarboxylation.

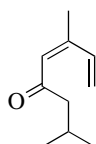
2,6,10-Trimethyl-9-undecenal is a richly fragrant substance that is used in flower compositions to obtain an aldehydic note.

FCT 1992 (30) p. 133 S.

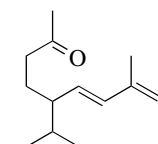
Trade Names. Adoxal (Giv.-Roure), Farenal (H&R).

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.



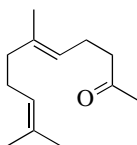
Tagetone



Solanone

6-Methyl-5-hepten-2-one 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 [1937-45-8] 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.

Geranylacetone [689-67-8], 6,10-dimethyl-5,9-undecadien-2-one



trans-Geranylacetone

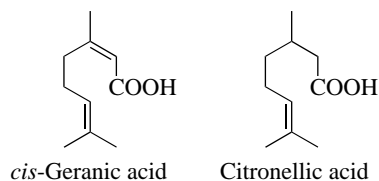
$C_{13}H_{22}O$, M_r 194.32, $bp_{1.3\text{kPa}}$ 124 °C, d_4^{20} 0.8729, n_D^{20} 1.4674, occurs in *cis* as well as *trans* form and has been identified in fruits and in essential oils. It is a colorless liquid with a fresh-green, slightly penetrating, roselike odor.

Geranylacetone is an intermediate in the synthesis of other fragrance substances. It is used in perfumery in rose compositions, for example, in soap perfumes.

FCT 1979 (17) p. 787.

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. 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

Geranyl formate [105-86-2]

$C_{11}H_{18}O_2$, M_r 182.26, $bp_{101.3\text{kPa}}$ 229 °C (decomp.), d_4^{25} 0.9086, 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.

FCT 1974 (12) p. 893.

Geranyl acetate [105-87-3]

$C_{12}H_{20}O_2$, M_r 196.29, $bp_{1.5\text{kPa}}$ 98 °C, d_4^{25} 0.9080, 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. FCT 1974 (12) p. 885.

Geranyl propionate [105-90-8]

$C_{13}H_{22}O_2$, M_r 210.32, $bp_{101.3\text{kPa}}$ 253 °C, d^{15} 0.902, n_D^{20} 1.459, has a fruity rose odor and is used in perfumery in heavy blossom fragrances with a secondary fruity note. FCT 1974 (12) p. 897.

Geranyl isobutyrate [2345-26-8]

$C_{14}H_{24}O_2$, M_r 224.34, $bp_{101.3\text{kPa}}$ 265 °C, d^{15} 0.8997, n_D^{20} 1.4576, is a liquid with a fruity rose odor. It is used in floral perfume compositions and in fruit flavors. FCT 1975 (13) p. 451.

Geranyl isovalerate [109-20-6]

$C_{15}H_{26}O_2$, M_r 238.37, $bp_{101.3\text{kPa}}$ 279 °C, $d^{15.5}$ 0.890, n_D^{20} 1.4640, is a liquid with a strongly fruity rose odor. It is used in perfume and flavor compositions. FCT 1976 (14) p. 785.

Neryl acetate [141-12-8]

$C_{12}H_{20}O_2$, M_r 196.29, $bp_{3.4\text{kPa}}$ 134 °C, d_{15}^{15} 0.903–0.907, 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). FCT 1976 (14) p. 625.

2.2.5.2 Linalyl and Lavandulyl Esters

Among the linalyl esters, 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, $bp_{1.3\text{kPa}}$ 100–103 °C, d_4^{25} 0.915, 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 eau de cologne. FCT 1975 (13) p. 833.

Linalyl acetate [115-95-7]

$C_{12}H_{20}O_2$ M_r 196.29, $bp_{101.3\text{kPa}}$ 220 °C, d_4^{20} 0.8951, n_D^{25} 1.4480, 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 [71]. 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 [34]. 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 [72].
2. Dehydrolinalool, obtained by ethynylation of 6-methyl-5-hepten-2-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 [73].

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, $bp_{101.3\text{kPa}}$ 226 °C, d^{15} 0.9000, 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.

FCT 1975 (13) p. 839.

Linalyl butyrate [78-36-4]

$C_{14}H_{24}O_2$, M_r 224.34, $bp_{101.3\text{kPa}}$ 232 °C, d^{15} 0.8977, 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.

FCT 1976 (14) p. 805.

Linalyl isobutyrate [78-35-3]

$C_{14}H_{24}O_2$, M_r 224.34, $bp_{0.02\text{ kPa}}$ 63–65 °C, d_4^{15} 0.8926, n_D^{25} 1.4450, 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.

FCT 1975 (13) p. 835.

Lavandulyl acetate [25905-14-0]

$C_{12}H_{20}O_2$, M_r 196.29, $bp_{1.7\text{ kPa}}$ 106–107 °C, d_4^{17} 0.9122, n_D^{17} 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 [74].

FCT 1978 (16) p. 805.

2.2.5.3 Citronellyl and Dihydromyrcenyl Esters

The following esters 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, $bp_{2\text{ kPa}}$ 97–98 °C, d_4^{15} 0.8919, 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.

FCT 1973 (11) p. 1073.

Citronellyl acetate [67650-82-2]

$C_{12}H_{22}O_2$, M_r 198.30, $bp_{101.3\text{ kPa}}$ 240 °C, d^{20} 0.8901, 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 eau 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.

FCT 1973 (11) p. 1069.

Citronellyl propionate [141-14-0]

$C_{13}H_{24}O_2$, M_r 212.33, $bp_{2\text{ kPa}}$ 120–124 °C, d_{15}^{15} 0.8950, 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.

FCT 1975 (13) p. 759.

Citronellyl isobutyrate [97-89-2]

$C_{14}H_{26}O_2$, M_r 226.36, $bp_{1.6\text{kPa}}$ 131–132 °C, d_{15}^{20} 0.8816, n_D^{20} 1.4418, is a liquid with a sweet-fruity note and is used in perfumery for fruity-floral nuances.

FCT 1978 (16) p. 693.

Citronellyl isovalerate [68922-10-1]

$C_{15}H_{28}O_2$, M_r 240.39, $bp_{4\text{kPa}}$ 194–196 °C, has a heavy, rosy-herbal odor and is used in oriental perfume compositions among others.

FCT 2000 (38, suppl. 3) p. S35.

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, $bp_{0.9\text{kPa}}$ 144–145 °C, d_{15}^{15} 0.9090, is a liquid with a flowery-rosy, fruity, mushroom-like odor. It is used in geranium oil reconstitutions.

FCT 2000 (38, suppl. 3) p. S37.

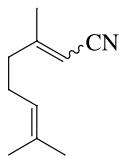
Dihydromyrcenyl acetate [53767-93-4], **2,6-dimethyl-7-octen-2-yl acetate**

$C_{12}H_{22}O_2$, M_r 198.31, is a colorless liquid, d_4^{20} 0.870–0.878, n_D^{20} 1.429–1.434 with a fresh, clean, citrus, floral odor (dihydromyrcenol see p. 31). It can be prepared by esterification of dihydromyrcenol with acetic acid in the presence of magnesium oxide as a catalyst [75]. It is used for flowery-citric topnotes, especially in soaps.

FCT 1983 (21) p. 847.

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 smaller than in the nonterpenoid 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.

Geranic acid nitrile [5146-66-7], **geranonitrile**

Geranic acid nitrile

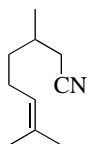
$C_{10}H_{15}N$, M_r 149.24, $bp_{1.3\text{kPa}}$ 110 °C, d^{20} 0.8709, n_D^{20} 1.4759, occurs as a mixture of its *cis* and *trans* isomers. It is a liquid with a crisp-fresh, lemon-like, green odor.

The nitrile can be prepared from citral by reaction with hydroxylamine and subsequent dehydration with acetic anhydride.

FCT 1976 (14) p. 787.

Trade Name. Citralva (IFF).

Citronellic acid nitrile [51566-62-2], citronellyl nitrile



Citronellic acid nitrile

$C_{10}H_{17}N$, M_r 151.25, $bp_{2\text{kPa}}$ 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.

FCT 1979 (17) p. 525.

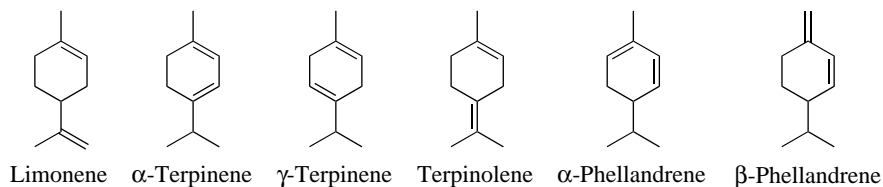
Trade Name. Agrunitril (Dragoco).

2.3 Cyclic Terpenes

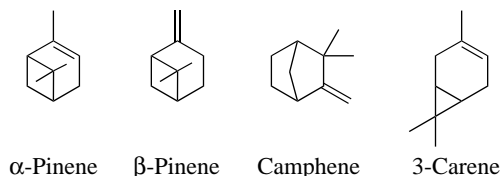
2.3.1 Hydrocarbons

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

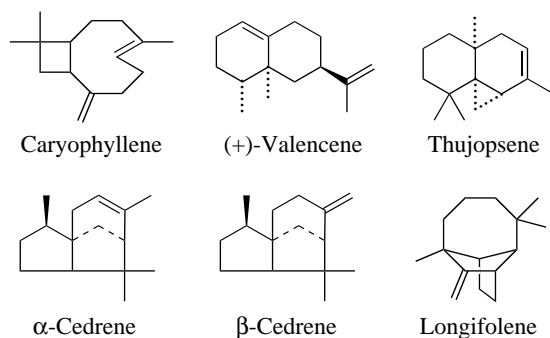
Of the various types of monocyclic terpene hydrocarbons, those with the *p*-menthadiene structure are the most important. Examples are as follows:



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 substances.

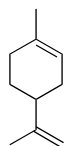


Many cyclic sesquiterpenes of various structural types have been isolated from essential oils. Typical examples are as follows:



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 substances or for the reconstitution of essential oils.

Limonene [138-86-3], 1,8-*p*-menthadiene



$C_{10}H_{16}$, M_r 136.24, $bp_{101.3\text{kPa}}$ 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 p. 61).

(+)-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 byproducts in many acid-catalyzed isomerizations of α - and β -pinene. Distillation of the so-called dipentene fraction yields limonenes in varying degrees of purity.

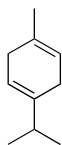
The limonenes are used as fragrance materials for perfuming household products and as components of artificial essential oils.

FCT 1975 (13) p. 825: (+)-limonene.

1978 (16) p. 809: (–)-limonene.

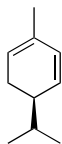
1974 (12) p. 703: (\pm)-limonene.

γ -Terpinene [99-85-4], 1,4-*p*-menthadiene



$C_{10}H_{16}$, M_r 136.24, $bp_{101.3\text{kPa}}$ 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. FCT 1976 (14) p. 875.

(–)- α -Phellandrene [4221-98-1], 1,5-*p*-menthadiene



$C_{10}H_{16}$, M_r 136.24, $bp_{99\text{kPa}}$ 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.

FCT 1978 (16) p. 843.

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 α -Pinene

$C_{10}H_{16}$, M_r 136.24, $bp_{101.3\text{kPa}}$ 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 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 [76]. 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. 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, borneol, and camphor.

FCT 1978 (16) p. 853.

 β -Pinene [127-91-3], 2(10)-pinene β -Pinene

$C_{10}H_{16}$, M_r 136.24, $bp_{101.3\text{kPa}}$ 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 is similar to α -pinene in its reactions. Pyrolytic cleavage 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.

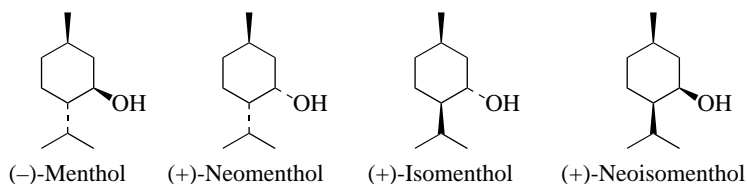
FCT 1978 (16) p. 859.

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 materials. 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 (Chapter 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 above; the other four are their mirror images.

(–)-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 [77]. (–)-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 racemates can be separated by fractional distillation. Boiling points (in °C at 101.3 kPa) are as follows:

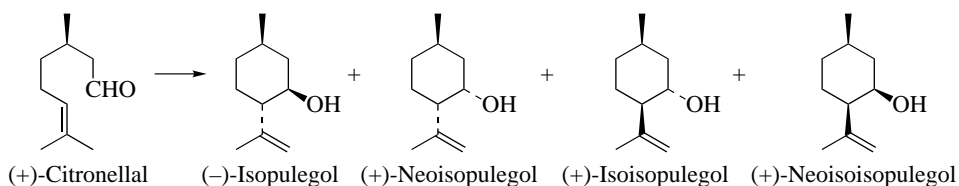
neomenthol	211.7
neoisomenthol	214.6
menthol	216.5
isomenthol	218.6

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

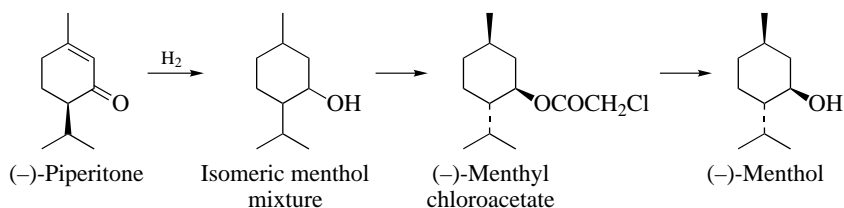
1. (–)-Menthol from Cornmint Oil. *Mentha arvensis* oils, which may contain 70–80% free (–)-menthol, are cooled and the crystals separated by centrifugation. Since the crystalline product contains traces of cornmint oil, this menthol has a slightly herbaceous-minty note. Pure (–)-menthol is obtained 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. Alternatively, it can be synthesized with a purity of 98% from dialkylgeranylamine (obtained from myrcene and a dialkylamine) by enantioselective isomerization to (+)-citronellaldialkylamine followed by hydrolytic cleavage to (+)-citronellal. Isomerization is effected in the presence of a chiral rhodium–phosphine complex as a catalyst [78]. (+)-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 [79].

However, 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.



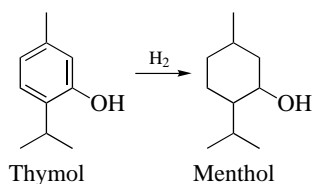
Analogously, (+)-*trans*-piperitol (obtained from α - or β -phellandrene via piperityl chloride [80]) can be hydrogenated to give a mixture of 97% (+)-isomenthol and 3% (+)-menthol. Pure (+)-isomenthol is obtained by crystallization and undergoes rearrangement to give an equilibrium mixture of (+)-neomenthol 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 [81].

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.

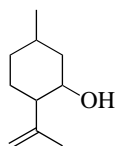
(b) (±)-Menthol can be resolved into its optical antipodes by several routes. A large-scale industrial process utilizes selective crystallization of either (+)- or (–)-menthyl benzoate by seeding saturated solutions or supercooled melts of (±)-menthyl benzoates with crystals of (+)- or (–)-menthyl benzoate. Pure (+)- or (–)-menthol is obtained following hydrolysis of the esters [82]. The undesired (+)-menthol can be reconverted into the racemate. Biochemical resolution methods have also been developed.

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.

FCT 1976 (14) p. 471: (–)-menthol.

1976 (14) p. 473: (±)-menthol.

Isopulegol, 8-*p*-menthen-3-ol



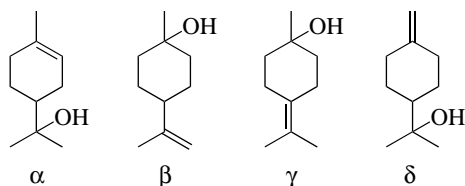
$C_{10}H_{18}O$, M_r 154.25, pure (–)-isopulegol [89-79-2], $bp_{1\text{ kPa}}$ 74 °C, d_4^{26} 0.9062, n_D^{26} 1.4690, $[\alpha]_D^{26} - 23.6^\circ$. Like menthol, isopulegol has three asymmetric carbon atoms and, therefore, four stereoisomers, each occurring as a pair of optically active antipodes.

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. FCT 1975 (13) p. 823.

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



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 (\pm)- 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

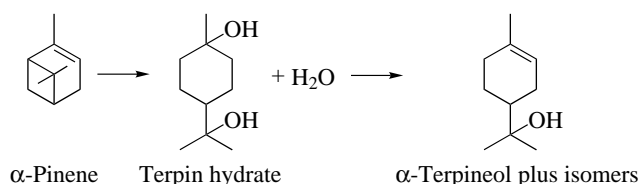
$C_{10}H_{18}O$, M_r 154.25, mp (enantiomers) 40–41 °C, mp (racemate) 35 °C, $bp_{101.3\text{ kPa}}$ 218–219 °C, d_4^{20} 0.9357, n_D^{20} 1.479, $[\alpha]_D + 106.4^\circ$ (solution in ether, 4%) is a colorless, crystalline solid, smelling of lilac. The most important commercial grade of terpineol consists 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 [83].

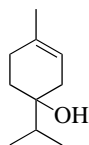


Selective conversion of pinene, 3-carene, and limonene or dipentene to terpineol, without terpin hydrate formation, is also used. Addition of organic acids (weak acids require catalytic amounts of mineral acids) produces terpinyl esters, which are subsequently hydrolyzed to terpineol, sometimes *in situ*.

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

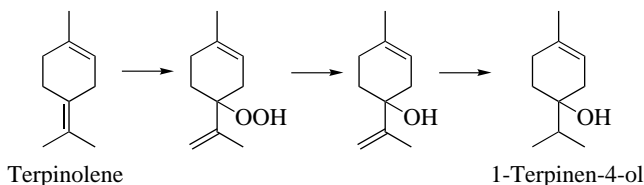
FCT 1974 (12) p. 997.

1-Terpinen-4-ol [562-74-3], 1-*p*-menthen-4-ol



$C_{10}H_{18}O$, M_r 154.25, $bp_{101.3\text{kPa}}$ 212 °C, $bp_{0.5\text{kPa}}$ 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.

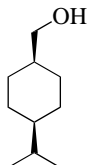
1-Terpinen-4-ol is a byproduct in the synthesis of terpineol from terpin hydrate, and occurs in commercial terpineol. Pure 1-terpinen-4-ol can be prepared from terpinolene by photosensitized oxidation, reduction of the resulting 1-methyl-4-isopropenyl-1-cyclohexene-4-hydroperoxide, and selective hydrogenation of the corresponding alcohol [84].



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

FCT 1982 (13) p. 833.

***cis*-Hexahydrocuminyll alcohol [13828-37-0], *p*-menthan-7-ol**



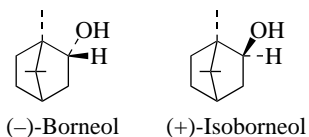
$C_{10}H_{20}O$, M_r 156.27, d_{20}^{20} 0.912–0.920, n_D^{20} 1.466–1.471 is a colorless liquid with a fresh soft and clean floral odor which recalls the fragrance associated with the white petals and blossoms of many flowers.

The title compound can be obtained by epoxidizing β -pinene (see p. 49) with peracetic acid, cleaving the oxirane ring by treating the epoxide with diatomaceous earth and reducing the resulting mixture over Raney nickel. The *cis*- and *trans*-isomer mixture is separated by distillation [85]. Because of its excellent stability the compound can be used in a wide range of products, e.g., soaps, detergents, cosmetics.

Trade Name. Mayol (Firmenich).

Borneol, 2-bornanol

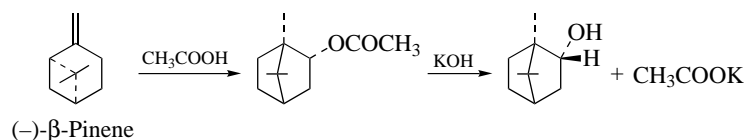
$C_{10}H_{18}O$, M_r 154.25, mp (enantiomers) 208 °C, mp (racemate) 210.5 °C, d_4^{20} 1.011, $[\alpha]_D^{20}$ + or – 37.7°, is a bicyclic terpene alcohol. Borneol is an endo isomer; the corresponding exo isomer is isoborneol [124-76-5]:



Borneol 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.

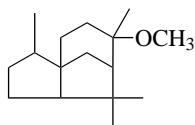
Borneol is oxidized to camphor with chromic or nitric acid; dehydration with dilute acids yields camphene. Borneol is readily esterified with acids, but on an industrial scale bornyl esters are prepared by other routes. For example, levorotatory borneol is synthesized industrially from levorotatory pinenes by Wagner–Meerwein rearrangement with dilute acid, followed by hydrolysis of the resulting esters [86].



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

FCT 1978 (16) p. 655: (–)-borneol.

Cedryl methyl ether [19870-74-7] and [67874-81-1]



$C_{16}H_{28}O$, 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.

FCT 1979 (17) p. 747.

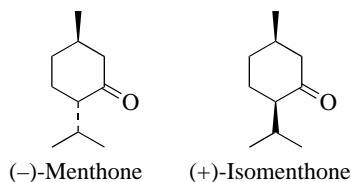
Trade Names. Cedramber (IFF) Cedranfix (Charabot).

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 substances. A few of the cyclic terpene ketones are commercially important as fragrance and flavor substances, 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). 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.

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 means of 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.

(\pm)-Menthone is prepared analogously from (\pm)-menthol. However, it can also be synthesized by hydrogenation of thymol in the presence of palladium-carbon catalysts [87].

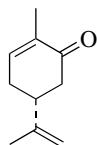
Table 1. Physical properties of industrially important menthone isomers

Compound	CAS registry number	bp , °C	d_4^{20}	n_D^{20}	$[\alpha]_D$
(-)-Menthone	[14073-97-3]	210	0.896*	1.450	-28.5°
(\pm)-Menthone	[1074-95-9]	210	0.896*	1.450	
(+)-Isomenthone	[1196-31-2]	212	0.900**	1.453	+95.0°
(\pm)-Isomenthone	[36977-92-1]	212	0.900**	1.453	

* $t = 20^\circ\text{C}$, ** $t = 4^\circ\text{C}$

Menthone and isomenthone are used for synthetic peppermint oils and bases. FCT 1976 (14) p. 475: (\pm)-menthone.

Carvone, 1,8-*p*-menthadien-6-one

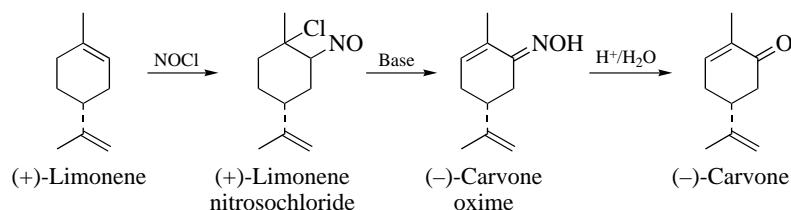


$C_{10}H_{14}O$, M_r 150.22, $bp_{101.3\text{kPa}}$ 230°C , d_4^{20} 0.960, n_D^{20} 1.499, $[\alpha]_D^{18}$ (+)-carvone $+64.3^\circ$, $[\alpha]_D^{20}$ (-)-carvone -62.5° , occurs as (+)-carvone [2244-16-8], (-)-carvone [6485-40-1], or racemic carvone [22327-39-5]. The optical isomers differ considerably in their sensory 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 a 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 synthetically, 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 [88].

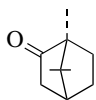


Uses. Both (+)- and (–)-carvone are used to flavor a number of foods and beverages. (–)-Carvone is produced in much larger quantities and is also used in oral hygiene products.

FCT 1978 (16) p. 673: (+)-carvone.

1973 (11) p. 1057: (–)-carvone.

Camphor, 1,7,7-trimethylbicyclo[2.2.1]heptan-2-one



(+)-Camphor

$C_{10}H_{16}O$, M_r 152.24, (+)-camphor: $bp_{101.3\text{kPa}}$ 204 °C, mp 178.8 °C, $[\alpha]_D^{20} + 44.3^\circ$; 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 is produced by fractional distillation and crystallization of camphor oil or, synthetically, by dehydrogenation of isoborneol (from isobornyl acetate, see p. 73) 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.

FCT 1978 (16) p. 665.

Fenchone, 1,3,3-trimethylbicyclo[2.2.1]heptan-2-one



(+)-Fenchone

$C_{10}H_{16}O$ M_r 152.24, $bp_{101.3\text{kPa}}$ 193 °C, d_4^{20} 0.9484, n_D^{20} 1.4628, $[\alpha]_D^{20} +$ or $- 66.8^\circ$, occurs as its (–)-isomer in a number of fennel oils. It is a colorless, slightly viscous liquid with a camphoraceous odor.

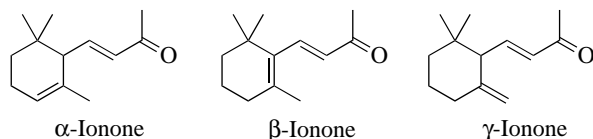
(+)-Fenchone [7787-20-4] containing a small amount of the (–)-isomer [4695-62-9] is prepared by dehydrogenation of (–)-fenchol. (–)-Fenchyl esters are obtained, along with other compounds, by addition of carboxylic acids to α -pinene. Hydrolysis of the esters yields (–)-fenchol.

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

FCT 1976 (14) p. 769.

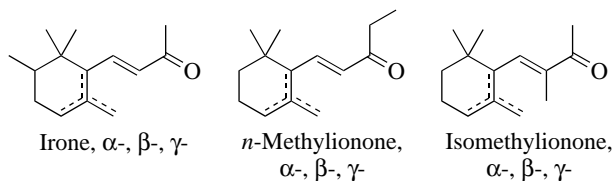
Ionones and Homologous Compounds

The C₁₃ ketones α - and β -ionone are cyclic terpenoids that occur in many essential oils. However, being metabolites of the corresponding carotenoids [89], they occur in only small amounts. A third isomer, γ -ionone, has not yet been observed in nature.



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*).



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 [90].

All ionones, irones, and methylionones, as well as the corresponding pseudo-compounds (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. 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

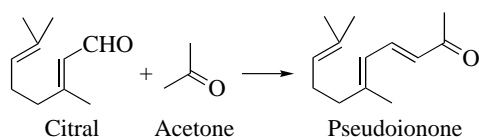
Name	Formula	CAS registry number	M_r	bp °C (p , kPa)	d_4^{20}	n_D^{20}	Odor
α -Ionone	$C_{13}H_{20}O$	[127-41-3]	192.30	121-122 (1.3)	0.9319	1.4982	sweet-floral, reminiscent of violets
β -Ionone	$C_{13}H_{20}O$	[79-77-6]	192.30	121.5 (0.93)	0.9461	1.5202	reminiscent of cedarwood, violet-like upon dilution
γ -Ionone	$C_{13}H_{20}O$	[76-76-5]	192.30	82 (0.16)	0.9317	1.4985	violet-like with woody-resinous tonality (intermediate in the synthesis of γ -dihydro-ionone, 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 - <i>n</i> -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 - <i>n</i> -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	1.5033	interesting, powdery, orris-like odor with slightly woody aspects
Allylionone	$C_{16}H_{24}O$	[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} .

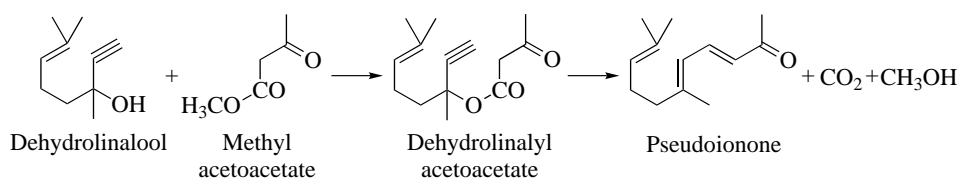
With Raney nickel–copper chromite catalysts, methylionones are converted into tetrahydromethylionols, which are also used as fragrance materials [91].

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.

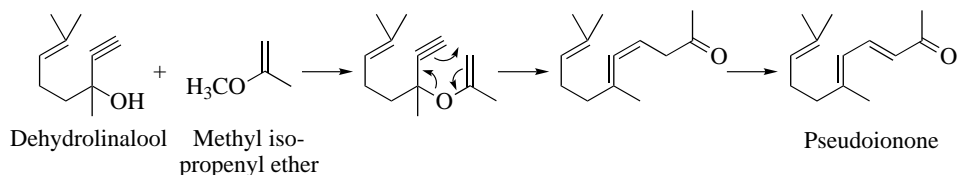
In all processes an acyclic precursor, called a pseudoionone, pseudoirone, etc., is prepared by base-catalyzed condensation of citral or 6-methylcitral with acetone, methyl ethyl ketone, or allylacetone, as appropriate.



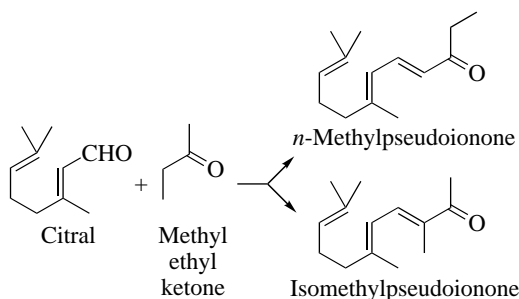
In the synthesis of vitamin A, the dependence on natural sources as well as steadily increasing production via β -ionone as an intermediate have led to the development of a method for synthesizing citral from dehydrolinalool (see p. 37). More recent routes employ dehydrolinalool as the starting material for pseudoionone. Dehydrolinalool is converted into pseudoionone by using either diketene [92] or a suitably substituted acetoacetate (Carroll reaction) [93]:



A milder reaction for synthesizing pseudoionone from dehydrolinalool is transesterification with an alkoxyalkene [94]:



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.



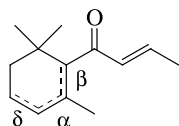
The ratio of the major isomers in the mixture depends on the condensation catalyst and the reaction conditions. In the presence of common alkaline catalysts (e.g., sodium hydroxide), straight-chain isomers are formed preferentially. Strongly alkaline catalysts, such as quaternary ammonium bases, favor the formation of isomethylpseudoionone [95]. 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 [96]. 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 [97]; 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.

FCT 1975 (13) p. 549: Ionone,
p. 551: α -Irone,
p. 863: Methylionone.

Damascones, 1-(2,6,6-trimethylcyclohexenyl)-2-buten-1-ones

$C_{13}H_{20}O$, M_r 192.30, are ionone isomers. Depending on the position of the double bond in the ring, various isomers may exist. Commercially important are α -, β - and δ -damascone.



Although having very similar structures, the different isomers show very different sensory properties and lead to very different effects when used in fragrance and flavour compositions.

α -Damascone, 1-(2,6,6-trimethyl-2-cyclohexenyl)-2-buten-1-one [43052-87-5]; (Z)-: [23726-94-5]; (E)-: [24720-09-0]

$C_{13}H_{20}O$, M_r 192.30, d_{20}^{20} 0.932–0.938, n_D^{20} 1.493–1.499, is a colorless to pale yellow liquid with a very diffusive floral fruity note. α -Damascone occurs in the natural flavor of tea and tobacco.

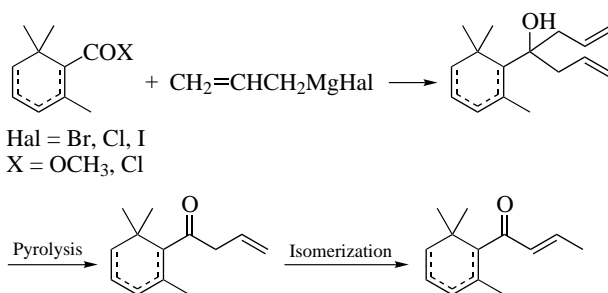
FCT 2000 (38, suppl. 3) p. S199. FEMA GRAS 3659.

β -Damascone, 1-(2,6,6-trimethyl-1-cyclohexenyl)-2-buten-1-one [35044-68-9]; (Z)-: [23726-92-3]; (E)-: [24726-91-2]

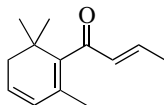
$C_{13}H_{20}O$, M_r 192.30, d_{20}^{20} 0.936–0.942, n_D^{20} 1.496–1.501, is a colorless to pale yellow liquid with a very powerful floral complex fruity note reminiscent of plum, rose and blackcurrant. β -Damascone is found as a volatile constituent of many natural materials, e.g., in rose oils and extracts.

FCT 2000 (38, suppl. 3) p. S205. FEMA GRAS 3243.

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 obtained by rearrangement of the double bond in the side-chain [98].



The α - and β -damascones are used in perfume compositions, especially rose perfumes, and in flavor compositions, to which they impart naturalness and body.

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, to the flavor of which it contributes an important role 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.

FCT 2000 (38, suppl. 3) p. S189.

 δ -Damascone, 1-(2,6,6-trimethyl-3-cyclohexenyl)-2-buten-1-one [57378-68-4];

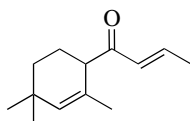
(*E*)-1 α ,2 β -: [71048-82-3]

$C_{13}H_{20}O$, M_r 192.30, d_{25}^{25} 0.926–0.934, n_D^{20} 1.489–1.494, is a colorless to slightly yellow liquid with a very diffusive fruity black currant odor. It has not been reported to occur in nature.

The material is prepared by Diels–Alder reaction of 1,3-pentadiene and mesityl oxide and subsequent aldol condensation of the resulting acetyl trimethyl cyclohexene with acetaldehyde [99]. δ -Damascone is used in perfumes to create masculine notes.

FCT 2000 (38, suppl. 3) p. S211. FEMA GRAS 3622.

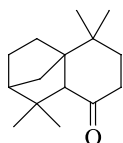
Trade Name. Delta Damascone (IFF).

1-(2,4,4-Trimethyl-2-cyclohexen-1-yl)-2-buten-1-one [39872-57-6]

$C_{13}H_{20}O$, M_r 192.30, d_4^{20} 0.917–0.925, n_D^{20} 1.485–1.493, is a colorless to slightly yellow liquid with a highly diffusive fruity-flowery odor. It is prepared from 1,5,5-trimethyl-1-cyclohexene by reaction with crotonic anhydride in the presence of catalysts [100].

It is used in perfumery for soaps, cosmetics, and toiletries to give naturalness and freshness.

Trade Name. Isodamascon (Dragoco).

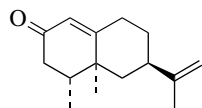
1,3,4,6,7,8a-Hexahydro-1,1,5,5-tetramethyl-2H-2,4a-methanonaphthalen-8(5H)-one
[23787-90-8]

$C_{15}H_{24}O$, M_r 220.36, a colorless liquid, d_{25}^{25} 0.997–1.005, n_D^{20} 1.498–1.503, with a dry woody, earthy-camphoraceous patchouly odor. Major use is in perfume oils for soaps and fabric detergents.

The material is not reported to occur in nature. It is prepared by oxidation of isolongifolene with a peroxide under acidic conditions, e.g., with hydrogen peroxide in formic acid [100a].

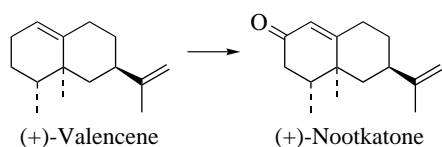
FCT 1983 (21), p. 859.

Trade Names. Isolongifolanone (Quest), Piconia (IFF), Valanone B (BBA).

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.

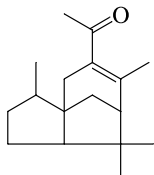


Nootkatone is used for flavoring beverages.
FCT 2000 (38, suppl. 3) p. S165.

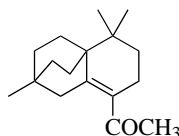
Cedryl methyl ketone

$C_{17}H_{26}O$, 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. 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 cedryl methyl ketone [32388-55-9], which results from the acetylation of α -cedrene. The odor-determining constituent is the so-called isomer G with a content of 5–10% which is formed by acetylation from thujopsene after rearrangement [100b, 100c], [32388-56-0]:



Cedryl methyl ketone/Acetylcedrene



'Isomer G'

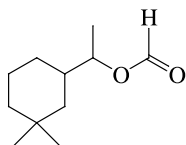
FCT 1978 (16) p. 639.

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

2.3.4 Esters

Esters mainly 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.

α ,3,3-Trimethylcyclohexane-1-methanol formate [25225-08-5]

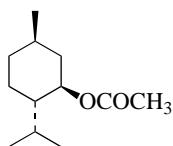


$C_{11}H_{20}O_2$, M_r 182.28, is a colorless liquid, d_{25}^{25} 0.935–0.943, n_D^{20} 1.445–1.453, with a fresh woody, herbal, seashore-like odor. It is used to create modern herbaceous top notes in perfume oils for nearly all applications.

The material is prepared by reaction of 3,7-dimethyl-1,6-octadiene (citronellene, see p. 33) with formic acid under acid catalysis [100d].

Trade Name. Aphermate (IFF).

(–)-Menthyl acetate [2623-23-6], **(–)-*p*-menthan-3-yl acetate**



$C_{12}H_{22}O_2$, M_r 198.30, $bp_{3\text{ kPa}}$ 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.

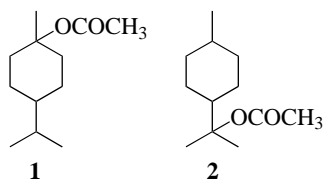
FCT 1976 (14) p. 477.

(±)-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.

FCT 1976 (14) p. 479.

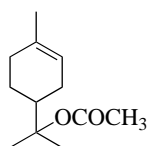
Menthanyl acetate, dihydroterpinyl acetate [58985-18-5]



$C_{12}H_{22}O_2$, M_r 198.30, $bp_{0.2\text{ kPa}}$ 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 (1) and *p*-menthan-8-yl (2) acetates. 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 [101]) or by esterification of a mixture of isomeric *p*-menthanols.

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**



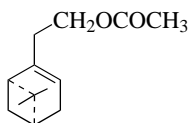
$C_{12}H_{20}O_2$, M_r 196.29, $bp_{5.3\text{ kPa}}$ 140 °C, d_4^{20} 0.9659, n_D^{21} 1.4689, $[\alpha]_D^{20}$ of the enantiomers + or – 79°; the enantiomers and the racemate occur in many essential oils (e.g., Siberian pine-needle oil and cypress oil), but generally not as the main component. Pure 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.

FCT 1974 (12) p. 999.

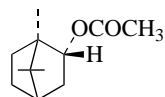
Nopyl acetate [35836-72-7], (–)-2-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-ethyl acetate



$C_{13}H_{20}O_2$, M_r 208.30, $bp_{1.5\text{kPa}}$ 122 °C, d_4^{20} 0.9811, n_D^{20} 1.4733, $[\alpha]_D - 30.9^\circ$, is not found in nature and has a fresh-fruity-woody odor. It 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.
FCT 1974 (12) p. 943.

Bornyl acetate, 2-endo-bornanyl acetate

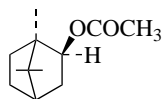


(–)-Bornyl acetate

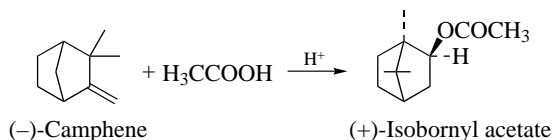
$C_{12}H_{20}O_2$, M_r 196.29, $bp_{101.3\text{kPa}}$ 223–224 °C, d_4^{20} 0.9838, n_D^{20} 1.4630, $[\alpha]_D^{20} +$ or -44.4° , mp (+) and (–) forms 29 °C, occurs in its optically active forms and as a racemate in many essential oils.

(–)-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 p. 59).

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**

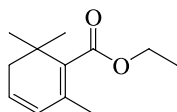
$C_{12}H_{20}O_2$, M_r 196.29, $bp_{1.6-1.7\text{kPa}}$ 102–103 °C, d_4^{20} 0.9841, n_D^{20} 1.4640, has been identified in a number of essential oils. It is a colorless liquid with a pleasant, pine-needle odor. Isobornyl acetate is prepared from camphene and acetic acid in the presence of acidic catalysts (e.g., sulfuric acid) [102], or on a styrene-divinylbenzene acid ion-exchanger [103].



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.

FCT 1975 (13) p. 552.

Ethyl 2,6,6,trimethyl-1,3-cyclohexadiene-1-carboxylate [35044-59-8]; the commercial quality also contains the α - [35044-57-6] and γ -isomers isomers [35044-58-7]



$C_{12}H_{18}O_2$, M_r 194.28, d_{20}^{20} 0.962–0.972, n_D^{20} 1.474–1.481, is a colorless to slightly yellow liquid with a natural rose odor with aspects of apple cider and woody cedar. It is recommended for use in floral and fruity fragrances for shampoos, toiletries and detergents.

The preparation of the material starts from of mesityl oxide and ethyl acetoacetate which are cyclized under acidic conditions. The resulting ethyl 4-oxo-2,6,6-trimethyl-2-cyclohexenecarboxylate is subsequently reduced and dehydrated.

FCT 2000 (38, suppl. 3) p. S93.

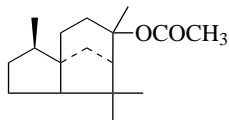
Trade Name. Ethyl Safranate (Quest).

Guaiyl acetate

$C_{17}H_{28}O_2$, M_r 264.41, $bp_{0.3\text{kPa}}$ 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). Guaiyl acetate is a yellow to amber liquid with a weak but lasting, woody odor. It is used in perfumery for tea-rose and wood nuances. FCT 1974 (12) p. 903.

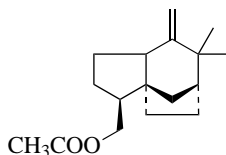
Cedryl acetate [77-54-3]



$C_{17}H_{28}O_2$, M_r 264.41, $bp_{0.4\text{kPa}}$ 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 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. FCT 1974 (12) p. 847.

Vetiveryl acetate [62563-80-8]

$bp_{0.3\text{kPa}}$ 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].



Khusimyl acetate

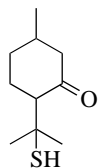
Vetiveryl acetate is prepared by esterification of the sesquiterpene alcohols isolated from vetiver oils.

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.

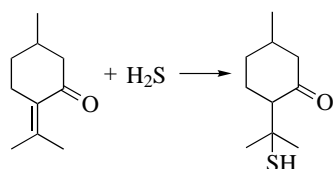
FCT 1974 (12) p. 1011.

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 materials.

8-Mercapto-*p*-menthan-3-one [38462-22-5]

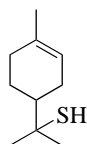
$C_{10}H_{18}OS$, M_r 186.31, bp_{1Pa} 57 °C, d_{20}^{20} 1.002–1.007, n_D^{20} 1.493–1.497, is an essential odoriferous constituent of buchu leaf oil. The commercial product is synthesized from pulegone and is a liquid mixture of *cis*–*trans* isomers with a typical blackcurrant odor. 8-Mercapto-*p*-menthan-3-one is prepared by reacting pulegone with hydrogen sulfide in the presence of a base (e.g., triethylamine) [104]:



Pulegone

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

Trade Name. Sulfox (Firmenich).

1-*p*-Menthene-8-thiol [71159-90-5]

$C_{10}H_{18}S$ M_r 170.31, $bp_{0.13Pa}$ 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} $\mu\text{g}/\text{kg}$ for the (+)-*R* and 8×10^{-5} $\mu\text{g}/\text{kg}$ for the (–)-*S* isomer [105].

2.4 Other Cycloaliphatic Compounds

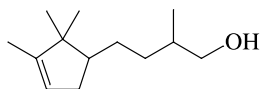
In addition to cyclic terpenoids, several other cycloaliphatic compounds have above-average importance as fragrance materials; some of them are structurally related to the terpenes.

Ketones are most widely represented and include cyclopentanone derivatives, such as the jasmin fragrance substances, and cyclic ketones with 15–17-membered carbon rings, such as muscone and civetone, which are constituents of the extremely expensive animal products, musk and civet. Cyclopentadecanone, a natural musk fragrance, and the unsaturated 5-cyclohexadecen-1-one, which has not yet been found in nature, have odor characteristics similar to those of muscone and civetone and are more easily synthesized. They are, therefore, often used as substitutes.

Some alicyclic alcohols are important as synthetic sandalwood fragrances. 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 and Ethers

2-Methyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)butanol [72089-08-8]



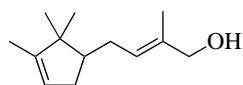
$C_{13}H_{24}O$, M_r 196.34, d_4^{20} 0.900–0.906, n_D^{20} 1.470–1.475, is a colorless liquid with a woody, tenacious sandalwood odor with a slight musk nuance. It is prepared by sequential aldol condensation of campholenaldehyde (2,2,3-trimethyl-3-cyclopenteneacetaldehyde, obtained by epoxidation of α -pinene and rearrangement of the epoxide) with propanal, hydrogenation and reduction [106].

It is used to perfume soaps and detergents.

FCT 2000 (**38, suppl. 3**) p. S157.

Trade Name. Brahmanol (Dragoco).

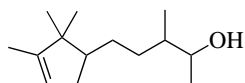
2-Methyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-buten-1-ol [28219-60-5]



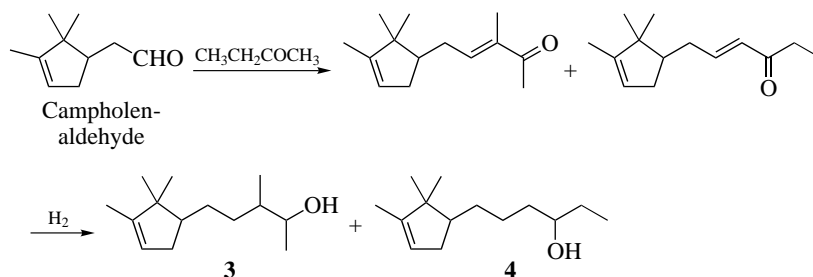
$C_{13}H_{22}O$, M_r 194.32, is not found in nature. It is a clear, colorless liquid, d_{20}^{20} 0.919–0.929, n_D^{20} 1.483–1.493, with a powerful sandalwood odor. It is prepared by condensation of campholenaldehyde with propionaldehyde and reduction of the formyl group.

It is used in perfume compositions for soaps and household products.

Trade Names. Sandalmysore Core (Kao), Sandelice (Cognis), Madrol (Dragoco).

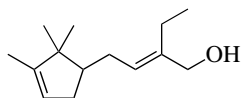
5-(2,2,3-Trimethyl-3-cyclopenten-1-yl)-3-methylpentan-2-ol [65113-99-7] (**3**)

$C_{14}H_{26}O$, M_r 210.36, d_4^{20} 0.896–0.904, n_D^{20} 1.470–1.476, is a sandalwood-like fragrance ingredient that does not occur in nature. It is prepared by condensation of campholenaldehyde with methyl ethyl ketone, followed by selective hydrogenation of the resulting unsaturated ketone [107].



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

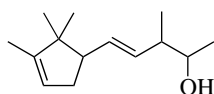
Trade Name. Sandalore (Giv.-Roure).

2-Ethyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-buten-1-ol [28219-61-6]

$C_{14}H_{24}O$, M_r 208.35, d_4^{20} 0.913–0.920, n_D^{20} 1.484–1.490, is a mixture of the *cis* and *trans* isomers. It does not occur in nature. It is a pale yellow liquid with a powerful sandalwood odor and a slight rose nuance. The mixture can be prepared starting from campholenaldehyde and butanal. The intermediate unsaturated aldehyde is partially hydrogenated to give the title alcohol.

It is used in perfume compositions for cosmetics, soaps and detergents. FCT 2000 (**38**, **suppl. 3**) p. S97.

Trade Names. Bacdanol (IFF), Bangalol (Quest), Sandolene (H&R), Sandranol (Dragoco).

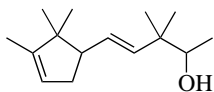
3-Methyl-5-(2,2,3-trimethyl-3-cyclopenten-1-yl)-4-penten-2-ol [67801-20-1]

$C_{14}H_{24}O$, M_r 208.35, is a mixture of isomers and not reported as being found in nature. It is a pale yellow liquid with a powerful woody, sandalwood odor with musk aspect. The mixture is obtained by condensation of campholenaldehyde with 2-butanone and isomerization of the reaction mixture with potassium *tert*-butylate in dimethyl formamide. Subsequent reduction with $NaBH_4$ yields a mixture of chiefly four diastereomeric title alcohols [108].

It is used in fine fragrances as well as in functional products.

Trade Name. Ebanol (Giv.-Roure).

3,3-Dimethyl-5-(2,2,3-trimethyl-3-cyclopenten-1-yl)-4-penten-2-ol [107898-54-4]

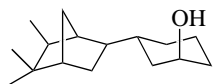


$C_{15}H_{26}O$, M_r 222.37, is not found in nature. It is a clear, colorless liquid, d_{25}^{25} 0.897–0.906, n_D^{20} 1.480–1.484, with a powerful, diffusive sandalwood odor and musk and cedarwood aspects. The compound is prepared starting from campholenaldehyde which is condensed with 2-butanone to give 3-methyl-5-(2,2,3-trimethyl-3-cyclopenten-1-yl)-3-penten-2-one. Methylation using phase transfer conditions gives the dimethylpentenone which is reduced with $NaBH_4$ to yield the title compound [109].

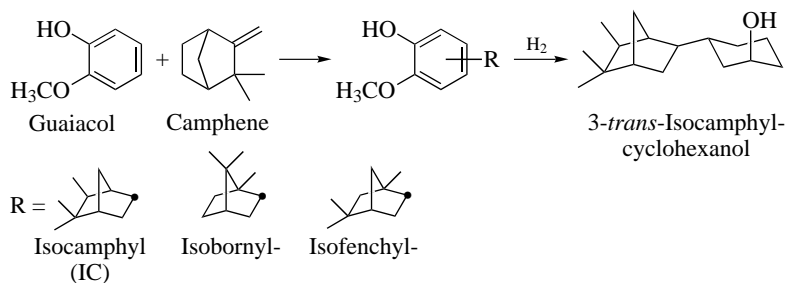
It is used in fine fragrances.

Trade Name. Polysantol (Firmenich).

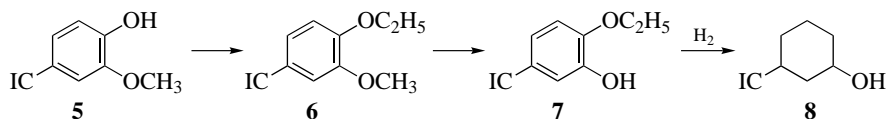
3-*trans*-Isocamphylcyclohexanol [4105-12-8]



$C_{16}H_{28}O$, M_r 236.40, does not occur in nature. It is the component responsible for the sandalwood odor of a synthetic mixture of terpenylcyclohexanol isomers. 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.



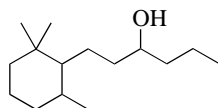
A process starting from catechol, instead of guaiacol, yields a mixture with a higher content of 3-*trans*-isocamphylcyclohexanol [110]. Moreover, the process starting from guaiacol has been improved by converting the main component formed in the first step, *p*-isocamphylguaiacol (**5**), into a mixed 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**) [111].



The mixture is used as such in large amounts as a replacement for sandalwood oil in soaps, cosmetics, and perfume compositions. FCT 1976 (**14**) p. 801.

Trade Names. Sandela (Giv.-Roure), Sandel H&R (H&R), IBCH (Rhodia), Santalex (Takasago), Candalum (Rhodia), Sandiff (IFF).

1-(2,2,6-Trimethylcyclohexyl)hexan-3-ol [70788-30-6]



$\text{C}_{15}\text{H}_{30}\text{O}$, M_r 226.41, $bp_{0.0133\text{ kPa}}$ 150 °C, d_4^{20} 0.896–0.902, n_D^{20} 1.470–1.476, is a colorless liquid with a highly diffusive, powdery-woody odor. It is a mixture of the *cis* and *trans* isomers. The *trans*-isomer has a more distinct animal and ambery character [112].

The title compound is prepared by condensation of citral (see p.36) with 2-pentanone in the presence of bases to give 8,12-dimethyltrideca-5,7,11-trien-4-one, which is cyclized and hydrogenated [113].

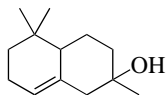
A high *trans*-mixture can be prepared starting from β -cyclocitral which is hydrogenated to 2,2,6-trimethylcyclohexane carboxaldehyde. Condensation with 2-pentanone in the presence of sodium ethoxide yields the corresponding 3-hexenone. Hydrogenation with nickel–copper chromite as a catalyst gives a mixture with up to 95% of the *trans*-isomer [114].

It is used in perfume compositions for soaps, detergents and household products.

FCT 2000 (38, suppl. 3) p. S219.

Trade Name. Timberol (Dragoco).

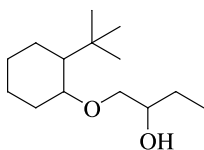
2,5,5-Trimethyl-1,2,3,4,4a,5,6,7-octahydronaphthalen-2-ol [41199-19-3], ambrinol



$C_{13}H_{22}O$, M_r 194.32, d_{20}^{20} 0.940–0.960, n_D^{20} 1.485–1.498, is a colorless to pale yellow liquid with an extremely powerful, amber, somewhat musty and animal odor. It is a constituent of ambergris (see p. 174). A synthesis starts with the thermolysis of β -ionone (see p. 63) which leads to dehydroambrinol. The title compound is obtained by hydrogenation over Raney nickel in methanolic solution [115].

It is used in small amounts in all perfume types for, for example, cosmetics, soaps, body care products, and detergents.

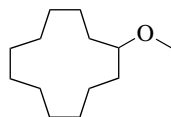
1-[[2-(1,1-Dimethylethyl)cyclohexyl]oxy]-2-butanol, [139504-68-0]



$C_{14}H_{28}O_2$, M_r 228.38, d_{20}^{20} 0.931–0.966, n_D^{20} 1.461–1.471, is a clear liquid with a typical woody amber odor. It is used as a woody fixative in many different perfume types with a wide range of applications.

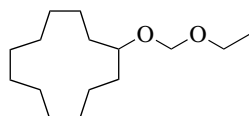
The material is prepared by reaction of 2-*tert*-butylcyclohexanol with sodium hydride and 1,2-epoxybutane [115a].

Trade Name. Amber Core (Kao).

Cyclododecyl methyl ether [2986-54-1], **methoxycyclododecane**

$C_{13}H_{26}O$, M_r 198.35, does not occur in nature. It is a clear, colorless to pale yellowish liquid, d_{25}^{25} 0.910–0.915, n_D^{20} 1.472–1.475, with a woody, cedarlike odor. It can be prepared from dodecanol sodium by reaction with methyl halogenide. It is used as a stable wood fragrance in technical perfumery.

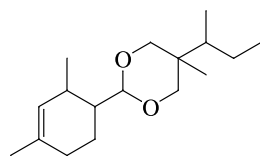
Trade Name. Palisandin (H&R).

(Ethoxymethoxy)cyclododecane [58567-11-6]

$C_{15}H_{30}O_2$, M_r 242.41, is not known in nature. It is a colorless liquid, $bp_{0.1 Pa}$ 94 °C, d_{25}^{25} 0.931, n_D^{20} 1.463–1.467, with a noble woody odor with ambergris nuances. It is prepared by reaction of cyclododecanol with paraformaldehyde/hydrochloric gas to give cyclododecyl chloromethyl ether which is treated with sodium ethylate [116]. (Ethoxymethoxy)cyclododecane is stable in alkaline media and can be used in perfume compositions for soaps and detergents.

FCT 1988 (26) p. 325.

Trade Name. Boisambrene forte (Cognis).

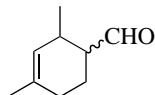
2-(2,4-Dimethyl-3-cyclohexenyl)-5-methyl-5-(1-methylpropyl)-1,3-dioxane
[117933-89-8]

$C_{17}H_{30}O_2$, M_r 266.43, d_{20}^{20} 0.960–0.966, n_D^{20} 1.478–1.484, a colorless liquid with a powerful and radiant woody amber odor of high tenacity. It is used to create special effects in fine fragrance perfume oils. The material is prepared by acetalization of 2,4-dimethyl-3-cyclohexene carboxaldehyde (see next chapter) with the corresponding diol [116a].

Trade Name. Karanal (Quest).

2.4.2 Aldehydes

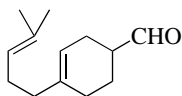
2,4-Dimethyl-3-cyclohexene carboxaldehyde [68039-49-6]



$C_9H_{14}O$, 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. Cyclal C (Giv.-Roure), Ligustral (Quest), Triplal (IFF), Vertocitral (H&R).

4-(4-Methyl-3-penten-1-yl)-3-cyclohexene carboxaldehyde [37677-14-8]

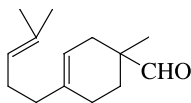


$C_{13}H_{20}O$, M_r 192.30, is prepared, together with its 3-isomer, by a Diels–Alder reaction of myrcene and acrolein. The mixture, d_4^{20} 0.927–0.935, n_D^{20} 1.488–1.492, has a fresh-fruity, slightly citrus-like odor and is used to perfume household products.

FCT 1976 (14) p. 803.

Trade Names. Empetal (Quest), Myrac aldehyde (IFF), Myraldene (Giv.-Roure), Vertomugal (H&R), Myrcenal (DRT).

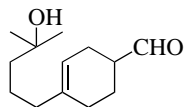
1-Methyl-4-(4-methyl-3-penten-1-yl)-3-cyclohexene carboxaldehyde [52474-60-9]



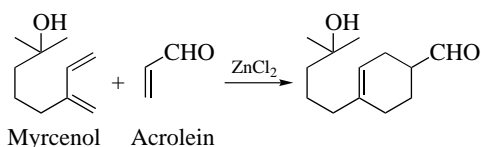
$C_{14}H_{22}O$, M_r 206.33, a colorless liquid, d_{25}^{25} 0.914–0.922, n_D^{20} 1.483–1.488, with an aldehydic ozone-like floral odor. It is used to create freshness in masculine perfume types, e.g., for use in fine fragrances, shower gels, and soaps. The materials prepared by Diels–Alder reaction of myrcene and methacrolein [116b]. A natural occurrence is not reported.

FCT 1976 (14), p. 803.

Trade Name. Precyclemone B (IFF).

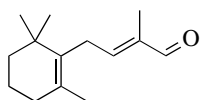
4-(4-Hydroxy-4-methylpentyl)-3-cyclohexene carboxaldehyde [31906-04-4]

$C_{13}H_{22}O_2$ M_r 210.32, $bp_{0.13\text{ kPa}}$ 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) [117]:



Reaction of myrcenol with acrolein at elevated temperatures, without a catalyst, yields a 70 : 30 mixture of the 4- and 3-substituted cyclohexene carboxaldehydes [118]. This mixture is a commercial product. The title compound has excellent fixative properties and is used especially in soap and cosmetics perfumery. FCT 1992 (30) p. 49 S.

Trade Names. Kovanol (Takasago), Lyrall (IFF).

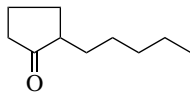
2-Methyl-4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2-butenal [3155-71-3]

$C_{14}H_{22}O$, M_r 206.33, $bp_{0.01\text{ kPa}}$ 100–103 °C, d_{25}^{25} 0.939–0.949, n_D^{20} 1.507–1.517, a clear yellowish liquid, does not occur in nature. Its floral odor is reminiscent of boronia absolute with violet accents. It can be prepared by reaction of β -ionone with ethyl chloroacetate and hydrolysis/decarboxylation of the intermediate glycidic ester. It is used in fine fragrances for ambra nuances in combination with sweet odor elements.

Trade Name. Boronal (H&R).

2.4.3 Ketones

2-Pentylcyclopentanone [4819-67-4]

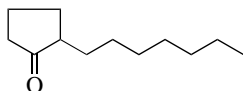


$C_{10}H_{18}O$, M_r 154.25, d_{20}^{20} 0.887–0.893, n_D^{20} 1.446–1.450, is a colorless liquid with a complex floral, aromatic and fruity odor, and a lactonic undertone. It is not found in nature.

2-Pentylcyclopentanone and its higher homologue 2-heptylcyclopentanone (see below) are prepared by condensation of cyclopentanone with the corresponding aliphatic aldehydes to give 2-alkylidenecyclopentanone and subsequent hydrogenation of the double bond. It is used in jasmin, herbal and lavender compositions.

Trade Name. Delphone (Firmenich).

2-Heptylcyclopentanone [137-03-1]



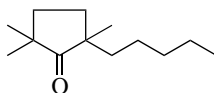
$C_{12}H_{22}O$, M_r 182.31, $bp_{1.3\text{kPa}}$ 130 °C, d_{20}^{20} 0.890, n_D^{20} 1.4530, is a colorless, viscous liquid with a fruity, slightly herbaceous, jasmin odor; it has not yet been found in nature.

2-Heptylcyclopentanone is used in, for example, jasmin, honeysuckle, and lavender compositions.

FCT 1975 (13) p. 452.

Trade Names. Alismone (Giv.-Roure), Fleuramone (IFF), Frutalone (PFW), Projasmon P (H&R), Heptone (Quest).

2,2,5-Trimethyl-5-pentylcyclopentanone [65443-14-3]



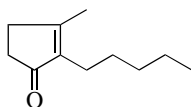
$C_{13}H_{24}O$, M_r 196.34, d_{20}^{20} 0.865–0.872, n_D^{20} 1.442–1.446, is a colorless to pale yellow liquid with a jasmin, lactonic and fruity odor. It is not found in nature. It is prepared by methylation of 2-pentylcyclopentanone with methyl iodide and sodium hydride in tetrahydrofuran [119].

Because of its stability combined with a soft floral note it has a wide use in jasmin and honeysuckle creations for, for example, body care products, soaps, and detergents.

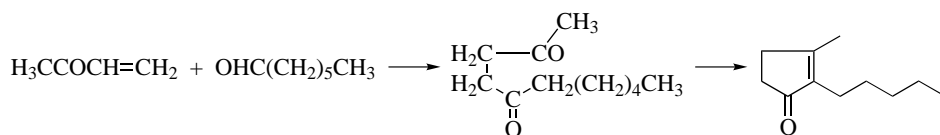
FCT 2000 (38, suppl. 3) p. S227.

Trade Name. Veloutone (Firmenich).

Dihydrojasmane [1128-08-1], 3-methyl-2-pentyl-2-cyclopenten-1-one



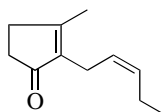
$C_{11}H_{18}O$, M_r 166.26, $bp_{2.7\text{kPa}}$ 87–88 °C, d^{25} 0.9157, n_D^{25} 1.4771, is a colorless, slightly viscous liquid with a typical jasmin odor, resembling that of the naturally occurring *cis*-jasmane. Dihydrojasmane can be synthesized by various routes. A preferred method is intramolecular 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 [120]:



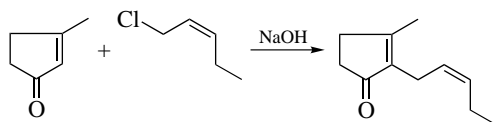
Dihydrojasmane is used in perfumery in jasmin bases and, more generally, in blossomy and fruity fragrances.

FCT 1974 (12) p. 523.

cis-Jasmone [488-10-8], 3-methyl-2-(2-*cis*-penten-1-yl)-2-cyclopenten-1-one

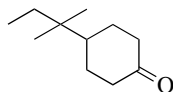


$C_{11}H_{16}O$, M_r 164.25, $bp_{1.6\text{kPa}}$ 78–79 °C, d^{20} 0.9423, n_D^{20} 1.4989, occurs in jasmin absolute and contributes to its typical jasmin odor. It is a pale yellow, viscous liquid with a strong jasmin odor. Various stereospecific syntheses for *cis*-jasmone have been reported. A patented 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., tricaprilmethylammonium chloride) [121]:



cis-Jasmone is used in perfumery in fine jasmin bases and floral compositions. FCT 1979 (17) p. 845.

4-*tert*-Pentylcyclohexanone [16587-71-6]

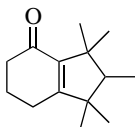


$C_{11}H_{20}O$, M_r 168.28, does not occur in nature. It is a colorless liquid, d_4^{20} 0.919–0.927, n_D^{20} 1.466–1.471, with a powerful orris type aroma. Hydrogenation of *p*-*tert*-amylphenol over palladium in the presence of borax is described for its synthesis [122].

It is useful in perfume compositions for, for example, laundry detergents. FCT 1974 (12) p. 819.

Trade Name. Orivone (IFF).

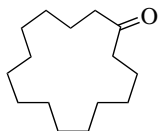
6,7-Dihydro-1,1,2,3,3-pentamethyl-4(5H)-indanone [33704-61-9]



$C_{14}H_{22}O$, M_r 206.33, is not found in nature. It is a pale yellow liquid, d_4^{20} 0.954–0.962, n_D^{20} 1.497–1.502, with a long lasting diffusive, conifer-like musk odor. A process for its production starts with the corresponding pentamethyltetrahydroindane which is treated with oxygen in the presence of cobalt naphthenate [123]. It is used in fine fragrances together with noble wood notes.

Trade Name. Cashmeran (IFF).

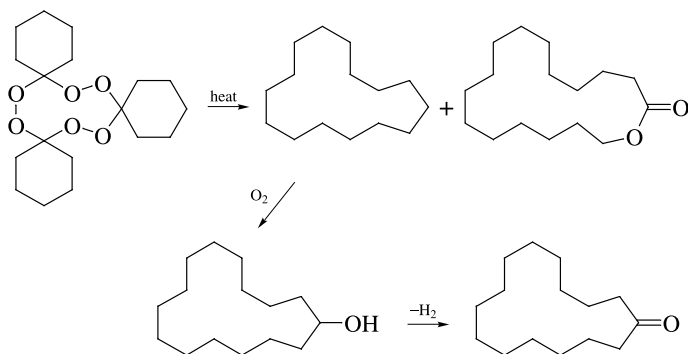
Cyclopentadecanone [502-72-7]



$C_{15}H_{28}O$, M_r 224.39, mp 65–67 °C, bp_{7Pa} 85 °C, is a musk fragrance found in the scent gland of the male civet cat.

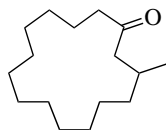
A number of syntheses have been developed for its manufacture. Among these, the so-called Story procedure is the only route which has the potential to make cyclopentadecanone available on a larger scale. But due to the handling of hydroperoxides, the process is difficult to control.

The process starts from tricyclohexylidene triperoxide which is obtained by oxidation of cyclohexanone with hydrogen peroxide. Pyrolysis leads to a mixture of 1,16-hexadecanolide and cyclopentadecane. The latter is oxidized by oxygen under boric acid catalysis to cyclopentadecanol which is subsequently oxidized to cyclopentadecanone [124,124a].



Cyclopentadecanone is used in fine fragrances.
FCT 1976 (14) p. 735.

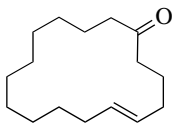
3-Methylcyclopentadecanone [541-91-3], muscone



$C_{16}H_{30}O$, M_r 238.42, d_{20}^{20} 0.918–0.925, n_D^{20} 1.477–1.482, is an odoriferous constituent of natural musk. It is a colorless liquid with very soft, sweet, musky odor and a perfumery, animal tonality. Numerous syntheses have been developed for its preparation [125].

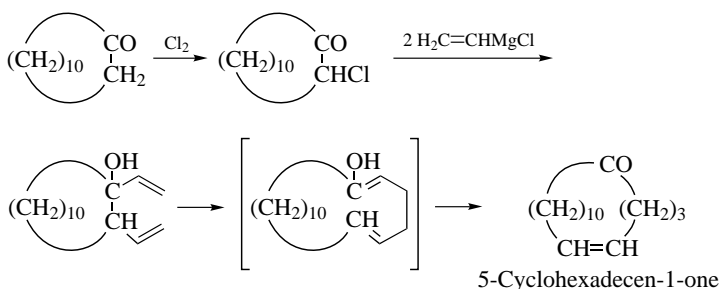
Because of its excellent stability it can be used in a wide range of products to give elegant, warm, animal notes. It is important for the reconstitution of natural musk.
FCT 1982 (20) p. 749.

Trade Name. Muscone (Firmenich).

5-Cyclohexadecen-1-one [37609-25-9]

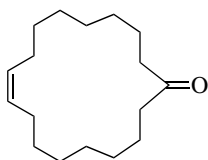
$C_{16}H_{28}O$, M_r 236.40, $bp_{0.01\text{ kPa}}$ 121 °C, n_D^{25} 1.4865, is commercially available as a 40:60 mixture of its *cis* and *trans* isomers. It is a colorless liquid with an intense musk odor.

A three-step synthesis starts from cyclododecanone. Reaction with chlorine gives 2-chlorocyclododecanone which is reacted with 2 mol of vinyl magnesium chloride to give 1,2-divinylcyclododecan-1-ol. This is finally converted into 5-cyclohexadecen-1-one by an oxy-Cope rearrangement [126]:



5-Cyclohexadecen-1-one can be added to perfume compositions as a substitute for the natural macrocyclic ketone musks.

Trade Name. Musk TM (Soda Aromatic), Velvione (Giv.-Roure), Ambretone (Takasago).

9-Cycloheptadecen-1-one [542-46-1], **civetone**

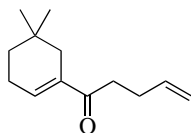
$C_{17}H_{30}O$, M_r 250.43, $bp_{0.007\text{ kPa}}$ 103 °C, d_{20}^{20} 0.923–0.940, n_D^{20} 1.485–1.492, is a colorless liquid with warm sensual animal and musky odor and extreme tenacity. It is the main odoriferous constituent of civet. A multistep synthesis, starting from cyclohexanone enol acetate has been patented. Two acyclic C_6 -fragments are linked to acetylene to give tetradeca-7-yne-1,14-dial. This is reacted with 1,3-bis(dimethylphosphono)propan-2-one. The resulting cyclohepta-2,16-dien-9-yn-1-one is hydrogenated over Pd/BaSO₄ to give civetone [127].

It is used in fine fragrance compositions for, for example, toiletries and body care products.

FCT 1976 (14) p. 727.

Trade Name. Civettone (Firmenich).

1-(5,5-Dimethyl-1-cyclohexen-1-yl)-4-penten-1-one [56973-85-4]

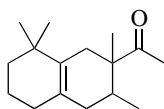


$C_{13}H_{20}O$, M_r 192.30, d_{20}^{20} 1.008–1.016, n_D^{20} 1.444–1.448, found not to occur in nature, is a colorless to pale yellow liquid with green, fruity, floral odor reminiscent of galbanum. One of several cited syntheses involves as a key step a double vinyl magnesium chloride addition to methyl 3,3-dimethyl-6-cyclohexene-1-carboxylate to give the title compound [128].

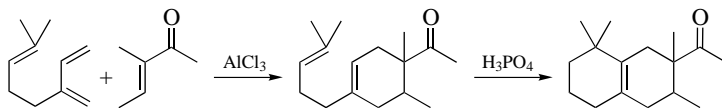
It can be used in all types of perfumes to give unique green, flora, and fruity effects. Its excellent stability permits the application in nearly all types of toiletries.

Trade Name. Dynascone 10 (Firmenich).

2,3,8,8-Tetramethyl-1,2,3,4,5,6,7,8-octahydro-2-naphthalenyl methyl ketone
[54464-57-2]

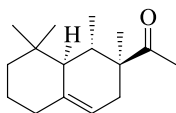


$C_{16}H_{26}O$, M_r 234.38, $bp_{0.37\text{kPa}}$ 134–135 °C, n_D^{20} 1.498–1.500, is a synthetic amber fragrance. It is prepared by a Diels–Alder reaction of myrcene and 3-methyl-3-penten-2-one in the presence of aluminum chloride and cyclization of the substituted



Myrcene

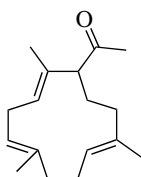
cyclohexenyl methyl ketone intermediate with phosphoric acid. Some of the corresponding 3-naphthalenyl methyl ketone is also formed [129]. The commercial product is a mixture of isomers. The typical woody odor is attributed to **1-[(1R*,2R*,8aS*)-1,2,3,5,6,7,8,8a-octahydro-1,2,8,8-tetramethylnaphthalen-2-yl]ethan-1-one** [140194-26-9], with less than 5% content a minor constituent of the mixture [129a–129c].



The ketone is used in perfume bases for soaps, eau de cologne, and detergent compositions.

Trade Name. Iso E Super (IFF), Amberone (Agan), Amboise (BBA).

Methyl 2,6,10-trimethyl-2,5,9-cyclododecatrien-1-yl ketone [28371-99-5]

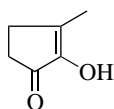


$C_{17}H_{26}O$, M_r 246.40, does not occur in nature. It is a pale yellow liquid, d_4^{20} 0.979–0.989, n_D^{20} 1.514–1.520, with a powerful, diffusive amber woody note with vetivert and smoky tobacco nuances. It is prepared from the corresponding trimethyl-cyclododecatriene by acetylation with acetic anhydride in the presence of boron trifluoride diethyl ether [130].

The product can be used to replace traditional materials such as sandalwood, vetivert and patchouli in perfume compositions.

Trade Name. Trimofix 'O' (IFF).

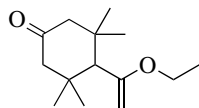
3-Methyl-2-cyclopenten-2-ol-1-one [80-71-7]



$C_6H_8O_2$, 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.

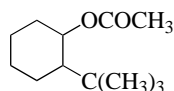
FCT 1976 (14) p. 809.

4-(1-Ethoxyvinyl)-3,3,5,5-tetramethylcyclohexanone [36306-87-3]

$C_{14}H_{24}O_2$, M_r 224.35, is not reported as being found in nature. It is a pale yellow liquid, $bp_{0.3\text{ kPa}}$ 80–82 °C, n_D^{15} 1.4758, with a rich, warm, and long lasting amber/woody note. The title compound is the main component of a mixture which is obtained by cyclodimerization of mesityl oxide in the presence of boron trifluoride etherate and reaction with ethyl orthoformate [131]. It is used in large proportions in almost every type of perfume composition.

FCT 1982 (20) p. 835.

Trade Name. Kephalis (Giv.-Roure).

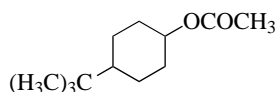
2.4.4 Esters**2-tert-Butylcyclohexyl acetate** [88-41-5], **OTBCHA**

$C_{12}H_{22}O_2$, M_r 189.30, 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.

FCT 1992 (30) p. 13 S.

Trade Names. Agrumex (H&R), Ortholate (Quest), Verdox (IFF).

4-tert-Butylcyclohexyl acetate [32210-23-4], **PTBCHA**

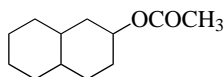
$C_{12}H_{22}O_2$, M_r 198.30, $bp_{1\text{ kPa}}$ 89–95 °C, d_{25}^{25} 0.933–0.939, n_D^{20} 1.450–1.454, does not occur in nature and exists in *cis* and *trans* forms. The *trans* isomer has a rich, woody odor, while the odor of the *cis* isomer is more intense and more flowery. Considerable variations 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 [132]. 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 [133].

4-*tert*-Butylcyclohexyl acetate is used particularly in soap perfumes.
FCT 1978 (16) p. 657.

Trade Names. Lorysia (Firmenich), Oryclon (H&R), Vertenex (IFF).

Decahydro- β -naphthyl acetate [10519-11-6]

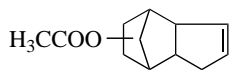


$C_{12}H_{20}O_2$, M_r 196.29, $bp_{0.65\text{ kPa}}$ 120 °C, d^{25} 1.005–1.015, n_D^{25} 1.475–1.482, is a fragrance substance that does not occur in nature. It consists of a mixture of several stereoisomers and is a colorless liquid with a sweet-fruity-herbaceous odor and a slight jasmin note.

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.

FCT 1979 (17) p. 755.

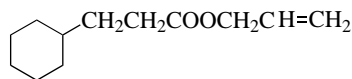
4,7-Methano-3a,4,5,6,7,7a-hexahydro-5 (or 6)-indenyl acetate [2500-83-6] (or [5413-60-5])



$C_{12}H_{16}O_2$, M_r 192.26, $bp_{1\text{ kPa}}$ 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.

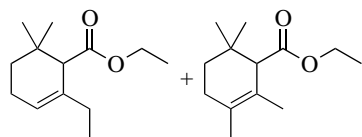
FCT 1976 (14) p. 889.

Trade Names. Cyclacet (IFF), Greenylacetate (Dragoco), Herbaflorat (H&R), Verdylacetate (Giv.-Roure), Jasmacyclene (Quest).

Allyl 3-cyclohexylpropionate [2705-87-5]

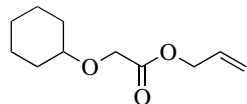
$C_{12}H_{20}O_2$, M_r 196.29, $bp_{0.13\text{ kPa}}$ 91 °C, has not yet been found in nature. It is a colorless liquid with a sweet-fruity odor, reminiscent of pineapples. The ester is prepared by esterification of 3-cyclohexylpropionic acid (obtained by hydrogenation of cinnamic acid) with allyl alcohol. It is used in perfumery to obtain fruity top notes as well as pineapple and chamomile nuances.

FCT 1973 (11) p. 491.

Ethyl 2-ethyl-6,6-dimethyl-2-cyclohexenecarboxylate [57934-97-1], and **Ethyl 2,3,6,6-tetramethyl-2-cyclohexenecarboxylate** [77851-07-1]

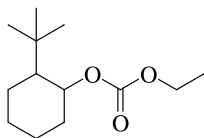
$C_{13}H_{22}O_2$, M_r 210.32 is a mixture of isomers, $bp_{0.8\text{ kPa}}$ 102 °C, n_D^{20} 1.4626, a colorless to pale yellow liquid with rosy, spicy, fruity, and woody odor. For its preparation 3,6-dimethyl-6-hepten-2-one and 7-methyl-6-octen-3-one are treated with ethyl diethylphosphoryl acetate to give a mixture of octadienoic acid esters. Cyclization with sulfuric/formic acid yields the title compounds as a mixture with isomers [134]. With its complex odor picture it is used in fine fragrances for shading.

Trade Name. Givescone (Giv.-Roure).

Allyl cyclohexyloxyacetate [68901-15-5], **cyclohexyloxyacetic acid allyl ester**

$C_{11}H_{18}O_3$, M_r 198.26, d_4^{20} 1.012–1.020, n_D^{20} 1.460–1.464, is a colorless to pale yellowish liquid with a strong, fruity, herbal-green odor reminiscent of galbanum. It is prepared by esterification of cyclohexyloxyacetic acid (from phenoxyacetic acid) with allyl alcohol and is used in fragrance compositions for toiletries and household products.

Trade Names. Cyclogalbanat (Dragoco), Cyclogabaniff (IFF), Isoananat (H&R).

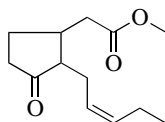
Ethyl 2-tert-butylcyclohexyl carbonate [67801-64-3]

$C_{13}H_{24}O_3$, M_r 228.33, d_4^{20} 0.973–0.977, n_D^{20} 1.449–1.453, is a colorless liquid with a spicy, woody, floral odor. The material is used for modifying floral fragrance compositions.

It is prepared by esterification of 2-tert-butylcyclohexanol with diethyl carbonate.

FCT 2000 (38, suppl. 3) p. S77.

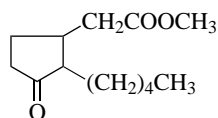
Trade Name. Floramat (Cognis)

cis-Methyl jasmonate [1211-29-6], **3-oxo-2-(2-cis-pentenyl)cyclopentaneacetic acid methyl ester**

$C_{13}H_{20}O_3$, M_r 224.30, is a volatile component of jasmin flower absolute. It is a colorless to pale yellow liquid, $bp_{0.25\text{kPa}}$ 116–118 °C, d_{20}^{20} 1.022–1.028, n_D^{20} 1.473–1.477, possessing an odor reminiscent of the floral heart of jasmin. Synthesis of the title compound is accomplished by reaction of *cis*-buten-1-yl bromide with Li in the presence of copper-(I) iodide, the product is treated with a mixture of 2-methylene- and 4-methylene-3-oxocyclopentylacetic acid methyl ester. The aforementioned ester mixture is obtained by reaction of methyl 3-oxocyclopentylacetate with formaldehyde [135].

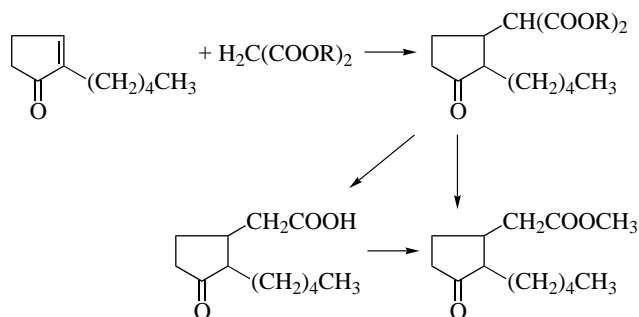
Methyl jasmonate is used in fine fragrances where it provides rich soft effects in jasmin and muguet compositions.

Trade Name. Methyl jasmonate (Firmenich).

Methyl dihydrojasmonate [24851-98-7], **methyl (3-oxo-2-pentylcyclopentyl)acetate**

$C_{13}H_{22}O_3$, M_r 226.32, bp_{1Pa} 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.

Of the four possible optical isomers, the (+)-(1*R*)-*cis*-isomer possesses the most characteristic jasmin odor. Methyl dihydrojasmonate is prepared by Michael addition of malonic acid esters to 2-pentyl-2-cyclopenten-1-one, followed by hydrolysis and decarboxylation of the resulting (2-pentyl-3-oxocyclopentyl) malonate, and esterification of the (2-pentyl-3-oxocyclopentyl)acetic acid [136].



Dealkoxycarbonylation of the malonate can also be accomplished directly with water at elevated temperature [137].

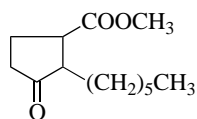
A recently developed industrially feasible process for the synthesis of a mixture with high (+)-(1*R*)-*cis*-isomer content comprises the catalytical hydrogenation of the corresponding cyclopenteneacetic acid in the presence of a ruthenium(II) complex with chiral ligands and subsequent esterification [138].

Methyl dihydrojasmonate is used in perfumery for blossom fragrances, particularly in jasmin types.

FCT 1992 (30) p. 85 S.

Trade Name. Cepionate (NZ), Hedion (Firmenich), MDJ Super (Quest).

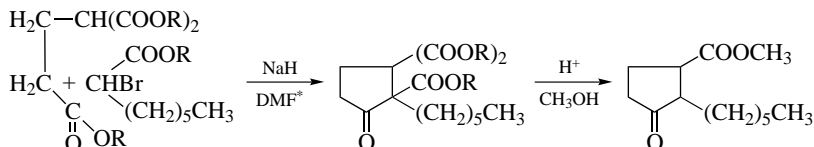
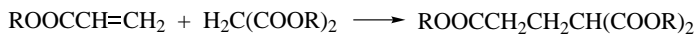
Methyl 2-hexyl-3-oxocyclopentanecarboxylate [37172-53-5]



$C_{13}H_{22}O_3$, M_r 226.32, bp_{8Pa} 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.

The title compound 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 [139]. Trialkyl propane-1,1,3-tricarboxylates can be prepared by Michael addition of dialkyl malonates to alkyl acrylates.



*DMF = dimethylformamide

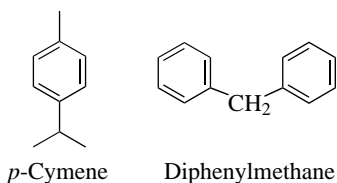
The compound is used in perfumery in floral compositions.

Trade Name. Jasmopol (PFW).

2.5 Aromatic Compounds

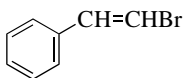
2.5.1 Hydrocarbons

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:



Slightly more important as a fragrance substance is the halogen-substituted hydrocarbon ω -bromostyrene.

ω -Bromostyrene [103-64-0]



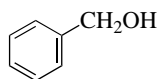
C_8H_7Br , M_r 183.05; *trans* isomer: mp 7 °C, $bp_{2.7\text{kPa}}$ 108 °C, d^{16} 1.4269, n_D^{20} 1.6093; the *trans* isomer has a strong hyacinth odor. It is prepared from cinnamic acid by addition of bromine and treatment of the resulting 3-phenyl-2,3-dibromopropionic acid with sodium carbonate. It is purified by fractional distillation. ω -Bromostyrene is used in soap perfumes.
FCT 1973 (11) p. 1043.

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]



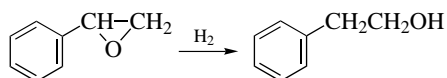
C_7H_8O , M_r 108.14, $bp_{101.3\text{kPa}}$ 205.4 °C, d_4^{20} 1.0419, n_D^{20} 1.5396, occurs in many essential oils and foods. It is a colorless liquid with a weak, slightly sweet odor. Benzyl alcohol can be oxidized to benzaldehyde, for example with nitric acid. Dehydrogenation over a copper–magnesium oxide–pumice catalyst also leads to the aldehyde. Esterification of benzyl alcohol results in a number of important fragrance and flavor materials. Diphenylmethane is prepared by a Friedel–Crafts reaction of benzyl alcohol and benzene with aluminum chloride or concentrated sulfuric acid. By heating benzyl alcohol in the presence of strong acids or strong bases dibenzyl ether is formed.

Synthesis. Benzyl alcohol is manufactured mainly by two processes.

1. Benzyl chloride is hydrolyzed by boiling with aqueous solutions of alkali or alkaline earth hydroxides or carbonates. Byproduct in this process is dibenzyl ether (up to 10%).

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.

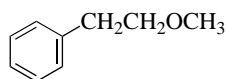
2. *Hydrogenation of Styrene Oxide.* Excellent yields of phenethyl alcohol are obtained when styrene oxide is hydrogenated at low temperature, using Raney nickel as a catalyst and a small amount of sodium hydroxide [140].



Uses. Phenethyl alcohol is used frequently and in large amounts as a fragrance material. 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.

FCT 1975 (13) p. 903.

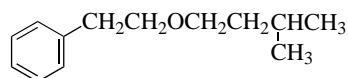
Phenethyl methyl ether [3558-60-9]



$C_9H_{12}O$, M_r 136.19, $bp_{94.6\text{kPa}}$ 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.

FCT 1982 (20) p. 807.

Phenethyl isoamyl ether [56011-02-0]

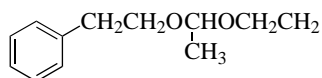


$C_{13}H_{20}O$, M_r 192.30, d_{25}^{25} 0.901–0.904, n_D^{20} 1.481–1.484, is a colorless liquid with a green, sweet-flowery odor of chamomile blossoms and a secondary, soapy note; it is used in perfumes.

FCT 1983 (21) p. 873.

Trade Name. Anther (Quest).

Acetaldehyde ethyl phenethyl acetal [2556-10-7]

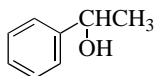


$C_{12}H_{18}O_2$, M_r 194.28, does not occur in nature. It is a colorless liquid, d_4^{20} 0.954–0.962, n_D^{20} 1.478–1.483, with powerful leafy-green, nasturtium, and hyacinth note. It can be synthesized by reaction of a 1:1 molar ratio of ethyl vinyl ether and phenethyl alcohol in the presence of cation exchange resin [141]. It imparts fresh, floral, green notes and is used in fine fragrances as well as in soap, cosmetics and detergents.

FCT 1992 (30) p. 1 S.

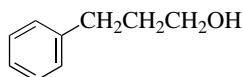
Trade Names. Efetaal (Quest), Hyacinth Body (IFF), Verotyl (PFW).

1-Phenylethyl alcohol [98-85-1], styrallyl alcohol



$C_8H_{10}O$, M_r 122.17, mp 20 °C, $bp_{101.3\text{kPa}}$ 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 materials.

Dihydrocinnamic alcohol [122-97-4], 3-phenylpropanol



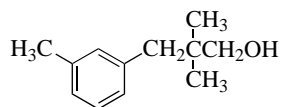
$C_9H_{12}O$, M_r 136.19, $bp_{100\text{kPa}}$ 237.5 °C, d_4^{20} 1.008, n_D^{20} 1.5278, occurs both in free and esterified form in resins and balsams (e.g., benzoe resin and Peru balsam). It has been identified in fruit and cinnamon.

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 materials.

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 [142].

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

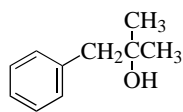
FCT 1979 (17) p. 893.

2,2-Dimethyl-3-(3-methylphenyl)propanol [103694-68-4]

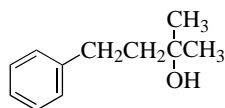
$C_{12}H_{18}O$, M_r 178.28, is not reported as being found in nature. It is a viscous liquid or crystalline mass, mp $22^\circ C$, $bp_{0.013\text{ kPa}}$ $74\text{--}76^\circ C$, d_4^{25} 0.960, n_D^{20} 1.515–1.518, with a fresh floral odor, reminiscent of lily of the valley and linden blossoms. It is prepared by reaction of 3-methylbenzyl chloride with 2-methylpropanal in the presence of tetrabutylammonium iodide and reduction of the resulting aldehyde with $NaBH_4$ [143].

It can be used in perfume compositions for toiletries, soaps, and detergents.

Trade Name. Majantol (H&R).

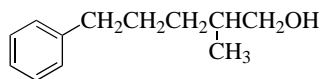
 α,α -Dimethylphenethyl alcohol [100-86-7], **1-phenyl-2-methyl-2-propanol**, **α,α -dimethyl benzyl carbinol**

$C_{10}H_{14}O$, M_r 150.22, mp $24^\circ C$, $bp_{101.3\text{ kPa}}$ $214\text{--}216^\circ C$, 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 benzyl magnesium 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 substances. FCT 1974 (12) p. 531.

4-Phenyl-2-methyl-2-butanol [103-05-9], **α,α -dimethylphenethyl carbinol**

$C_{11}H_{16}O$, M_r 164.25, $bp_{1.9\text{ kPa}}$ $124\text{--}125^\circ C$, $d_4^{20.7}$ 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 methyl magnesium chloride. It is used in blossom compositions.

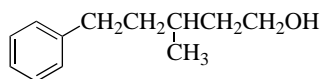
FCT 1974 (12) p. 537.

2-Methyl-5-phenylpentanol [25634-93-9]

$C_{12}H_{18}O$, M_r 178.28, is not reported to be found in nature. It is a colorless to pale yellow liquid, d_{25}^{25} 0.958–0.962, n_D^{20} 1.510–1.515, with a rose blossom, slightly waxy odor. It can be prepared by condensation of cinnamaldehyde with propanal and hydrogenation of the resulting unsaturated aldehyde.

Because of its excellent stability and relatively low price it is used in many perfumery fields.

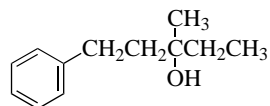
Trade Name. Rosaphen (H&R).

3-Methyl-5-phenylpentanol [55066-48-3]

$C_{12}H_{18}O$, M_r 178.28, does not occur in nature. It is a colorless liquid, $bp_{0.013\text{ kPa}}$ 86–91 °C, d_{20}^{20} 0.960–0.964, n_D^{20} 1.511–1.514, with a long lasting diffusive, fresh, floral, rose odor. The alcohol is prepared by hydrogenation of tetrahydro-4-methylene-5-phenylpyran which is obtained by cyclocondensation of benzaldehyde with 3-methyl-3-buten-1-ol in the presence of *p*-toluenesulfonic acid [144].

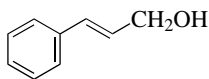
It can be used in all perfume types for a wide range of products, e.g., soaps, detergents and body care products.

Trade Names. Phenoxanol (IFF), Phenylhexanol (Firmenich), Mefrosol (Quest).

1-Phenyl-3-methyl-3-pentanol [10415-87-9], **phenethyl methyl ethyl carbinol**

$C_{12}H_{18}O$, M_r 178.28, $bp_{1.7\text{ kPa}}$ 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 ethyl magnesium chloride by a Grignard reaction. It is used to perfume soap, cosmetics, and detergents.

FCT 1979 (17) p. 891.

Cinnamic alcohol [104-54-1], 3-phenyl-2-propen-1-ol*trans*-Cinnamic alcohol

$C_9H_{10}O$, 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.

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 materials.

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 [145].
3. High yields of cinnamic alcohol can be obtained by reduction of cinnamaldehyde with alkali borohydrides. Formation of dihydrocinnamic alcohol is thus avoided [146].

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 materials. 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).

FCT 1974 (12) p. 855.

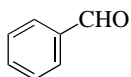
2.5.3 Aldehydes and Acetals

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 -methylidihydrocinnamaldehyde. 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 materials. However, both compounds are used in large quantity for the production of the corresponding cinnamic and dihydrocinnamic aldehydes.

Benzaldehyde [100-52-7]



C_7H_6O , M_r 106.12, $bp_{101.3\text{kPa}}$ 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. In the absence of inhibitors, benzaldehyde undergoes autoxidation to perbenzoic acid, which reacts with a second molecule of benzaldehyde to benzoic acid.

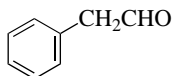
Hydrogenation of benzaldehyde yields benzyl alcohol, condensation with aliphatic aldehydes leads to additional fragrance substances or their unsaturated intermediates. Unsaturated araliphatic acids are obtained through the Perkin reaction, for example, the reaction with acetic anhydride to give cinnamic acid.

Benzaldehyde is prepared by hydrolysis of benzal chloride, for example in acidic media in the presence of a catalyst such as ferric chloride, or in alkaline media with aqueous sodium carbonate. Part of the commercially available benzaldehyde originates from a technical process for phenol. In this process, benzaldehyde is a byproduct in the oxidation, with air, of toluene to benzoic acid.

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 materials.

FCT 1976 (14) p. 693.

Phenylacetaldehyde [122-78-1]



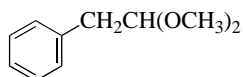
C_8H_8O , M_r 120.15, $bp_{101.3\text{kPa}}$ 195 °C, d_4^{20} 1.0272, n_D^{20} 1.5255, has been identified in many essential oils and as a volatile constituent of foods. It is a colorless liquid with a sweet-green odor, reminiscent of hyacinth. Since it readily undergoes oxidation and polymerizes, it 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 [147]. 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 [148].

Phenylacetaldehyde is used in perfume compositions, in particular for hyacinth and rose notes.

FCT 1979 (17) p. 377.

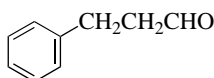
Phenylacetaldehyde dimethyl acetal [101-48-4]



$C_{10}H_{14}O_2$, M_r 166.22, $bp_{100.2\text{kPa}}$ 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.

FCT 1975 (13) p. 899.

Dihydrocinnamaldehyde [104-53-0], 3-phenylpropanal

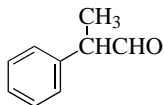


$C_9H_{10}O$, M_r 134.18, $bp_{2.7\text{kPa}}$ 112 °C, d_4^{20} 1.019, n_D^{20} 1.5266, occurs in Sri Lanka cinnamon oil, among others. The aldehyde is a colorless liquid with a strong, flowery, slightly balsamic, heavy hyacinth-like odor. It tends to undergo self-condensation.

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

FCT 1974 (12) p. 967.

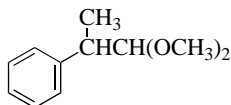
Hydratropaldehyde [93-53-8], 2-phenylpropanal



$C_9H_{10}O$, M_r 134.18, $bp_{1.5\text{kPa}}$ 92–94 °C, d_4^{20} 1.0089, n_D^{20} 1.5176, identified in dried mushroom, 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 material. Hydratropaldehyde is obtained from styrene by oxo

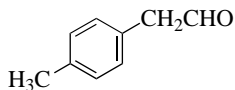
synthesis; small quantities of the isomeric dihydrocinnamaldehyde are formed as a byproduct. Hydratropaldehyde is used in perfumery in blossom compositions. FCT 1975 (13) p. 548.

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. FCT 1979 (17) p. 819.

4-Methylphenylacetaldehyde [104-09-6]



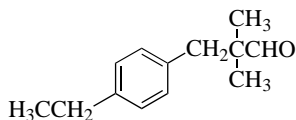
$C_9H_{10}O$, M_r 134.18, $bp_{101.3\text{kPa}}$ 221–222 °C, d_4^{20} 1.0052, n_D^{20} 1.5255, which has been identified in corn oil, is a colorless liquid with a strong green odor. It can be prepared by reaction of 4-methylbenzaldehyde with chloroacetates, followed by hydrolysis of the resulting glycidates and decarboxylation. The aldehyde is used in flower compositions for green notes. FCT 1978 (16) p. 877.

3-Methyl-5-phenylpentanal [55066-49-4]

$C_{12}H_{16}O$, M_r 176.26, d_{20}^{20} 0.957–0.965, n_D^{20} 1.503–1.509, a colorless liquid with a fresh, aldehydic, floral, citrus, lilly of the valley odor. The material is mainly used in cosmetics, toiletries, and alcoholic fragrances to modify and lift floral notes. It is not reported to occur in nature.

Trade Name. Mefranal (Quest).

3-(4-Ethylphenyl)-2,2-dimethylpropanal [67634-15-5]



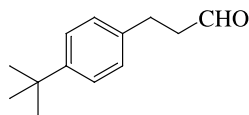
$C_{13}H_{18}O$, M_r 190.29, does not occur in nature. It is a colorless liquid, d_4^{20} 0.951–0.959, n_D^{20} 1.504–1.509, with a powerful, clean, fresh air tone, reminiscent of ocean breeze. It can be prepared by reaction of *p*-ethylbenzyl chloride and isobutyric

aldehyde in the presence of catalysts. The product is used in perfumes for, e.g., household products.

FCT 1988 (26) p. 307.

Trade Names. Floralozone (IFF), Florazon (Dragoco).

3-[4-(1,1-Dimethylethyl)phenyl]propanal [18127-01-0]

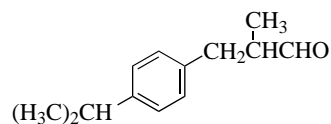


$C_{13}H_{18}O$, M_r 190.29, d_{20}^{20} 0.956–0.962, n_D^{20} 1.508–1.512, is a colorless to pale yellow liquid with a powerful green aquatic aldehydic lily of the valley odor. It is recommended for use in toiletries and alcoholic fragrances, but also for use in soaps and detergents. 3-[4-(1,1-Dimethylethyl)phenyl]propanal can be prepared from 4-*tert*-butylbenzaldehyde by aldol reaction with acetaldehyde and subsequent selective hydrogenation of the double bond of the resulting 4-*tert*-butylcinnamaldehyde [149] or by reaction of *tert*-butylbenzene with acrolein diacetate in the presence of a Lewis-catalyst and saponification of the resulting 3-[4-(1,1-dimethylethyl)phenyl]-1-propen-1-yl acetate [149a].

FCT 1988 (26), p. 287.

Trade Name. Bourgeonal (Quest).

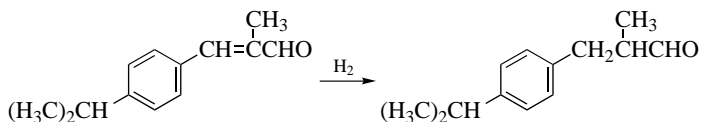
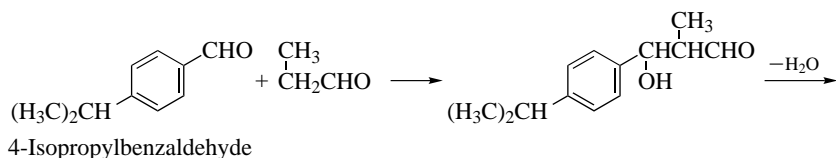
Cyclamenaldehyde [103-95-7], 2-methyl-3-(4-isopropylphenyl)propanal



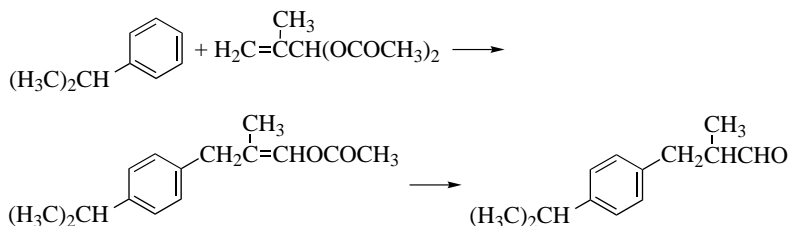
$C_{13}H_{18}O$, M_r 190.28, $bp_{0.3\text{kPa}}$ 108–108.5 °C, d_4^{20} 0.9502, n_D^{20} 1.5068. The commercially available racemate is a colorless to yellowish liquid with an intense flowery odor reminiscent of *Cyclamen europaeum* (cyclamen, sowbread).

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

1. Alkaline condensation of 4-isopropylbenzaldehyde and propanal results, via the aldol, in the formation of 2-methyl-3-(4-isopropylphenyl)-2-propenal. The unsaturated aldehyde is hydrogenated selectively to the saturated aldehyde in the presence of potassium acetate and a suitable catalyst, such as palladium–alumina [150]:



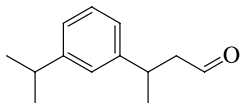
2. Friedel–Crafts reaction of isopropylbenzene and 2-methylpropenal diacetate (methacrolein diacetate) in the presence of titanium tetrachloride/boron trifluoride etherate gives cyclamenaldehyde enolacetate, which is hydrolyzed to the aldehyde [151]:



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.

FCT 1974 (12) p. 397.

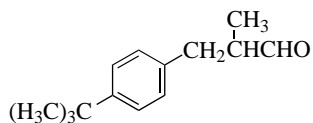
3-(3-Isopropylphenyl)butanal [125109-85-5]



$\text{C}_{13}\text{H}_{18}\text{O}$, M_r 190.29, d_{25}^{25} 0.9480–0.9540, n_D^{20} 1.5040–1.5080, a clear colorless to pale yellow liquid with a powerful fresh, green, floral, lily of the valley like odor. It is recommended for use in all areas of perfumery. The preparation is effected by hydroformylation of 1,3-diisopropenylbenzene and subsequent hydrogenation [151a].

Trade name. Florhydral (Giv.-Roüre).

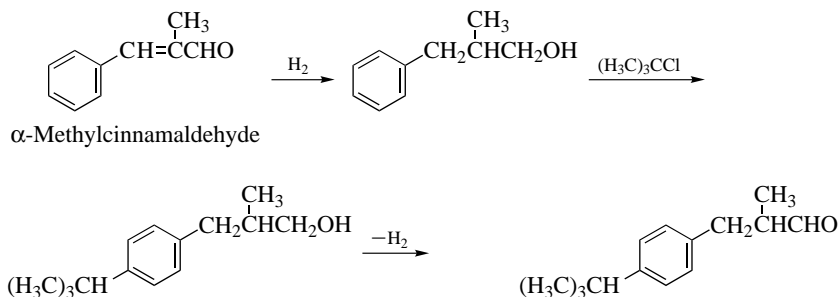
4-*tert*-Butyl- α -methyl-dihydrocinnamaldehyde [80-54-6],
2-methyl-3-(4-*tert*-butyl-phenyl)propanal



$C_{14}H_{20}O$, M_r 204.31, $bp_{0.8\text{kPa}}$ 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.

More recent patents describe the following preparation from α -methylcinnamaldehyde. α -Methylcinnamaldehyde (from benzaldehyde and propionaldehyde) is hydrogenated to α -methylcinnamyl alcohol. The alcohol is alkylated with *tert*-butyl chloride or isobutene to 4-*tert*-butyl- α -methylcinnamyl alcohol, which is subsequently dehydrogenated to the desired aldehyde [152, 153].

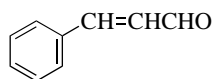


The compound is more stable than cyclamenaldehyde and is a popular component of flower compositions, particularly lily of the valley and linden types, because of its mild, pleasant, blossom fragrance. Large quantities are used in soap and cosmetic perfumes.

FCT 1978 (16) p. 659.

Trade Names. Lilestralis (BBA), Lilial (Giv.-Roure), Lysmeral (BASF), Lilialdehyde (Kuraray).

Cinnamaldehyde [14371-10-9], **3-phenyl-2-propenal**



C_9H_8O , M_r 132.16, *trans* isomer: $bp_{101.3\text{kPa}}$ 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.

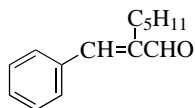
trans-Cinnamaldehyde is a yellowish liquid with a characteristic spicy odor, strongly reminiscent of cinnamon. Being an α,β -unsaturated aldehyde, it undergoes many reactions, of which hydrogenation to cinnamic alcohol, dihydrocinnamaldehyde, and dihydrocinnamic alcohol are important. Cinnamic acid is 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 [154].

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.

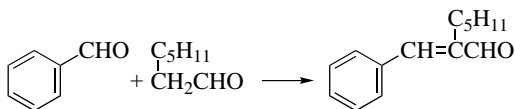
FCT 1979 (17) p. 253.

α -Amylcinnamaldehyde [122-40-7], 2-pentyl-3-phenyl-2-propenal



$\text{C}_{14}\text{H}_{18}\text{O}$, M_r 202.30, $bp_{0.7\text{kPa}}$ 140 °C, d_4^{20} 0.9710, n_D^{20} 1.5381, has been identified as an aroma volatile of black tea. 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.

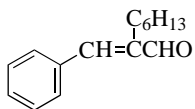
It is prepared from benzaldehyde and heptanal in the same way as cinnamaldehyde.



α -Amylcinnamaldehyde 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.

FCT 1973 (11) p. 855.

α -Hexylcinnamaldehyde [101-86-0], 2-hexyl-3-phenyl-2-propenal

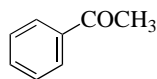


$C_{15}H_{20}O$, M_r 216.32, $bp_{2\text{ kPa}}$ 174–176 °C, d_4^{24} 0.9500, n_D^{25} 1.5268, has been identified in rice. It is a yellow liquid with a mild, slightly fatty, flowery, somewhat herbal odor, and a distinct jasmine note. Like the α -amyl homologue, α -hexylcinnamaldehyde must be protected 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., jasmine and gardenia) and, because of its stability to alkali, in soap perfumes.
FCT 1974 (12) p. 915.

2.5.4 Ketones and Acetals

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.

Acetophenone [98-86-2], methyl phenyl ketone

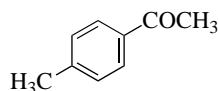


C_8H_8O , M_r 120.15, mp 20.5 °C, $bp_{101.3\text{ kPa}}$ 202.0 °C, d_4^{20} 1.0281, n_D^{20} 1.5372, is a naturally occurring component of a large number of foods and essential oils. It is a colorless liquid with a penetrating sweet odor, reminiscent of orange blossom.

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. The quantities 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 materials.
FCT 1973 (11) p. 99.

4-Methylacetophenone [122-00-9], *p*-tolyl methyl ketone

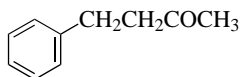


$C_9H_{10}O$, M_r 134.18, mp 28 °C, $bp_{101.3\text{ kPa}}$ 226 °C, d_4^{20} 1.0051, n_D^{20} 1.5335, has been identified in Brazilian rosewood oil and in pepper. It occurs as colorless crystals with a flowery-sweet odor that is milder than that of acetophenone. 4-Methylacetophenone is prepared from 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.

FCT 1974 (12) p. 933.

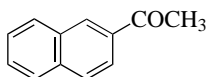
Benzylacetone [2550-26-7], 4-phenyl-2-butanone



$C_{10}H_{12}O$, M_r 148.20, $bp_{101.3\text{kPa}}$ 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.

FCT 1983 (21) p. 647.

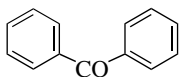
Methyl β -naphthyl ketone [93-08-3]



$C_{12}H_{10}O$, M_r 170.21, $bp_{1.7\text{kPa}}$ 171–173 °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 (mp 56 °C). 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 eau de cologne, soap perfumes, and detergents. It is a good fixative.

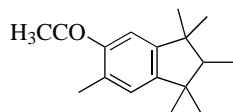
FCT 1975 (13) p. 876.

Benzophenone [119-61-9], diphenyl ketone

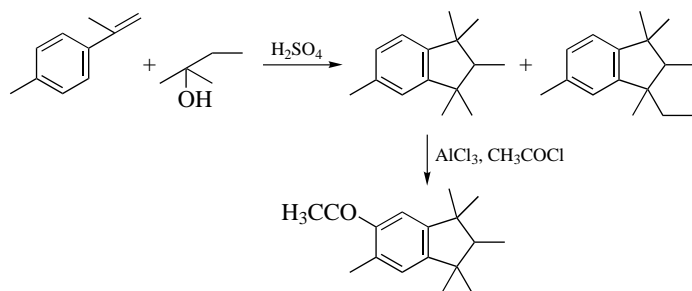


$C_{13}H_{10}O$, M_r 182.22, $bp_{6.3\text{kPa}}$ 200.5 °C, d^{50} 1.976, has been identified as a flavor component of grapes. It is a colorless crystalline solid (mp 48.1 °C) with a rosy, slightly geranium-like odor. It can be prepared in several ways, for example, by Friedel–Crafts reaction of benzene 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.

FCT 1973 (11) p. 873.

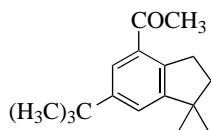
5-Acetyl-1,1,2,3,3,6-hexamethylindane [15323-35-0]

$C_{17}H_{24}O$, M_r 244.38, mp $35^\circ C$, 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 [155]:

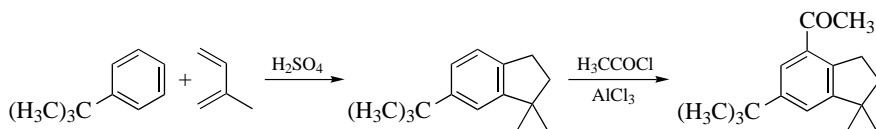


The indane ketone is a musk fragrance that is stable to light and in soap. It is used in perfumes and cosmetics for its fixative properties as well as its fragrance. FCT 1975 (13) p. 693.

Trade Name. Phantolide (PFW).

4-Acetyl-1,1-dimethyl-6-tert-butylindane [13171-00-1]

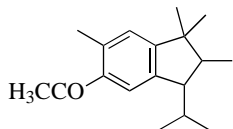
$C_{17}H_{24}O$, M_r 244.38, mp $76.7\text{--}77.2^\circ C$, is a musk fragrance that does not occur in nature. It is prepared by reacting *tert*-butylbenzene with isoprene in the presence of sulfuric acid, followed by acetylation of the resulting 1,1-dimethyl-6-*tert*-butylindane [156]:



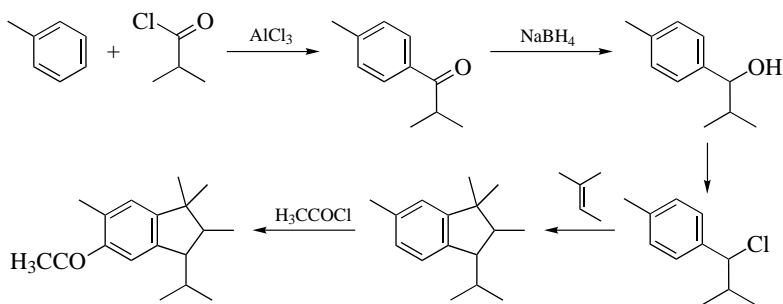
The indane is light-stable and is mainly used for perfuming soap and cosmetics. FCT 1976 (14) p. 699.

Trade Name. Celestolide (IFF).

5-Acetyl-1,1,2,6-tetramethyl-3-isopropylindane [68140-48-7]



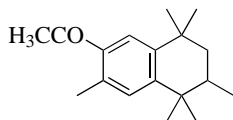
$C_{18}H_{26}O$, M_r 258.40, $bp_{0.13\text{kPa}}$ 144–146 °C, n_D^{20} 1.5301, is also a musk fragrance that does not occur in nature. It is prepared from toluene and isobutyryl chloride by a Friedel–Crafts reaction that yield *p*-tolyl isopropyl ketone; the ketone is reduced to the corresponding alcohol. 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 [157]:



It is used in perfume compositions for soap and detergents. FCT 1983 (21) p. 645.

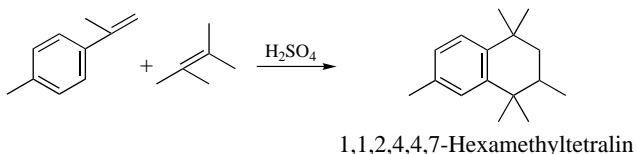
Trade Name. Traseolide (Quest).

1-(5,6,7,8-Tetrahydro-3,5,5,6,8,8-hexamethyl-2-naphthalenyl)-ethanone [1506-02-1], [21145-77-7]

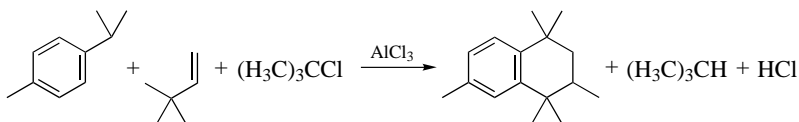


$C_{18}H_{26}O$, M_r 258.40, mp 55.5 °C, $bp_{0.25\text{kPa}}$ 119 °C, is a synthetic musk fragrance. It is prepared from 1,1,2,4,4,7-hexamethyltetralin, which is obtained by one of the following routes:

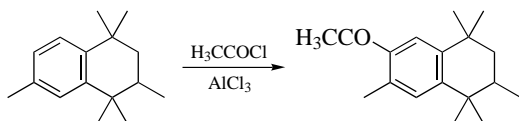
1. Reaction of α,p -dimethylstyrene with tetramethylethene [158] or 2,3-dimethylbutan-2-ol [155] in an acetic acid–sulfuric acid mixture yields the desired hexamethyltetralin, in addition to polymerized starting materials:



2. Reaction of *p*-cymene with 3,3-dimethyl-1-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 [159].



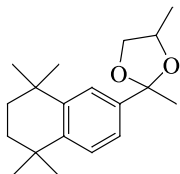
1,1,2,4,4,7-Hexamethyltetralin is subsequently acetylated to 6-acetyl-1,1,2,4,4,7-hexamethyltetralin, e.g., with acetyl chloride and aluminum chloride.



The product is a light-stable, versatile musk fragrance that is used in soap and cosmetics.

Trade Names. Ganolide (Agan), Tetralide (BBA), Tonalide (PFW).

2,4-Dimethyl-2-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-1,3-dioxolane [131812-67-4]



$C_{19}H_{28}O_2$, M_r 288.43, d_4^{20} 1.0030–1.0070, n_D^{20} 1.510–1.515, a colorless to pale yellow viscous liquid with a woody-ambery, camphoraceous, tobacco and

musk-like odour of a remarkable long-lastingness [159a]. It is recommended for use in nearly all fragrance applications.

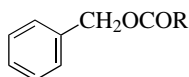
Trade Name. Okoumal (Giv.-Roure).

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.

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 = CH₃, C₉H₁₀O₂, M_r 150.18, $bp_{101.3\text{ kPa}}$ 215 °C, d_4^{20} 1.0550, n_D^{20} 1.5232, is the main component of jasmin absolute 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. In terms of volume, benzyl acetate is one of the most important fragrance and flavor chemicals.

FCT 1973 (11) p. 875.

Benzyl propionate [122-63-4]

R = CH₂CH₃, C₁₀H₁₂O₂, M_r 164.20, $bp_{101.3\text{ kPa}}$ 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.

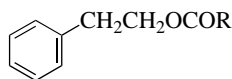
FCT 1975 (13) p. 723.

Benzyl isovalerate [103-38-8]

R = CH₂CH(CH₃)₂, C₁₂H₁₆O₂, M_r 192.26, $bp_{101.3\text{ kPa}}$ 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.

FCT 1974 (12) p. 829.

The most commonly used *phenethyl esters* are the following:



Phenethyl acetate [103-45-7]

R = CH₃, C₁₀H₁₂O₂, M_r 164.20, $bp_{101.3\text{kPa}}$ 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.
FCT 1974 (12) p. 957.

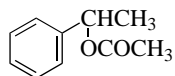
Phenethyl isobutyrate [103-48-0]

R = CH(CH₃)₂, C₁₂H₁₆O₂, M_r 192.26, $bp_{2\text{kPa}}$ 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.
FCT 1978 (16) p. 847.

Phenethyl isovalerate [140-26-1]

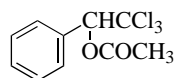
R = CH₂CH(CH₃)₂, C₁₃H₁₈O₂, M_r 206.28, $bp_{7.2\text{kPa}}$ 141–145 °C, d^{15} 1.9845, n_D^{20} 1.4855, has been identified as a volatile aroma component of peppermint oils. The fruitiness of its odor is even more pronounced than that of the isobutyrate. It is used in small quantities for the same purposes as phenethyl isobutyrate.
FCT 1974 (12) p. 961.

1-Phenylethyl acetate [50373-55-2], **styrallyl acetate**



C₁₀H₁₂O₂, M_r 164.20, $bp_{1.3\text{kPa}}$ 92.5 °C, d_4^{20} 1.0277, n_D^{20} 1.4954, has not been reported as occurring in nature. It 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.
FCT 1976 (14) p. 611.

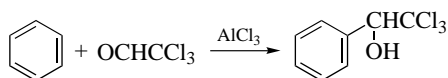
α-Trichloromethylbenzyl acetate [90-17-5]



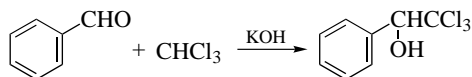
$C_{10}H_9Cl_3O_2$, M_r 267.54, is a fragrance substance that does not occur in nature. It forms white crystals (mp 88 °C) and has a weak, very natural, lasting rose odor.

The ester is prepared from α -trichloromethylbenzyl alcohol, for example, by reaction with acetic anhydride. The alcohol can be prepared by one of the following methods:

1. Addition of trichloroacetaldehyde (chloral) to benzene in the presence of aluminum chloride [160].

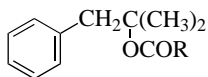


2. Reaction of benzaldehyde with chloroform in the presence of potassium hydroxide [161].



α -Trichloromethylbenzyl acetate is a stable rose fragrance with excellent fixative properties. It is preferentially used in soap, powders, and bath salts.

The following α,α -dimethylphenethyl esters are commercially important:



α,α -Dimethylphenethyl acetate [151-05-3]

$R = \text{CH}_3$, $C_{12}H_{16}O_2$, M_r 192.26, mp ca. 30 °C, $bp_{0.4\text{kPa}}$ 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.

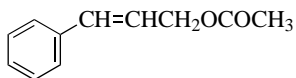
FCT 1974 (12) p. 533.

α,α -Dimethylphenethyl butyrate [10094-34-5]

$R = (\text{CH}_2)_2\text{CH}_3$, $C_{14}H_{20}O_2$, M_r 220.31, $bp_{0.4\text{kPa}}$ 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.

FCT 1980 (18) p. 667.

Cinnamyl acetate [21040-45-9]

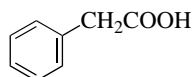


$C_{11}H_{12}O_2$, M_r 176.21, $bp_{1.3\text{kPa}}$ 139–140 °C, d^{22} 1.0520, n_D^{20} 1.5420, is the only ester of cinnamic alcohol of any importance. *trans*-Cinnamyl acetate occurs in cassia oil and is a colorless liquid with a sweet-flowery-fruity, slightly balsamic odor. It is a good fixative and is used in blossom compositions (e.g., lilac and jasmín) and for oriental notes. In aroma compositions, it is used for cinnamon-fruity effects. FCT 1973 (11) p. 1063.

2.5.6 Aromatic Acids

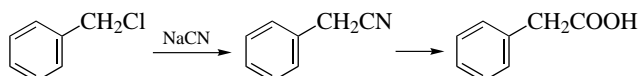
Aromatic acids (e.g., benzoic acid) and araliphatic acids (e.g., phenylacetic, cinnamic, and dihydrocinnamic acids) occur in numerous essential oils and have also been identified in the aromas of many foods. However, phenylacetic acid is the only acid that is used in significant quantities as a fragrance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

Phenylacetic acid [103-82-2]



$C_8H_8O_2$, M_r 136.15, $bp_{101.3\text{kPa}}$ 265.5 °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 (mp 78 °C) that have a honey odor.

The common route to phenylacetic acid is conversion of benzyl chloride into benzyl cyanide by reaction with sodium cyanide, followed by hydrolysis.



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.

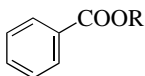
FCT 1975 (13) p. 901.

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.

2.5.7.1 Benzoates

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



Methyl benzoate [93-58-3]

R = CH₃, C₈H₈O₂, *M_r* 136.15, *bp*_{101.3 kPa} 199.6 °C, *d*₄²⁰ 1.0888, *n*_D²⁰ 1.5164, has been found in essential oils (e.g., ylang-ylang oil). It is a colorless liquid with a strong, dry-fruity, slightly phenolic odor. Methyl benzoate can be converted simply into other benzoates by transesterification. Since methyl benzoate is a fairly large by-product in the manufacture of terylene, earlier synthetic routes such as those starting from benzoic acid or benzoyl chloride have largely been abandoned.

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

FCT 1974 (12) p. 937.

Hexyl benzoate [6789-88-4]

R = (CH₂)₅CH₃, C₁₃H₁₈O₂, *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.

FCT 1979 (17) p. 813.

Benzyl benzoate [120-51-4]

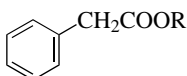
R = CH₂C₆H₅, C₁₄H₁₂O₂, *M_r* 212.25, *bp*_{2.0 kPa} 170–171 °C, *d*₄²⁵ 1.1121, *n*_D²⁰ 1.5680, is the main component of Peru balsam oil. It occurs in fairly large amounts in a number of blossom concretes and absolutes (e.g., tuberose and hyacinth). It forms either a viscous liquid or solid flakes (*mp* 21–22 °C) and has a weak, sweet-balsamic odor. It is prepared either by transesterification of technical methyl benzoate with benzyl alcohol, or from benzyl chloride and sodium benzoate. A third process starts with benzaldehyde which is converted in high yield into benzyl benzoate in the presence of sodium or aluminum benzylate (Tishchenko reaction).

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

FCT 1973 (11) p. 1015.

2.5.7.2 Phenylacetates

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



Ethyl phenylacetate [101-97-3]

$R = \text{CH}_2\text{CH}_3$, $\text{C}_{10}\text{H}_{12}\text{O}_2$, M_r 164.20, $bp_{101.3\text{kPa}}$ 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.

FCT 1975 (13) p. 99.

Geranyl phenylacetate [102-22-7]

$R = \text{CH}_2\text{CH} = \text{C}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH} = \text{C}(\text{CH}_3)_2$, $\text{C}_{18}\text{H}_{24}\text{O}_2$, 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.

FCT 1974 (12) p. 895.

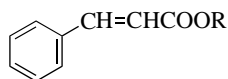
Phenethyl phenylacetate [102-20-5]

$R = \text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$, $\text{C}_{16}\text{H}_{16}\text{O}_2$, M_r 240.30, $bp_{0.6\text{kPa}}$ 177–178 °C, d_{25}^{25} 0.880, n_D^{20} 1.5496–1.5504, has been identified in e.g., the flower concrete of *Michelia champaca* L. It is a colorless liquid or crystals (mp 26.5 °C), 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.

FCT 1975 (13) p. 907.

2.5.7.3 Cinnamates

Three cinnamates are of some importance in perfumery:

**Methyl cinnamate** [1754-62-7]

$R = \text{CH}_3$, $\text{C}_{10}\text{H}_{10}\text{O}_2$, M_r 162.19, $bp_{101.3\text{kPa}}$ 261.9 °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 (mp 36.5 °C) 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.

FCT 1975 (13) p. 849.

Benzyl cinnamate [103-41-3]

$R = \text{CH}_2\text{C}_6\text{H}_5$, $\text{C}_{16}\text{H}_{14}\text{O}_2$, M_r 238.29, occurs in balsams and balsam oils. It forms white, sweet-balsamic-smelling crystals (mp 35–36 °C). Benzyl cinnamate is used as a fixative in perfumes and as a component of heavy, oriental perfumes.

FCT 1973 (11) p. 1017.

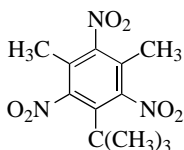
Phenethyl cinnamate [103-53-7]

R = CH₂CH₂C₆H₅, C₁₇H₁₆O₂, M_r 252.31, occurs in extracts from *Populus balsamifera* buds. It is a crystalline solid (mp 65–68 °C) with a heavy, rosy-balsamic odor. It is used as a fixative in blossom fragrances.

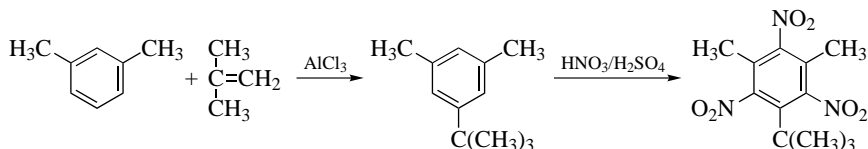
FCT 1978 (16) p. 845.

2.5.8 Miscellaneous Compounds

Of the few aromatic, nitrogen-containing fragrance substances, the nitro musks, musk xylol and musk ketone, are still considerably important commercially as inexpensive and adhesive musk fragrances. Musk ambrette, another artificial nitro musk, has lost its significance on account of its toxic properties. Methyl anthranilate and its *N*-methyl derivative are also aromatic, nitrogen-containing compounds that are used as fragrances and flavors in fairly large amounts. Schiff's bases of methyl anthranilate are of increasing importance as perfumery ingredients. A number of aromatic nitriles have been introduced; they are stable to alkali and, therefore, used in soap perfumes.

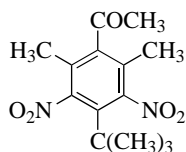
Musk xylol [81-15-2], **2,4,6-trinitro-1,3-dimethyl-5-*tert*-butylbenzene**

C₁₂H₁₅N₃O₆, 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.

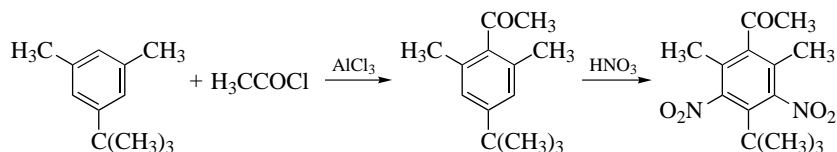


Musk xylol is used in large quantities in inexpensive perfumes for soap and household products.

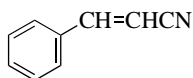
FCT 1975 (13) p. 881.

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 $137^\circ C$, 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 is widely used as a fixative in blossom and phantasy compositions. FCT 1975 (13) p. 877.

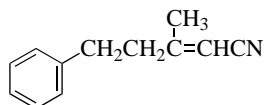
Cinnamitrile [4360-47-8]

C_9H_7N , M_r 129.16, $bp_{1.7kPa}$ $135-135.5^\circ C$, d^{25} 1.0244, n_D^{25} 1.6001; *trans*-cinnamitrile is a colorless crystalline solid (mp $23.5-24^\circ C$) or a colorless viscous liquid with a spicy, slightly flowery odor.

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

FCT 1976 (14) p. 721.

Trade Name. Cinnamalva (IFF).

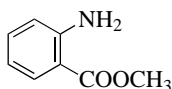
5-Phenyl-3-methyl-2-pentenitrile [93893-89-1]

$C_{12}H_{13}N$, M_r 171.24, $bp_{0.02\text{kPa}}$ 82–88 °C, d_4^{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.

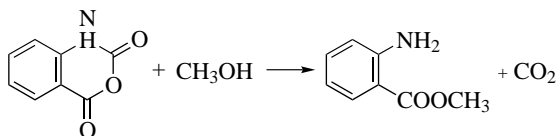
The nitrile is prepared by condensation of benzylacetone with cyanoacetic acid in the presence of pyridine and by elimination of carbon dioxide. The mixture is used in soap and detergent perfumes [162].

Trade Name. Citronitril (H&R).

Methyl anthranilate [134-20-3]



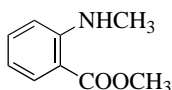
$C_8H_9NO_2$, M_r 151.16, $bp_{2\text{kPa}}$ 135.5 °C, d_4^{19} 1.1682, n_D^{20} 1.5815, occurs in a large number of blossom essential oils (e.g., neroli, ylang-ylang, and jasmin oils), grapes, and citrus oils. It occurs as white crystals (mp 24–25 °C), or a yellowish liquid, that show blue fluorescence 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 [163].



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

FCT 1974 (12) p. 935.

Methyl *N*-methylantranilate [85-91-6]



$C_9H_{11}NO_2$, M_r 165.19, $bp_{1.6\text{kPa}}$ 130–131 °C, d_4^{20} 1.1295, n_D^{20} 1.5796, is the main component of petitgrain oils from mandarin leaves and is also found in mandarin 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.

FCT 1975 (13) p. 791.

Some Schiff's bases of methyl anthranilate are interesting fragrance materials:

(a) with hydroxycitronellal [89-43-0]

Trade Names. Auralva (IFF), Aurantha (Takasago), Aurantiol Pure (Giv.-Roure), Aurantion (Quest),

(b) with 2,4-dimethyl-3-cyclohexene carbaldehyde [68845-02-3]

Trade Names. Ligantraal (Quest), Vertosine (H&R),

(c) with 4-*tert*-butyl- α -methylidihydrocinnamaldehyde [91-51-0]

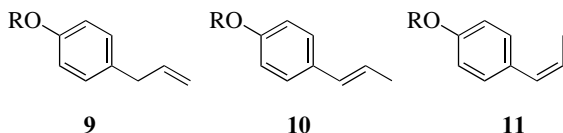
Trade Name. Verdantiol (Giv.-Roure).

All of them have a heavy blossom odor and a high tenacity.

2.6 Phenols and Phenol Derivatives

2.6.1 Phenols, Phenyl Esters, and Phenyl Ethers

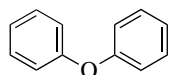
Of the phenols and phenyl ethers used as fragrance and flavor substances, 4-allyl- (**9**, R=H) and 4-propenylphenols (**10** and **11**, R=H) and their methyl ethers (**9-11**, R=CH₃) occur particularly frequently in essential oils.



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.

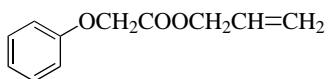
Although 1,2-methylenedioxy-4-allylbenzene and 1,2-methylenedioxy-4-propenylbenzene are really heterocyclic compounds, they are discussed here because of their close biogenetic relationship to the 2-methoxy-4-alkenylphenols.

Diphenyl ether [101-84-8]



$C_{12}H_{10}O$, M_r 170.21, $bp_{1.34\text{kPa}}$ 121 °C, d_4^{20} 1.0748, has not been observed in nature. It is a colorless liquid or a crystalline solid (mp 26.8 °C) 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. 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). FCT 1974 (12) p. 707.

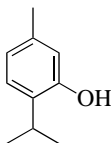
Phenoxyacetic acid 2-propenyl ester [7493-74-5], phenoxyacetic acid allyl ester



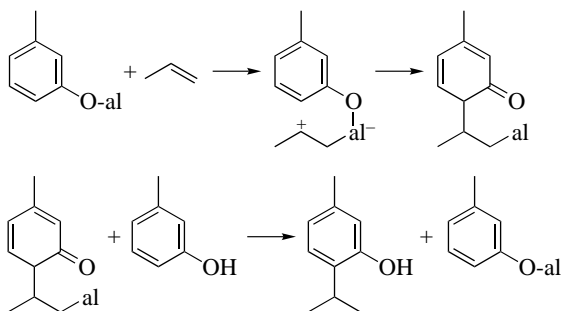
$C_{11}H_{12}O_3$ M_r 192.22, d_{25}^{25} 1.100–1.105, n_D^{20} 1.514–1.517, is a clear, colorless to yellowish liquid with a green, sweet, herbal-fruity odor with nuances of galbanum and pineapple.

It is prepared by reaction of phenoxyacetic acid alkali salts with allyl halogenide and used in technical perfumery.

Thymol [89-83-8], 2-isopropyl-5-methylphenol



$C_{10}H_{14}O$, M_r 150.22, $bp_{101.3\text{kPa}}$ 232.5 °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 (mp 51.5 °C) with a spicy-herbal, slightly

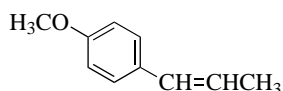


medicinal odor reminiscent of thyme. Thymol is prepared on a technical scale in a continuous high-temperature, high-pressure, liquid-phase, ortho-alkylation process, from *m*-cresol and propylene, in the presence of activated aluminum oxide hydrate.

The crude thymol mixture, consisting of approximately 60% thymol, unreacted *m*-cresol (ca. 25%), and other (iso)propyl-substituted products, is separated by fractional distillation. Most of the byproducts are recycled.

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

Anethole [104-46-1], 1-methoxy-4-(1-propenyl)benzene

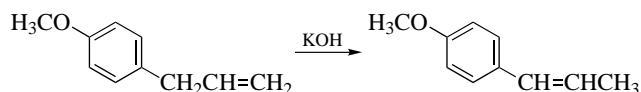


$C_{10}H_{12}O$, M_r 148.20, *trans* isomer: $bp_{101.7\text{kPa}}$ 234 °C, $bp_{1.6\text{kPa}}$ 115 °C, d_4^{20} 0.9883, n_D^{20} 1.5615, occurs both as its *cis* and *trans* isomers in nature; however, *trans*-anethole is always the main isomer. Anethole occurs in anise oil (80–90%), star anise oil (>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. Anethole is isolated from anethole-rich essential oils as well as from sulfate turpentine oils.

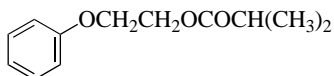
1. Anethole can be crystallized from oils in which it occurs as a major component (star anise and sweet fennel oils), and estragole containing oils (e.g., basilicum oil).
2. A fraction of American sulfate turpentine oil (0.5% of the total) consists mainly of an azeotropic mixture of anethole and caryophyllene. *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 $bp_{101.3\text{kPa}}$ 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.



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.

FCT 1973 (11) p. 863.

2-Phenoxyethyl isobutyrate [103-60-6]



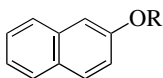
$C_{12}H_{16}O_3$, M_r 208.26, $bp_{0.53\text{ kPa}}$ 125–127 °C, d_{25}^{25} 1.044–1.050, n_D^{20} 1.492–1.496, is a fragrance material that does not occur in nature. It is a colorless liquid with a sweet, flowery-fruity odor.

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.

FCT 1974 (12) p. 955.

Trade Name. Phenirat (H&R).

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, $bp_{1.3\text{ kPa}}$ 138 °C, forms white crystals (mp 73–74 °C) with an intense orange blossom odor.

FCT 1975 (13) p. 885.

β -Naphthyl ethyl ether [93-18-5]

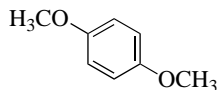
$R = CH_2CH_3$, $C_{12}H_{12}O$, M_r 172.23, $bp_{1.3\text{ kPa}}$ 148 °C, forms white crystals (mp 37–38 °C), with a mild, long-lasting, orange blossom fragrance.

FCT 1975 (13) p. 883.

β -Naphthyl isobutyl ether [2173-57-1]

$R = CH_2CH(CH_3)_2$, $C_{14}H_{16}O$, M_r 200.28, forms white crystals (mp 33–33.5 °C) with a fruity, orange blossom odor.

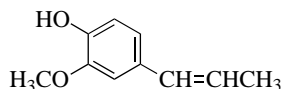
FCT 1992 (30) p. 95 S.

Hydroquinone dimethyl ether [150-78-7], 1,4-dimethoxybenzene

$C_8H_{10}O_2$, M_r 138.17, $bp_{2.7\text{kPa}}$ 109 °C, occurs in hyacinth oil and has also been identified in tea. It is a white crystalline solid (mp 57–58 °C) with an intensely sweet, somewhat herbal, nutlike odor.

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

FCT 1978 (16) p. 715.

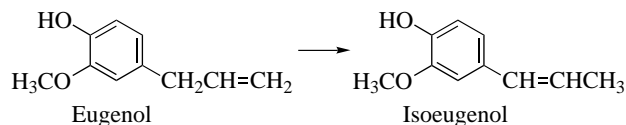
Isoeugenol [97-54-1], 2-methoxy-4-(1-propenyl)phenol

$C_{10}H_{12}O_2$, M_r 164.22; *cis* isomer [5912-86-7]: $bp_{1.7\text{kPa}}$ 134–135 °C, d_4^{20} 1.0837, n_D^{20} 1.5726; *trans* isomer [5932-68-3]: mp 33–34 °C, $bp_{1.7\text{kPa}}$ 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 materials are prepared by esterification or etherification of the hydroxyl group.

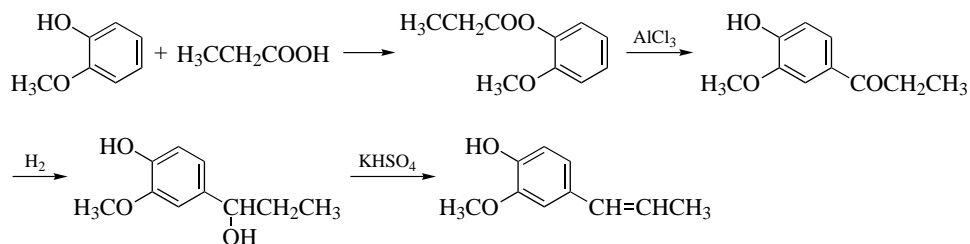
Production. Starting materials for the synthesis of isoeugenol are eugenol and guaiacol.

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 [164] or rhodium [165] compounds.



2. *Synthesis from Guaiacol.* In a process developed in the former Soviet Union, guaiacol is esterified with propionic acid, and the resulting guaiacyl propionate

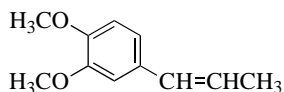
rearranges in the presence of aluminum chloride to give 4-hydroxy-3-methoxypropiophenone. Reduction of the ketone to the corresponding secondary alcohol and dehydration finally yield isoeugenol [166–168].



Uses. Isoeugenol is used in perfumery in a large number of blossom compositions, mostly for clove and carnation types, but also in oriental perfumes. Small amounts are employed in aromas and in reconstituted essential oils.

FCT 1975 (13) p. 815.

Isoeugenol methyl ether [93-16-3]

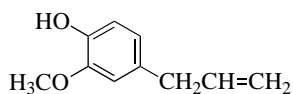


$\text{C}_{11}\text{H}_{14}\text{O}_2$, M_r 178.23, *cis* isomer [6380-24-1]: $bp_{0.9\text{kPa}}$ 137–137.5 °C, d_4^{20} 1.0530, n_D^{20} 1.5628; *trans* isomer [6379-72-2]: $bp_{0.7\text{kPa}}$ 126 °C, d_4^{20} 1.0556, n_D^{20} 1.5699, occurs in small quantities in several essential oils. It is a colorless 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.

FCT 1975 (13) p. 865.

Eugenol [97-53-0], 2-methoxy-4-allylphenol



$\text{C}_{10}\text{H}_{12}\text{O}_2$, M_r 164.20, $bp_{1.3\text{kPa}}$ 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.

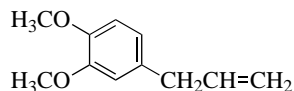
Catalytic hydrogenation (e.g., in the presence of noble-metal catalysts) yields dihydroeugenol. Isoeugenol is obtained from eugenol by shifting the double bond. Esterification and etherification of the hydroxyl group of eugenol yield valuable fragrance and flavor materials (e.g., eugenyl acetate and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

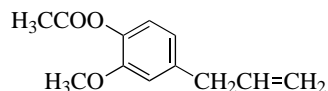
FCT 1975 (13) p. 545.

Eugenol methyl ether [93-15-2]



$C_{11}H_{14}O_2$, M_r 178.23, $bp_{1.5\text{kPa}}$ 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.

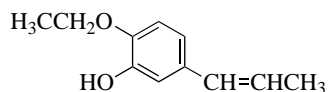
Eugenyl acetate [93-28-7]



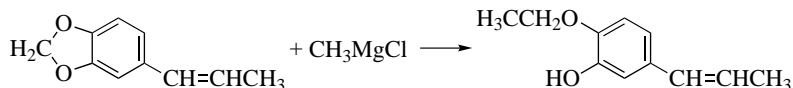
$C_{12}H_{14}O_3$, M_r 206.24, $bp_{0.4\text{kPa}}$ 120–121 °C, d_4^{20} 1.0806, n_D^{20} 1.5205, occurs in clove oil, together with eugenol. It is a crystalline solid (mp 29 °C) or yellowish liquid with a slightly fruity, clove odor. Eugenyl acetate is prepared by acetylation of eugenol with acetic anhydride and is used in clove compositions to accentuate flowery character.

FCT 1974 (12) p. 877.

Propenylguethol [94-86-0], 2-ethoxy-5-(1-propenyl)phenol

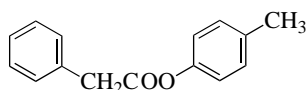


$C_{11}H_{14}O_2$, M_r 178.23, exists in *cis* (*mp* 35–36 °C) and in *trans* (*mp* 86 °C) forms. The *trans* isomer has a sweet vanilla-like odor. Propenylguethol can be prepared from isosafrole by reaction with methyl magnesium chloride or by ethylation of isoeugenol followed by selective demethylation with alkali [169].



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

***p*-Cresyl phenylacetate [101-94-0]**



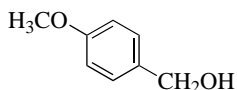
$C_{15}H_{14}O_2$, M_r 226.27, is prepared by esterification of *p*-cresol with phenylacetic acid. It forms crystals (*mp* 75–76 °C) with a narcissus odor and a honey note. It is used in blossom compositions with a slight animal note.

FCT 1975 (13) p. 775.

2.6.2 Phenol Alcohols and their Esters

In comparison with the araliphatic alcohols discussed in Section 2.5.2, very few phenol alcohols are used as fragrance and flavor materials. Neither the alcohols corresponding to vanillin, ethylvanillin, and heliotropin nor 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.

Anise alcohol [105-13-5], 4-methoxybenzyl alcohol



$C_8H_{10}O_2$, M_r 138.17, $bp_{1.3\text{kPa}}$ 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.

FCT 1974 (12) p. 825.

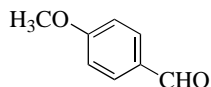
Anisyl acetate [104-21-2]

$C_{10}H_{12}O_3$, M_r 180.20, $bp_{1.5\text{kPa}}$ 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.

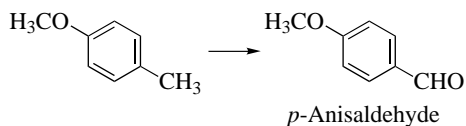
FCT 2000 (38, suppl. 3) p. S7.

2.6.3 Phenol Aldehydes

Phenol aldehydes are generally pleasant-smelling products. Some of them are particularly important as fragrance and flavor materials. 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 material. Other important derivatives of this aldehyde are veratraldehyde (dimethyl ether) and heliotropin (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, $bp_{1.85\text{kPa}}$ 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 [170].

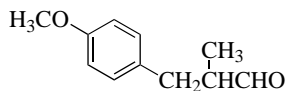


Other industrial processes are the liquid-phase oxidation in the presence of cobalt catalysts [171] and the electrochemical oxidation in the presence of lower aliphatic alcohols via the corresponding anisaldehyde dialkyl acetal [172].

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 hydrogen sulfite derivative is used as a brightener for metals in galvanic baths. FCT 1974 (12) p. 823.

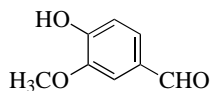
2-Methyl-3-(4-methoxyphenyl)propanal [5462-06-6]



$C_{11}H_{14}O_2$, M_r 178.23, d_4^{20} 1.039–1.047, n_D^{20} 1.517–1.522, is a pale yellow liquid with licorice, anise note with slight fruity modification. It does not occur in nature. It can be prepared by condensation of anisaldehyde (see above) with propanal and selective hydrogenation of the resulting 2-methyl-3-(4-methoxyphenyl)-2-propenal. It fits well with flowery notes and is used in fine fragrances and cosmetics. FCT 1988 (26) p. 377.

Trade Names. Canthoxal (IFF), Anisylpropanal (BASF).

Vanillin [121-33-5], 4-hydroxy-3-methoxybenzaldehyde



$C_8H_8O_3$, M_r 152.15, $bp_{1.3\text{kPa}}$ 155 °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.

Properties. Vanillin is a colorless crystalline solid (*mp* 82–83 °C) 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 Cannizzarro reaction. Numerous derivatives can be prepared by etherification or esterification of the hydroxyl group and by aldol condensation at the aldehyde group. Several of these derivatives are intermediates, for example, in the synthesis of pharmaceuticals.

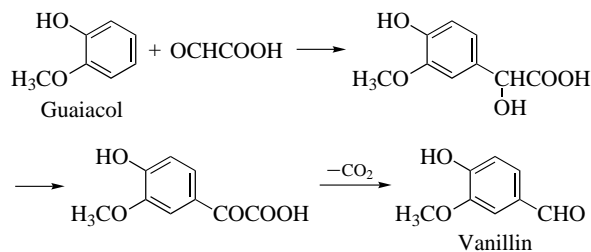
Production. Commercial vanillin is obtained by processing waste sulfite liquors or is synthesized from guaiacol. Preparation by oxidation of isoeugenol is of historical interest only.

1. *Preparation from Waste Sulfite Liquors.* The starting material for vanillin production is the lignin present in sulfite wastes from the cellulose industry. 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 [173]. 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.

2. *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 [174]. 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.



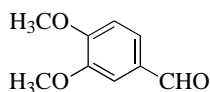
This process has the advantage that, under the reaction conditions, the glyoxyl radical enters the aromatic guaiacol ring almost exclusively *para* to the phenolic hydroxyl group. Tedious separation procedures are thus avoided.

Much research and development for the biotechnological manufacture of vanillin has been done [175].

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.

FCT 1977 (15) p. 633.

Veratraldehyde [120-14-9], 3,4-dimethoxybenzaldehyde

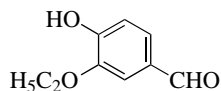


$C_9H_{10}O_3$, M_r 166.18, occurs in a few essential oils and is a crystalline solid (*mp* 44.5–45 °C) with a woody, vanilla-like odor.

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.

FCT 1975 (13) p. 923.

Ethylvanillin [121-32-4], 3-ethoxy-4-hydroxybenzaldehyde

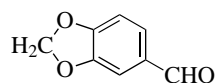


$C_9H_{10}O_3$, M_r 166.18, *mp* 77–78 °C, does not occur in nature. Its odor resembles that of vanillin but is approximately three times as strong. Ethylvanillin can be prepared by method 2 as described for vanillin, using guethol instead of guaiacol as the starting material.

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

FCT 1975 (13) p. 103.

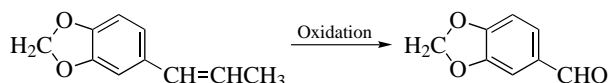
Heliotropin [120-57-0], piperonal, 3,4-methylenedioxybenzaldehyde



$C_8H_6O_3$, M_r 150.13, $bp_{1.6\text{kPa}}$ 139.4 °C, $d_4^{43.2}$ 1.2792, occurs in a number of essential oils, but never as the main component. It forms white crystals (mp 37 °C) with a sweet-flowery, slightly spicy, heliotrope-like odor.

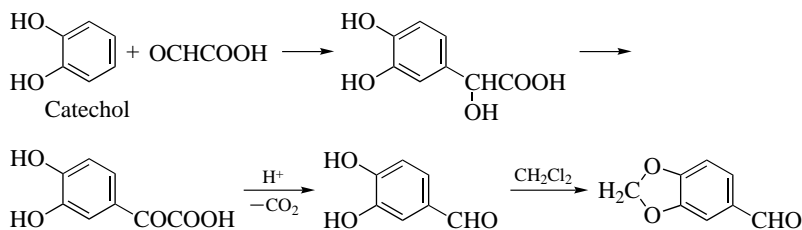
Production. Heliotropin is produced by two main routes:

1. *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 heliotropin are chromium(VI) salts, oxygen, and ozone.

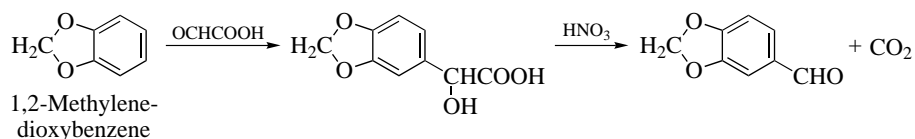


This method is still used currently because safrole (the starting material for isosafrole) can be isolated from essential oils relatively inexpensively and in sufficient quantity.

2. *From Catechol.* Several routes have recently been developed for the synthesis of heliotropin 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 [176]. The latter product is converted into heliotropin, for example, by reaction with methylene chloride in the presence of quaternary ammonium salts [177].



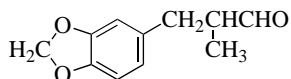
In another route, catechol is first reacted with methylene chloride and converted into 1,2-methylenedioxybenzene [177]. Reaction with glyoxylic acid in strongly acidic media yields 3,4-methylenedioxymandelic acid [178]. Subsequent oxidation and decarboxylation with nitric acid affords heliotropin.



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

FCT 1974 (12) p. 907.

2-Methyl-3-(3,4-methylenedioxyphenyl)propanal [1205-17-0]



$C_{11}H_{12}O_3$, M_r 192.22, is not found in nature. It is a colorless to slightly yellow liquid, d_4^{20} 1.159–1.167, n_D^{20} 1.531–1.536, with green, floral odor with top notes of ozone and new mown hay. It can be prepared by condensation of heliotropin (see previous page) with propanal and partial hydrogenation of the intermediately formed unsaturated aldehyde.

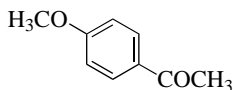
Title compound can be used in perfumes for toiletries, e.g., shaving creams and detergents.

Trade Names. Heliofolal (H&R), Helional (IFF), Aquanal (Quest), Heliobouquet (Takasago).

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 material. 4-Hydroxybenzylacetone, a higher mass phenol ketone, has a characteristic raspberry aroma.

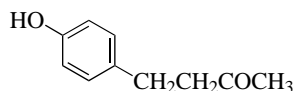
4-Methoxyacetophenone [100-06-1], acetanisole



$C_9H_{10}O_2$, 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.

FCT 1974 (12) p. 927.

4-(4-Hydroxyphenyl)-2-butanone [5471-51-2], raspberry ketone



$C_{10}H_{12}O_2$, M_r 164.20, is a highly characteristic component of raspberry aroma. It forms colorless crystals (mp 82–83 °C) 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 4-(4-hydroxyphenyl)-2-butanone with methyl vinyl ketone (e.g., in the presence of phosphoric acid) [179] or with 4-hydroxy-2-butanone in the presence of concentrated sulfuric acid [180].

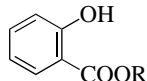
The ketone is used in fruit flavors, particularly in raspberry compositions. FCT 1978 (16) p. 781.

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

2.6.5 Phenolcarboxylates

2.6.5.1 Salicylates

Alkyl and aralkyl salicylates, are sensorially important phenolcarboxylates 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, $bp_{1.6\text{kPa}}$ 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.

FCT 1978 (16) p. 821.

Isoamyl salicylate [87-20-7]

$R = CH_2CH_2CH(CH_3)_2$, $C_{12}H_{16}O_3$, M_r 208.26, $bp_{2\text{kPa}}$ 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.

FCT 1973 (11) p. 859.

Hexyl salicylate [6259-76-3]

$R = (CH_2)_5CH_3$, $C_{13}H_{18}O_3$, M_r 222.28, $bp_{1.6\text{kPa}}$ 167–168 °C, d_{25}^{25} 1.035, n_D^{25} 1.5049, has been reported in carnation flower absolute [181]. 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. FCT 1975 (13) p. 807.

***cis*-3-Hexenyl salicylate** [65405-77-8]

R = *cis*-(CH₂)₂CH = CHCH₂CH₃, C₁₃H₁₆O₃, M_r 220.27, bp_{0.15 kPa} 125 °C, d₂₅²⁵ 1.0589, n_D²⁰ 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. FCT 1979 (17) p. 373.

Cyclohexyl salicylate [25485-88-5]

R = cyclo-C₆H₁₁, C₁₃H₁₆O₃, M_r 220.27 is not found in nature. It is a colorless liquid, bp_{4 Pa} 115 °C, d₂₅²⁵ 1.112, n_D²⁰ 1.532–1.536, with aromatic, floral balsamic odor. It is used in perfumery instead of benzyl salicylate.

Benzyl salicylate [118-58-1]

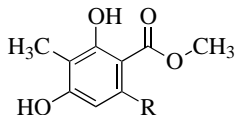
R = CH₂C₆H₅, C₁₄H₁₂O₃, M_r 228.25, bp_{1.3 kPa} 186–188 °C, d₄²⁰ 1.1799, n_D²⁵ 1.5805, which occurs in several essential oils, is a colorless, viscous liquid with a weak, sweet, slightly balsamic odor. Benzyl salicylate is used as a fixative in flowery-spicy perfume compositions and in flavors. FCT 1973 (11) p. 1029.

Phenethyl salicylate [87-22-9]

R = CH₂CH₂C₆H₅, C₁₅H₁₄O₃, M_r 242.27, which has been reported to occur in some essential flower oils, is a crystalline solid (mp 44 °C) with a weak, long-lasting, balsamic, blossom odor, reminiscent of rose and hyacinth. It is used in perfumery for spicy and balsamic blossom compositions. FCT 1978 (16) p. 849.

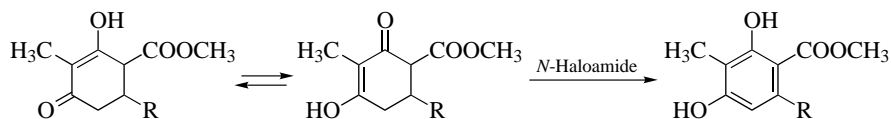
2.6.5.2 Resorcylic Acid Esters

Two *alkyl-substituted resorcylic acid esters* are important as oakmoss fragrance substances.

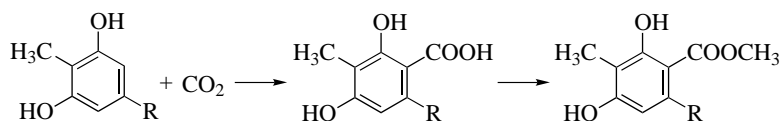


They can be prepared from acyclic compounds. In an industrial process, dimethyl malonate is condensed with 4-alken-3-ones (or a mixture of the respective ketones with 5-chloroalkan-3-ones) to give a substituted 3-hydroxy-2-cyclohexenone. Aromatization, in good yield is achieved by reaction of the hydroxycyclohexenones

with a suitable *N*-haloamide. The intermediate 3-hydroxy-2-cyclohexenones can also be obtained by condensation of methyl 3-oxoalkanoate with methyl crotonate [182].



Another route starts from the corresponding (di)methyl-1,3-dihydroxybenzene which is carboxylated, and the resulting dihydroxymethylbenzoic acid is esterified.



Methyl 3-methylresorcyate [33662-58-7], **methyl 2,4-dihydroxy-3-methylbenzoate**
 R = H, C₉H₁₀O₄, *M_r* 182.18, *mp* 130.5–131.6 °C, forms an off-white powder with long-lasting moss odor, slightly reminiscent of oakmoss and strong seaside in character. It is used in small amounts to provide marine effects to perfumes.

Trade Name. Seamoss (PFW).

Methyl 3,6-dimethylresorcyate [4707-47-5],
methyl 2,4-dihydroxy-3,6-dimethylbenzoate

R = CH₃, C₁₀H₁₂O₄, *M_r* 196.20, is an odor determining constituent of oakmoss absolute extract and forms colorless crystals (*mp* 145 °C) with a mossy-earthy odor. It is used as a substitute for oakmoss extract in fine fragrances, soap, and cosmetics.

Trade Names. Atralone (Agan), Evernyl (Giv.-Roure), Veramoss (IFF).

2.7 O- and O,S-Heterocycles

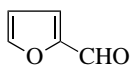
2.7.1 Cyclic Ethers

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. Caryophyllene oxide [1139-30-6], which has a woody,

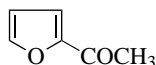
slightly ambergris-like odor can be prepared by treatment of β -caryophyllene with organic peracids. α -Cedrene oxide [11000-57-0] is another wood-fragrance compound, that can be easily prepared by epoxidation of cedarwood oil hydrocarbons.

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-hexahydro-penta[g]benzopyran, a musk fragrance that is used in large amounts.

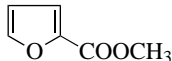
Numerous furan and pyran derivatives, many of which originate from heat treatment of carbohydrates, largely determine the odor of processed foods. Of this group, 2,5-dimethyl-4-hydroxy-2*H*-furan-3-one and maltols are used in fairly large quantities in flavors. The following compounds are used in relatively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



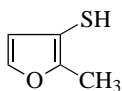
2-furaldehyde [98-01-1]: freshly baked bread odor



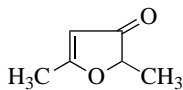
2-acetylfuran [1192-62-7]: sweet balsamic odor



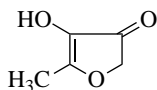
methyl 2-furoate [611-13-2]: fruity, mushroom-like odor



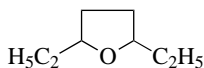
2-methylfuran-3-thiol [28588-74-1]: roast beef aroma



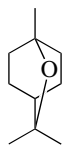
2,5-dimethyl-3(2*H*)-furanone [14400-67-0]: roast coffee odor



4-hydroxy-5-methyl-3(2*H*)-furanone [19322-27-1]: roast meat odor



2,5-diethyltetrahydrofuran [41239-48-9]: fruity, herbal-minty note

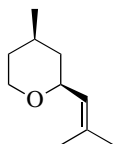
1,8-Cineole [470-82-6], 1,8-epoxy-*p*-menthane, eucalyptol

$C_{10}H_{18}O$, M_r 154.25, $bp_{101.8\text{ kPa}}$ 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 large quantities by fractional distillation of *Eucalyptus globulus* oil. A product essentially free from other products can be obtained by crystallization of cineole-rich eucalyptus oil fractions.

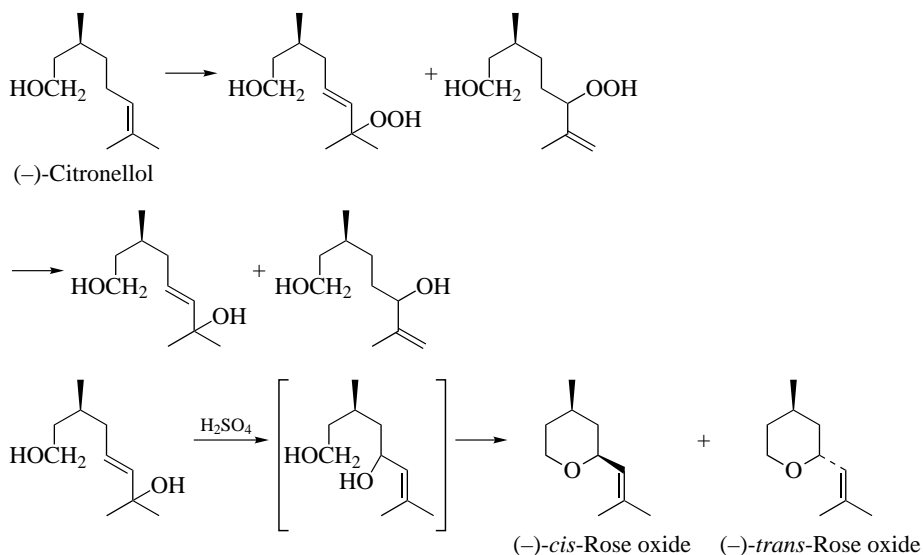
1,8-Cineole has a fresh odor and is used in large quantities in fragrances as well as in flavors (e.g., in oral hygiene products).

FCT 1975 (13) p. 105.

Rose oxide [16409-43-1], 4-methyl-2-(2-methyl-1-propenyl)tetrahydropyran

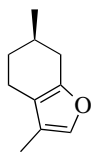
$C_{10}H_{18}O$, M_r 154.25, $bp_{1.6\text{ kPa}}$ 70 °C, d_4^{20} 0.875, n_D^{20} 1.4570, $[\alpha]_D$ for the optically pure (–)-*cis* form -58.1° , occurs in small quantities, mainly the levorotatory *cis* form, in essential oils (e.g., Bulgarian rose oil and geranium oil). Commercial synthetic products 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 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 [183]. 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.



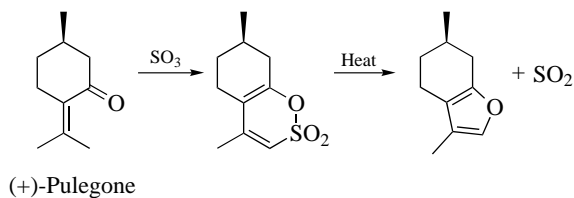
Rose oxide is used in rose and geranium perfumes.
FCT 1976 (14) p. 855.

Menthofuran [494-90-6], 3,6-dimethyl-4,5,6,7-tetrahydrobenzofuran

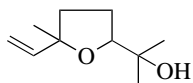


$C_{10}H_{14}O$, M_r 150.22, $bp_{1.3\text{kPa}}$ 78–79 °C, d_4^{20} 0.9676, n_D^{20} 1.4855, $[\alpha]_D^{20} + 94.6^\circ$, occurs mainly as the (+) isomer, in numerous essential oils (e.g., *Mentha* oils). It is a colorless liquid with a minty odor.

(+)-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.

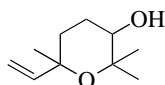


Menthofuran is used mainly in peppermint oil reconstitutions.

Linalool oxide, 2-methyl-2-vinyl-5-(α -hydroxyisopropyl)tetrahydrofuran

$C_{10}H_{18}O_2$, M_r 170.25, $bp_{101.3\text{kPa}}$ 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.

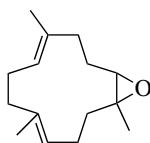
Linalool oxide is prepared by oxidation of linalool, e.g., with peracids. The isomeric compound 2,2,6-trimethyl-6-vinyltetrahydro-2*H*-pyran-3-ol [14049-11-7], which also occurs in nature, is formed as a byproduct:



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.

FCT 1983 (21) p. 863.

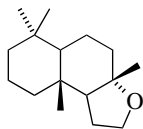
1,5,9-Trimethyl-13-oxabicyclo[10.1.0]trideca-4,8-diene [13786-79-3]

$C_{15}H_{24}O$, M_r 220.36, d_{20}^{20} 0.962–0.980, n_D^{20} 1.504–1.509, is a colorless to pale yellow liquid with powerful complex woody and amber odor. It does not occur in nature. It is prepared by monoepoxidation of 1,5,9-trimethyl-1,5,9-dodecatriene with, e.g., peracids.

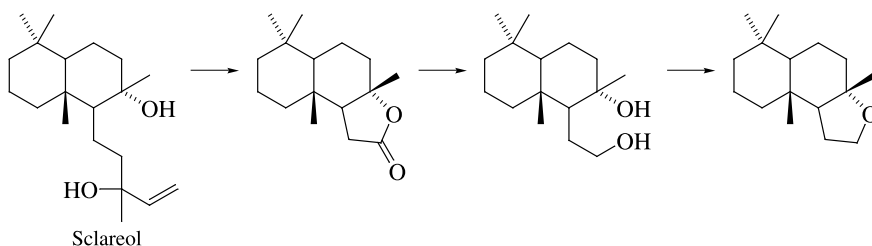
It is used in perfumery for cosmetics and detergents.

FCT 2000 (38, suppl. 3) p. S185.

Trade Name. Cedroxyde (Firmenich).

3a,6,6,9a-Tetramethyldodecahydronaphtho[2,1-*b*]furan [6790-58-5]

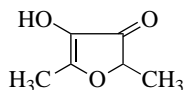
$C_{16}H_{28}O$, M_r 236.40, mp 75–76 °C, is a crystalline autoxidation product of ambrein (see Ambergris) with a typical ambergris odor. It is prepared from sclareol, a diterpene alcohol obtained from extraction of clary sage plants (see Sage Oils, p. 217). Oxidative degradation to a lactone, hydrogenation of the latter to the corresponding diol and dehydration yield



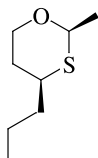
The lactone intermediate is prepared in another industrial process by cyclization of homofarnesic acid in the presence of $SnCl_4$ as a catalyst [184]. Pure diastereomers are obtained by acid cyclization of *trans*- and *cis*-4-methyl-6-(2,6,6-trimethylcyclohex-1(2)enyl)-3-hexen-1-ol, prepared from 2-methyl-4-(2,6,6-trimethylcyclohex-1(2)enyl)-2-butenal [185].

The product is used in perfumery for creating ambergris notes.

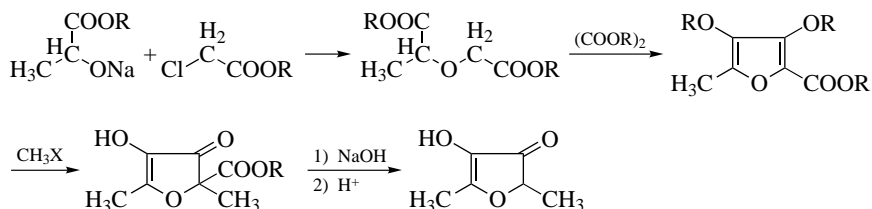
Trade Names. Compound starting from natural sclareol: Ambermore (Aromor), Ambrox (Firmenich), Ambroxan (Cognis), Ambroxid (H&R); compound starting from homofarnesic acid derivatives: Ambrox DL (Firmenich), Synambrane (H&R); compound starting from 2-methyl-4-(2,6,6-trimethylcyclohex-1(2)enyl)-2-butenal: Cetalox (Firmenich).

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 and strawberry 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 [186]. The dione is the ozonization product of 2,5-hexyenediol, which is obtained by ethynylation of acetaldehyde.



In another process, a dialkyl α -methylglycolate (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 [187].

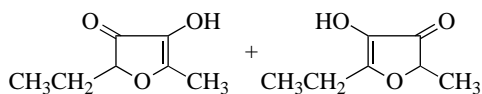


It is also manufactured in a multistep bioprocess from rhamnose [188].

The compound is used in the flavoring of foods.

Trade Name. Furaneol (Firmenich).

2-Ethyl-4-hydroxy-5-methyl-3(2*H*)-furanone [27538-10-9] and 5-Ethyl-4-hydroxy-2-methyl-3(2*H*)-furanone [27538-09-6]

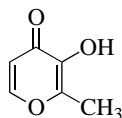


$\text{C}_7\text{H}_{10}\text{O}_3$, M_r 142.16, has been identified in, e.g., coffee and melon. The tautomer mixture is a clear slightly yellowish liquid, $bp_{0.02\text{kPa}}$ 82–83 °C, d_4^{20} 1.137, n_D^{20} 1.511 with sweet, caramel, fruity, bread-like odor. One commercially applied synthesis is the condensation of 2-pentene nitrile with ethyl lactate followed by oxidation of the intermediate 4-cyano-5-ethyl-2-methyldihydro-3(2*H*)-furanone with monoperoxy-sulfate [189].

It is used in fruit flavors as well as flavor compositions with caramel, coffee, meat, or bread character.

Trade Name. Homofuronol (Giv.-Roure).

Maltol [118-71-8], 3-hydroxy-2-methyl-4*H*-pyran-4-one

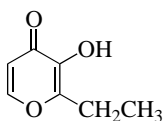


$C_6H_6O_3$, M_r 126.11, occurs in pine needles and the bark of young larch trees. It is produced when cellulose or starch are heated and is a constituent of wood tar oils. It forms crystals (mp 162–164 °C) with a caramel-like odor, reminiscent of freshly baked cakes.

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).

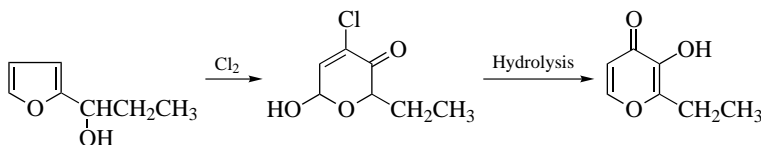
FCT 1975 (13) p. 841.

Ethylmaltol [4940-11-8], 2-ethyl-3-hydroxy-4H-pyran-4-one



$C_7H_8O_3$, M_r 140.14, does not occur in nature. It forms white crystals (mp 90–91 °C) with very sweet caramel-like odor, four to six times more potent than maltol.

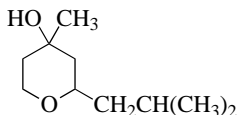
Several syntheses have been developed for its preparation. In a one pot process, e.g., α -ethylfurfuryl alcohol is treated with halogen to give 4-halo-6-hydroxy-2-ethyl-2H-pyran-3(6H)-one, which need not be isolated and can be converted to ethylmaltol by aqueous hydrolysis [190]



Ethylmaltol is used in aroma compositions and as a flavor enhancer in food, beverages and tobacco.

FCT 1975 (13) p. 805.

2-Isobutyl-4-methyltetrahydro-2H-pyran-4-ol [63500-71-0]



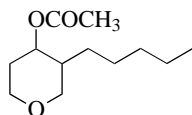
$C_{10}H_{20}O_2$, M_r 172.27, d_{20}^{20} 0.948–0.955, n_D^{20} 1.455–1.460, is a colorless to pale yellow liquid with a fresh, soft and natural floral odor. It does not occur in nature.

Cyclocondensation of 3-methyl-3-buten-1-ol with 3-methylbutanal on silica gel and alumina in the absence of solvents is proposed for synthesis [191].

It can be used in almost all perfume types to give elegant floral diffusion without changing the fragrance character. Its stability allows application in soap, toiletries, and household products.

Trade Names. Florol (Firmenich), Florosa Q (Quest).

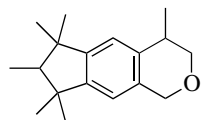
3-Pentyltetrahydro-2H-pyran-4-ol acetate [18871-14-2]



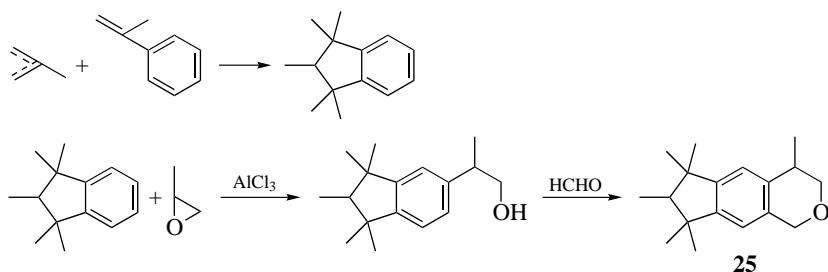
$C_{12}H_{22}O_3$, M_r 214.30, $bp_{0.13\text{ kPa}}$ 102–103 °C, d_{25}^{25} 0.974–0.978, n_D^{20} 1.448–1.451, is a colorless to pale yellow liquid with a sweet-floral, fruity, slightly woody, jasmine-like odor. It is prepared by a Prins reaction of 1-octene with formaldehyde and acetic acid and is used in perfumes for various flower types, especially jasmine. FCT 1992 (30) p. 5 S.

Trade Names. Jasmal (IFF), Jasmonyl LG (Giv.-Roure), Jasmophyll (H&R), Jasmopyrane (Quest).

4,6,6,7,8,8-Hexamethyl-1,3,4,6,7,8-hexahydrocyclopenta[g]benzopyran [1222-05-5]



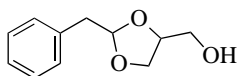
$C_{18}H_{26}O$, M_r 258.40, $bp_{1.1\text{ kPa}}$ 129 °C, d_4^{20} 1.0054, n_D^{20} 1.5342, is a viscous liquid with a musklike odor. It is one of the most frequently used synthetic, artificial musk fragrances. The starting material for its synthesis is 1,1,2,3,3-pentamethylindane, which is prepared 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 phenethyl alcohol from benzene and ethylene oxide (see p. 99)). Ring closure of the resulting 1,1,2,3,3-pentamethyl-5-(β -hydroxyisopropyl)indane is accomplished with paraformaldehyde and a lower aliphatic alcohol via the acetal [192] or with paraformaldehyde and a carboxylic acid anhydride via the acylate [193].



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 soap, detergents, and cosmetics and is used in large amounts. FCT 1976 (14) p. 793.

Trade Names. Abbalide (BBA), Galaxolide (IFF), Musk 50 (Agan), Pearlide (Kao).

Phenylacetaldehyde glycerine acetal [29895-73-6], 2-benzyl-1,3-dioxolan-4-methanol



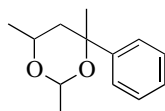
$C_{11}H_{14}O_3$, M_r 194.23, is not found in nature. It is a colorless slightly viscous liquid, d_4^{20} 1.154–1.162, n_D^{20} 1.529–1.534, with a tenacious honey, cyclamen, and rose note. It is prepared by acetalization of phenylacetaldehyde with glycerine.

It is used for tenacious compositions with green and broom character, e.g., for detergents.

FCT 1976 (14) p. 829.

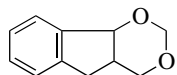
Trade Name. Acetal CD (Giv.-Roure).

2,4,6-Trimethyl-4-phenyl-1,3-dioxane [5182-36-5]



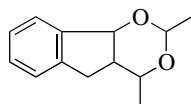
$C_{13}H_{18}O_2$, M_r 206.29, does not occur in nature. It is a colorless to pale yellow liquid, d_4^{20} 1.018–1.023, n_D^{20} 1.501–1.506, with a herbal-fresh odor, reminiscent of grapefruit. It is prepared by a Prins reaction of α -methylstyrene with acetaldehyde and used in perfume compositions for soap, detergents, and household products.

Trade Names. Floropal (H&R), Vertacetal (Dragoco).

4,4a,5,9b-Tetrahydroindeno[1,2-d]-m-dioxin [18096-62-3]

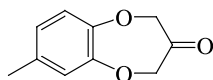
$C_{11}H_{12}O_2$, M_r 176.21, $bp_{1.3\text{kPa}}$ 134 °C, $d_{15.5}^{15.5}$ 1.159, n_D^{20} 1.559, forms crystals (mp 35–36 °C) with an indole-like odor. It is prepared by a Prins reaction from indene and formaldehyde in the presence of dilute sulfuric acid [194]. It is used in perfumes for soap and detergents.

Trade Names. Indoflor (H&R), Indolal (Dragoco), Indolarome (IFF).

4,4a,5,9b-Tetrahydro-2,4-dimethylindeno[1,2-d]-m-dioxin [27606-09-3]

$C_{13}H_{16}O_2$, M_r 204.27, d_{25}^{25} 1.085–1.089, n_D^{20} 1.527–1.531, is a clear colorless to pale yellow liquid with a transparent floral green odor reminiscent of magnolia, geranium, and grapefruit. It is utilized to create special floral notes. Due to its excellent stability it is recommended for use in a wide range of applications. The material is prepared by reaction of indene with acetaldehyde [195].

Trade Name. Magnolan (H&R).

7-Methyl-2H-1,5-Benzodioxepin-3(4H)-one [28940-11-6], watermelon ketone

$C_{10}H_{10}O_3$, M_r 178.19, is a white powder with a fresh marine odor, mp 35–41 °C. It is used to create fresh aquatic marine notes in perfume oils for many applications, e.g., for fine fragrances, soaps, and shower gels.

The material is prepared by etherification of 4-methylpyrocatechol with two equivalents of alkyl 2-bromoacetate, and subsequent Dieckmann condensation followed by hydrolysis and decarboxylation [195a].

Trade Name. Calone 1951 (Calchauvet).

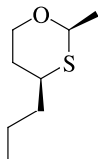
Ethyl 2-methyl-1,3-dioxolane-2-acetate [6413-10-1], **2-methyl-1,3-dioxolane-2-acetic acid ethyl ester**

$C_8H_{14}O_4$, M_r 174.20, is not found in nature. It is a colorless liquid, d_4^{20} 1.084–1.092, n_D^{20} 1.431–1.435, with a strong, fruity, apple-like, slightly green odor. It can be prepared by acetalization of ethyl acetoacetate with ethyleneglycol.

It is used in perfume bases for soap, toiletries, and detergents.
FCT 1988 (26) p. 315.

Trade Names. Applinal (Quest), Fructone (IFF), Jasmapunat (H&R).

***cis*-2-Methyl-4-propyl-1,3-oxathiane** [59323-76-1]



$C_8H_{16}OS$, M_r 160.28. d_{20}^{20} 1.045–1.055, n_D^{20} 1.458–1.463, is a colorless liquid with a typical note of tropical fruits. The material is reported to occur in the flavor of yellow passion fruit and is mainly used in passion fruit and grapefruit type flavors. It is also recommended for use in citrus and fruity fragrance materials for a wide range of applications.

cis-2-Methyl-4-propyl-1,3-oxathiane is prepared by reaction of 3-mercaptohexanol with acetaldehyde [195b].

FEMA-GRAS 3578.

Trade Name. Oxane (Firmenich).

2.7.2 Lactones

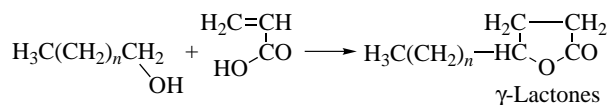
Naturally occurring organoleptically important lactones are mainly saturated and unsaturated γ - and δ -lactones, and to a lesser extent macrocyclic lactones. The occurrence of these types of lactones reflects their ready formation from natural acyclic precursors.

The lactones are the intramolecular esters of the corresponding hydroxy fatty acids. They contribute to the aroma of butter and various fruits. 15-Pentadecanolide is responsible for the musk-like 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 materials. Like the well-known macrocyclic ketones, 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 [196].



Because of the demand for natural γ - and δ -lactones in the flavor industry biosynthetic processes have been developed for their production [197].

γ -Octalactone [104-50-7], ($n = 3$)

$\text{C}_8\text{H}_{14}\text{O}_2$, M_r 142.20, $bp_{1.3\text{kPa}}$ 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.

FCT 1976 (14) p. 821.

γ -Nonalactone [104-61-0], ($n = 4$), so-called ‘aldehyde C_{18} ’

$\text{C}_9\text{H}_{16}\text{O}_2$, M_r 156.22, $bp_{1.7\text{kPa}}$ 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.

FCT 1975 (13) p. 889.

Trade Name. Abricolin (H&R).

γ -Decalactone [706-14-9], ($n = 5$)

$\text{C}_{10}\text{H}_{18}\text{O}_2$, M_r 170.25, $bp_{2.3\text{kPa}}$ 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.

FCT 1976 (14) p. 741.

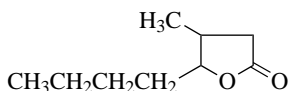
γ -Undecalactone [104-67-6], ($n = 6$), so-called ‘aldehyde C_{14} ’

$\text{C}_{11}\text{H}_{20}\text{O}_2$, M_r 184.28, $bp_{2.0\text{kPa}}$ 167–169 °C, d_4^{20} 0.944, n_D^{20} 1.4514, occurs in foods and is an almost colorless liquid with a peach-like 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.

FCT 1975 (13) p. 921.

β -Methyl- γ -octalactone [39212-23-2], whiskey lactone

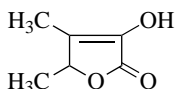


$C_9H_{16}O_2$, M_r 156.23, $bp_{0.5\text{kPa}}$ 96 °C, d_{20}^{20} 0.961–0.971, n_D^{20} 1.443–1.449, is found as its *cis* and *trans* isomers in whiskey and in oakwood volatiles, the *cis* isomer is the more important in sensory terms. It is a clear, almost colorless liquid with an intense, warm, sweet, coumarin-like odor.

A *cis*–*trans*-mixture can be prepared by radical addition reaction of pentanal with crotonic acid followed by reductive cyclization of the resulting γ -oxo acid with sodium boron hydride/sulfuric acid [198]. It is used in aroma compositions, e.g., for beverages.

Trade Name. Methyl octalactone (PFW).

4,5-Dimethyl-2(5H)-furanone [28664-35-9], sotolone

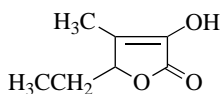


$C_6H_8O_3$, M_r 128.13, was found in, e.g., fenugreek, coffee, sake, and flor-sherry. Its aroma characteristic changes from caramel-like at low concentrations to curry-like at high concentrations. A method described for its preparation comprises condensation of ethyl propionate with diethyl oxalate and reaction of the intermediately formed diethyl oxalylpropionate with acetaldehyde. Acidic decarboxylation of the ethyl 4,5-dimethyl-2,3-dioxodihydrofuran-4-carboxylate gives the title compound [199].

It is used in food flavoring.

Trade Names. Sugar lactone (Treatt), Fenugreek lactone (Vioryl).

5-Ethyl-3-hydroxy-4-methyl-2(5)-furanone [698-10-2], abhexone

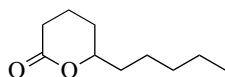


$C_7H_{10}O_3$, M_r 142.16, has been found in, e.g., lovage and roast coffee. It has a bouillon-like, coffee and lovage aroma, depending on its concentration. It can be

synthesized by condensation of 2-oxobutanoic acid (from acrylic aldehyde with acetic anhydride and sodium cyanide, followed by reaction with methanol/hydrochloric acid) with methanol/sodium methylate and subsequent decarbo-methoxylation [200]. It is used for aromatization of food.

Trade Name. Ethyl fenugreek lactone (Vioryl).

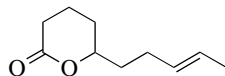
δ -Decalactone [705-86-2]



$C_{10}H_{18}O_2$, M_r 170.25, bp_{3Pa} 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, peach-like aroma.

δ -Decalactone can be prepared by peracid oxidation of 2-pentylcyclopentanone. It is used in perfumes and for cream and butter flavorings. FCT 1976 (14) p. 739.

Tetrahydro-6-(3-pentenyl)-2H-pyran-2-one [32764-98-0]

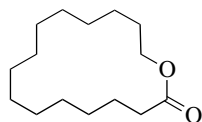


$C_{10}H_{16}O_2$, M_r 168.24, d_4^{20} 0.995–1.005, n_D^{20} 1.475–1.480, does not occur in nature. It is a colorless liquid with an oily-fruity odor with floral, petal-like notes. For synthesis, 1,3-cyclohexanedione is reacted with crotyl bromide in the presence of potassium hydroxyde to give the 2-alkenyl-substituted 1,3-diketone. Ring cleavage with sodium hydroxyde leads to the unsaturated keto acid which is reduced with $NaBH_4$ under formation of the title compound [201].

It is used in compositions with fantasy notes for toiletries.

Trade Name. Jasmolactone (Firmenich).

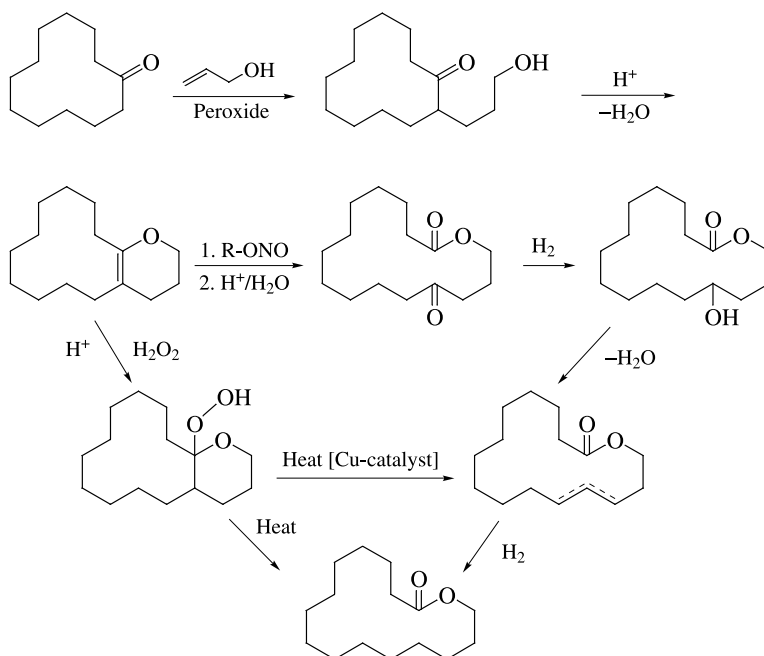
15-Pentadecanolide [106-02-5], 15-hydroxypentadecanoic acid lactone



$C_{15}H_{28}O_2$, M_r 240.39, $bp_{1.3-1.4kPa}$ 169 °C, d_4^{40} 0.940, occurs in small quantities in, for example, angelica root oil. It forms colorless crystals (mp 37–38 °C) with a delicate, musk-like odor.

Production. The main industrial syntheses start from compounds produced from cyclododecatriene: either by ring expansion of cyclododecanone or by depolymerization of polyesters of 15-hydroxypentadecanoic acid (from 1,12-dodecanediol).

1. *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. This is converted into 13-oxabicyclo[10.4.0]hexadec-1(12)-ene by acid-catalyzed dehydration [202]. Addition of hydrogen peroxide, in the presence of sulfuric acid, gives 12-hydroperoxy-13-oxabicyclo[10.4.0]hexadecane. 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 12-hydroxy-15-penta-decanolide [203].

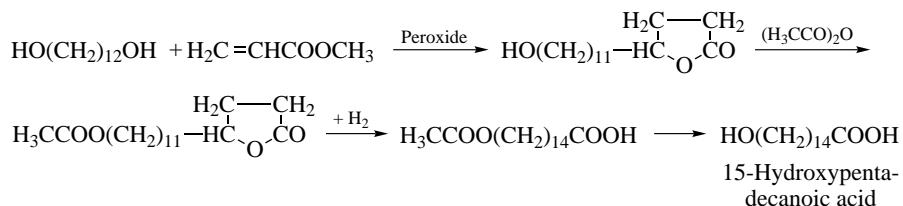


In another process, 13-oxabicyclo[10.4.0]hexadec-1(12)-ene is reacted with isopropyl nitrite to give 12-oxo-15-pentadecanolide, which is hydrogenated to the corresponding hydroxy compound. The hydroxy group is derivatized and the reaction product pyrolyzed to the unsaturated lactone. Hydrogenation of the latter yields 15-pentadecanolide [204].

The unsaturated lactone may also be obtained by decomposition of the hydroperoxide under copper catalysis [204a, 204b].

2. *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 [205].



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. FCT 1975 (13) p. 787.

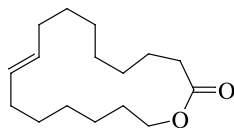
Trade Names. Cyclopentadecanolid (H&R), Exaltolide, Exaltex (Firmenich), Pentalide (Soda Aromatic).

15-Pentadec-11-enolide/15-Pentadec-12-enolide (mixture of *cis* and *trans* isomers) [34902-57-3]

$\text{C}_{15}\text{H}_{26}\text{O}_2$, M_r 238.37, d_{25}^{25} 0.958–0.967, n_D^{20} 1.478–1.484. It is a colorless to pale yellow liquid with a powerful very elegant musk odor with waxy and nitromusk undertones. The material is recommended for use in a wide range of fragrance products, e.g., antiperspirants, soaps, shampoos, detergent powder, and fabric conditioner. It is prepared as described under 15-Pentadecanolide [204a], see foregoing paragraph.

Trade Names. Habanolide (Firmenich), Globalide (H&R).

9-Hexadecen-16-olide [28645-51-4], **oxacycloheptadec-10-en-2-one**



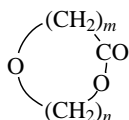
$\text{C}_{16}\text{H}_{28}\text{O}_2$, M_r 252.40, is not reported as being found in nature in contrast to (*Z*)-7-hexadecen-16-olide which occurs in ambrette seed oil (see p. 172) and which is also

referred to as ambrettolide. It is a colorless to slightly yellow liquid, d_4^{20} 0.949–0.957, n_D^{20} 1.477–1.482, with an intense and powerful musk odor. It is prepared by treating aleuritic acid (9,10,16-trihydroxyhexadecanoic acid) with trimethyl orthoformate to give a dioxolane derivative. Reaction with acetic anhydride yields ω -acetoxy 9-*trans*-hexadecenoic acid methyl ester. This is lactonized with potassium hydroxide to give the title compound [206].

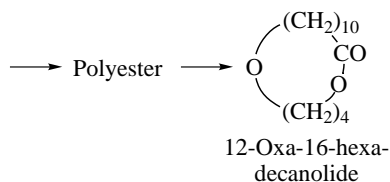
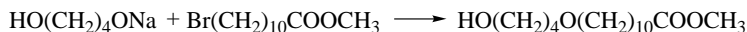
It is used in perfumery for fine fragrances, highly appreciated for its diffusion and fixative properties.

Trade Names. Ambrettolide (Giv.-Roure), Ambrettolide (IFF).

12-Oxa-16-hexadecanolide [6707-60-4], 16-hydroxy-12-oxahexadecanoic acid lactone



($m = 10$, $n = 4$) $C_{15}H_{28}O_3$, 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 11-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.



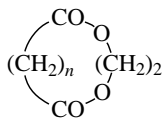
12-Oxa-16-hexadecanolide as well as the stronger smelling 11-oxa ($m = 9$, $n = 5$) [3391-83-1], and 10-oxa ($m = 8$, $n = 6$) [1725-01-5] isomers which are obtained in the same way from the corresponding hydroxy-oxa acids, are used as long-lasting musks mainly in fine fragrances.

FCT 1982 (20) p. 789: 12-Oxa-

1982 (20) p. 787: 11-Oxa-

1992 (30) p. 99 S: 10-Oxa-

Trade Names. 12-Oxa-16-hexadecanolide = Cervolide (Quest), Musk 781 (IFF); 11-Oxa-16-hexadecanolide = Musk R 1 (Quest); 10-Oxa-16-hexadecanolide = Oxalide (Takasago).

1,12-Dodecanedioic acid ethylene ester [54982-83-1], ($n = 10$)

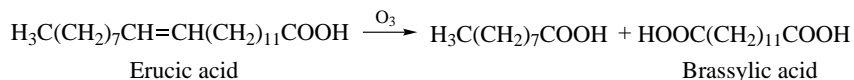
$C_{14}H_{24}O_4$, M_r 256.34, mp 18 °C, $bp_{2.7\text{kPa}}$ 139–141 °C, d_4^{60} 1.0303, n_D^{20} 1.4588, is a synthetic musk that is prepared by thermal depolymerization of the polyester obtained from 1,12-dodecanedioic acid and ethylene glycol in the presence of a catalyst (e.g., stannous salts of aliphatic monocarboxylic acids) [207].

The compound is used in perfumery as a musk fragrance, but is not as long-lasting as the following homologous compound, ethylene brassylate.

Trade Names. Arova N (Degussa.), MC-4 (Soda Aromatic), Musk C14 (Takasago).

1,13-Tridecanedioic acid ethylene ester [105-95-3], ethylene brassylate, ($n = 11$)

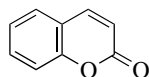
$C_{15}H_{26}O_4$, M_r 270.37, $bp_{1.3\text{kPa}}$ 140 °C, d_4^{20} 1.0180, n_D^{20} 1.4702, is an artificial fragrance material, with a sweetish, slightly fatty, musk odor. Like the previous compound, the ester is obtained by depolymerization of the corresponding polyester. Brassylic acid (1,13-tridecanedioic acid) is prepared by ozonolysis of erucic acid [208]:



Ethylene brassylate is used in large amounts in perfumery as a fixative and for rounding off sweet-flowery odor notes.

FCT 1975 (13) p. 91

Trade Names. Musk T (Takasago), MC-5 (Soda Aromatic).

Coumarin [91-64-5], 2H-1-benzopyran-2-one

$C_9H_6O_2$, M_r 146.15, $bp_{1.33\text{kPa}}$ 153.9 °C, d_4^{20} 0.935, occurs widely in nature and determines, for example, the odor of woodruff. It forms white crystals (mp 70.6 °C) with a haylike, 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 synthesis from salicylaldehyde. 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.



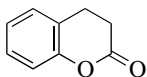
In a special process, the sodium acetate catalyst is retained in the reactor by a built-in filter and is reused [209].

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.

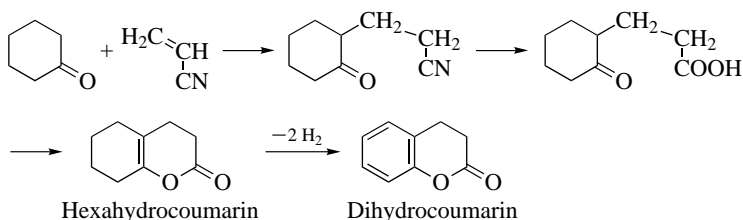
Uses. Coumarin is one of the most widely used fragrance materials. It is used in fine fragrances as well as in soap perfumes for spicy green notes. It is also used in galvanization as a brightener.

FCT 1974 (12) p. 385.

Dihydrocoumarin [119-84-6], 3,4-dihydro-2H-benzopyran-2-one



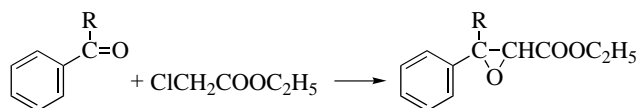
$\text{C}_9\text{H}_8\text{O}_2$ M_r 148.16, $bp_{2.3\text{kPa}}$ 145 °C, n_D^{25} 1.5528, occurs in a few essential oils and forms colorless crystals (mp 24 °C) with a sweet-herbal odor. Dihydrocoumarin is prepared by hydrogenation of coumarin, for example, in the presence of a Raney nickel catalyst. Another process employs the vapor-phase dehydrogenation of hexahydrocoumarin in the presence of Pd or Pt– Al_2O_3 catalysts [210]. Hexahydrocoumarin is prepared by cyanoethylation of cyclohexanone and hydrolysis of the nitrile group, followed by ring closure to the lactone [211].



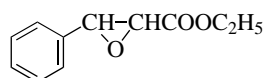
Dihydrocoumarin is used in woodruff-type flavor compositions.
FCT 1974 (12) p. 521.

2.7.3 Glycidates

A number of glycidates are important intermediates in the synthesis of fragrance materials. A few glycidates are fragrance materials in themselves. 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 ‘aldehyde C₁₆ special’

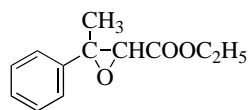


C₁₁H₁₂O₃, M_r 192.21, bp_{0.04kPa} 104 °C, d²⁰ 1.1023, n_D³⁰ 1.5095, is a colorless liquid with a strawberry-like odor; it is not known to occur in nature.

It is prepared by treating ethyl cinnamate with peracetic acid [212] or by condensation of benzaldehyde with ethyl chloroacetate (in the above Darzens reaction, R = H). The glycidate is used as a long-lasting fragrance material for creating harmonic, fruity notes in household and fine fragrances.

FCT 1975 (13) p. 101.

Ethyl 3-methyl-3-phenylglycidate [77-83-8], so-called ‘aldehyde C₁₆’, strawberry aldehyde



C₁₂H₁₄O₃, M_r 206.24, bp_{2.4kPa} 153–155 °C, d₂₅²⁵ 1.506–1.513, occurs in two optically active pairs of *cis* and *trans* isomers; each isomer has a characteristic odor [213]. 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 = CH₃) and ethyl chloroacetate depends on the base used in the reaction.

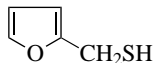
The glycidate is used in household perfumery for fruity notes.

FCT 1975 (13) p. 95.

Trade Name. Strawberry pure (Giv.-Roure).

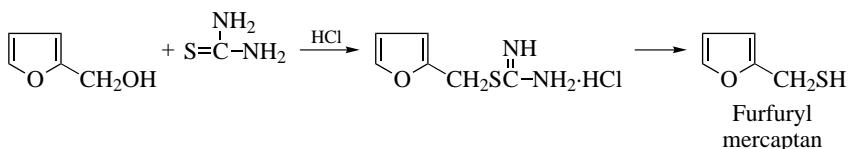
2.7.4 Miscellaneous Compounds

2-Furylmethanethiol [98-02-2], furfuryl mercaptan



C_5H_6OS , M_r 114.16, $bp_{101.3\text{ kPa}}$ 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*-furfurylisothiuronium chloride is cleaved with sodium hydroxide to give furfuryl mercaptan.



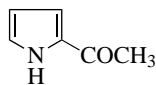
The thiol is used in coffee aromas.

2.8 N- and N,S-Heterocycles

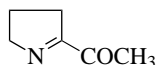
Many nitrogen- and sulfur-containing heterocycles have been identified in the aroma fractions of foods [214]. In roasted products (e.g., coffee) and heat-treated foods (e.g., baked bread or fried meat), these heterocycles are formed from reducing sugars and simple or sulfur-containing amino acids by means of Maillard reactions [215, 216]. Their odor threshold values are often extremely low and even minute amounts may significantly contribute to the aroma quality of many products [217, 218]. 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 substances. 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.

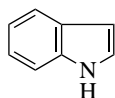
Representatives of the above-mentioned classes are as follows:



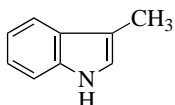
2-acetylpyrrole [1072-83-9]: roast odor



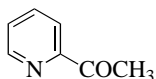
2-acetyl-3,4-dihydro-5H-pyrrole [85213-22-5]:
characteristic odor of white bread crust



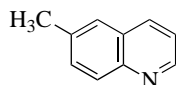
indole [120-72-9]: fecal odor, floral in high dilution



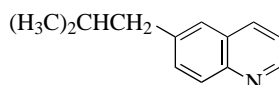
3-methylindole, skatole [83-34-1]: indole-like odor



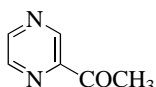
2-acetylpyridine [1122-62-9]: roast odor



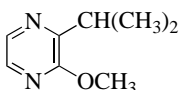
6-methylquinoline [91-62-3]: blossom odor, sweet-animalic upon dilution



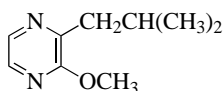
6-isobutylquinoline [68141-26-4]: mossy-earthy odor



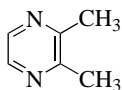
2-acetylpyrazine [22047-25-2]: popcorn-like odor



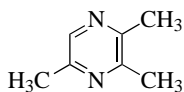
2-methoxy-3-isopropylpyrazine [25773-40-4]:
green pea odor



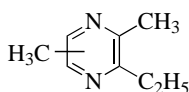
2-methoxy-3-isobutylpyrazine [24683-00-9]:
green-pepper odor
FCT 2000 (38, suppl. 3) p. S125.



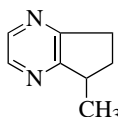
2,3-dimethylpyrazine [5910-89-4] and its
2,5-[123-32-0] and 2,6-[108-50-9] isomers: roast
odor, reminiscent of nuts



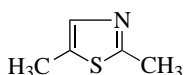
trimethylpyrazine [14667-55-1]: roast odor,
reminiscent of coffee and cocoa



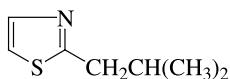
mixture of 3-ethyl-2,5-dimethylpyrazine
[13360-65-1] and 2-ethyl-3,5-dimethylpyrazine
[13925-07-0]: roast odor, reminiscent of nuts



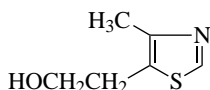
5-methyl-6,7-dihydro[5H]cyclopentapyrazine
[23747-48-0]: nutty, roast odor



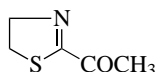
2,5-dimethylthiazole [4175-66-0]: meat-like odor



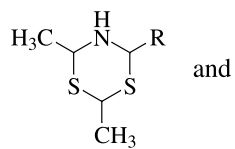
2-isobutylthiazole [18640-74-9]: tomato odor



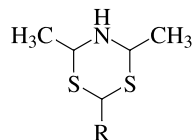
4-methyl-5-thiazolethanol [137-00-8]: meaty,
roast odor



2-acetyl-2-thiazoline [29926-41-8]: cooked beef
odor



and



alkyldimethyl-1,3,5-dithiazines: roast odor

R = Methyl, isopropyl, isobutyl, 2-butyl