Kurt Bauer, Dorothea Garbe, Horst Surburg

Common Fragrance and Flavor Materials

Preparation, Properties and Uses
Third Completely Revised Edition

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Preface to the Third Edition

Twelve years after its first publication comes the third edition of "Common Fragrance and Flavor Materials". The content has been updated in many respects while retaining the proven concept.

In the case of the single-component fragrance and flavor materials, those compounds have been included which have become established on the market, as well as those which have attracted considerable interest on account of their outstanding organoleptic properties and have contributed to the composition of new fragrance types. The production processes for all fragrance and flavor materials described in the book have been critically reviewed. New processes have been taken into account, and those that are clearly outdated have been eliminated. A few compounds that have declined in importance or whose use is now restricted for toxicological reasons have been removed from the text, as have several essential oils. The latest publications and standards concerning essential oils and natural raw materials have been included in the new edition, making it an up-to-date reference work. For the first time references are cited for all essential oils, giving newcomers to the field a quick overview of the original literature. The chapters on quality control and product safety have been expanded and brought up to date.

The authors wish to thank all the colleagues whose specialist advice assisted us in revising the book.

Holzminden, February 1997

K. Bauer
D. Garbe
H. Surburg

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Preface to the Second Edition

Within three years of publication the first edition of "Common Fragrance and Flavor Materials" was out of print and is now followed by this second edition. As in the case of the first edition this book is based mainly on a chapter on "Flavors and Fragrances" which has since been published in English in Ullmann's Encyclopedia of Industrial Chemistry.

We would like to thank our readers for their suggestions for improvement and further development of the contents which were contained in several book reviews. We have not followed up all the suggestions for the simple reason that we did not wish to change the character of the book, which is expressely aimed at a general audience interested in commonly used fragrance and flavor materials, and not at experts in the field.

The chapter on "Single Fragrance and Flavor Compounds" has been updated to include new developments. production methods have been brought up-to-date and CAS registry numbers have been added to all single compounds described. The former chapters "Essential Oils" and "Animal Secretions" have been grouped together under the heading "Natural Raw Materials in the Flavor and Fragrance Industry" and thoroughly revised to include new literature references.

Holzminden, February 1990

K. Bauer
D. Garbe
H. Surburg

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Preface to the First Edition

Fragrance and flavor materials are used in a wide variety of products, such as soaps, cosmetics, toiletries, detergents, alcoholic and non-alcoholic beverages, ice cream, confectioneries, baked goods, convenience foods, tobacco products, and pharmaceutical preparations. This book presents a survey of those natural and synthetic fragrance and flavor materials which are produced commercially on a relatively large scale, or which are important because of their specific organoleptic properties. It provides information concerning their properties, methods employed in their manufacture, and areas of application. Therefore, the book should be of interest to anyone involved or interested in fragrance and flavor, *e.g.*, perfumers, flavorists, individuals active in perfume and flavor application, food technologists, chemists, and even laymen.

The book is, essentially, a translation of the chapter on fragrance and flavor materials in *Ullmanns Encyklopädie der technischen Chemie*, Volume 20, 4th Edition, Verlag Chemie GmbH, Weinheim (Federal Republic of Germany), 1981. The original (German) text has been supplemented by inclusion of recent developments and of relevant information from other sections of the Encylopedia. The present English version will make the information available to a wider circle of interested readers.

The condensed style of presentation of "Ullmann's" has been maintained. A more detailed treatment of various items and aspects was considered but was believed to be outside the scope of this book. Additional information, however, can be obtained from the literature cited.

To improve its usefulness, the book contains

- a formula index, including CAS registry numbers;
- an alphabetical index of single fragrance and flavor compounds, essential oils, and animal secretions.

Starting materials and intermediates are not covered by these indexes.

The authors wish to express their gratitude to:

- Haarmann & Reimer Company, in particular to its General Manager, Dr. C. Skopalik, who suggested the publication of this book in English and who, at an earlier stage, provided time and facilities for writing the chapter on fragrance and flavor materials in *Ullmanns Encyklopädie der technischen Chemie* (1981), and to Dr. Hopp, Vice President Research, for valuable additions to his book;
- all others who provided information and suggestions for the chapter in Ullmann's Encyclopedia and thereby for this book.

The authors are most grateful to Dr. J. J. Kettenes-van den Bosch and Dr. D. K. Kettenes for translating the original German text into English and for their suggestions and help in shaping the present book. Drs. Kettenes thank Mr. W. S. Alexander, Hockessin, Delaware (USA), for critically reviewing the English.

Holzminden, June 1984

K. Bauer
D. Garbe

Contents

1 Introduction

1.1 History

Since early antiquity, spices and resins from animal and plant sources have been used extensively for perfumery and flavor purposes, and to a lesser extent for their observed or presumed preservative properties. Fragrance and flavor materials vary from highly complex mixtures to single chemicals. Their history began when people discovered that components characteristic of the aroma of natural products could be enriched by simple methods. Recipes for extraction with olive oil and for distillation have survived from pre-Christian times to this day.

Although distillation techniques were improved, particularly in the 9th century A.D. by the Arabs, the production and application of these concoctions remained essentially unchanged for centuries. Systematic development began in the 13th century, when pharmacies started to prepare so-called remedy oils and later recorded the properties and physiological effects of these oils in pharmacopoeias. Many essential oils currently used by perfumers and flavorists were originally prepared by distillation in pharmacies in the 16th and 17th centuries.

Another important step in the history of natural fragrance materials occurred in the first half of the 19th century, when the production of essential oils was industrialized due to the increased demand for these oils as perfume and flavor ingredients. Around 1850, single organic compounds were also used for the same purposes. This development resulted from the isolation of cinnamaldehyde from cinnamon oil by DUMAS and PÉLIGOT in 1834, and the isolation of benzaldehyde from bitter almond oil by LIEBIG and WÖHLER in 1837. The first synthetic 'aroma oils' were introduced between 1845 and 1850. These consisted of lower molecular mass fatty acid esters of several alcohols and were synthesized by the chemical industry for their fruity odor. Methyl salicylate followed in 1859 as 'artificial wintergreen oil' and benzaldehyde in 1870 as 'artificial bitter almond oil.' With the industrial synthesis of vanillin (1874) and coumarin (1878) by Haarmann & Reimer (Holzminden, Federal Republic of Germany), a new branch of the chemical industry was founded.

The number of synthetically produced fragrance and flavor chemicals has since expanded continually as a result of the systematic investigation of essential oils and fragrance complexes for odoriferous compounds. Initially, only major components were isolated from natural products; their structure was then elucidated and processes were developed for their isolation or synthesis. The present trend, however, is to isolate and identify characteristic fragrance and flavor substances that occur in the natural products in only trace amounts. The isolation and structure elucidation of these components requires the use of sophisticated chromatographic and spectroscopic techniques. Interesting products can then be synthesized.

1.2 Definition

Fragrance and flavor substances are comparatively strong-smelling organic compounds with characteristic, usually pleasant odors. They are, therefore, used in perfumes and perfumed products, as well as for the flavoring of foods and beverages. Whether a particular product is called a fragrance or a flavor substance depends on whether it is used as a perfume or a flavor. Fragrances and flavors are, like taste substances, chemical messengers, their receptors being the olfactory cells in the nose, [1], [2].

1.3 Physiological Importance

Chemical signals are indispensable for the survival of many organisms which use chemoreceptors to find their way, to hunt for and inspect food, to detect enemies and harmful objects, and to find members of the opposite sex (pheromones). These functions are no longer vitally important for humans. The importance of flavor and fragrance substances in humans has evolved to become quantitatively and qualitatively different from that in other mammals; this is because humans depend to a greater extent on acoustic and optical signals for orientation. However, humans have retained the ability to detect odors and human behavior can undoubtedly be affected by fragrances and aromas.

Sensory information obtained from the interaction of fragrance and flavor molcules with olfactory and taste receptors is processed in defined cerebral areas, resulting in perception. During the past 10 years much research has been done concerning sensory perception and results have been published in, e.g., [2], [3], [4].

Although food acceptance in humans is determined mainly by appearance and texture, flavor is nevertheless also important. For example, spices are added to food not for their nutritional value, but for their taste and flavor. Furthermore, aromas that develop during frying and baking enhance the enjoyment of food.

Unlike flavoring substances, fragrances are not vitally important for humans. The use of fragrances in perfumery is primarily directed toward invoking pleasurable sensations by shifting the organism's emotional level. Whereas 'naturalness' is preferred in aromas (generally mixtures of many compounds), the talent and imagination of the perfumer is essential for the creation of a perfume.

1.4 Natural, Nature-identical, and Artificial Products

Natural products are obtained directly from plant or animal sources by physical procedures. *Nature-identical* compounds are produced synthetically, but are chemically identical to their natural counterparts. *Artificial* flavor substances are compounds that have not yet been identified in plant or animal products for human consumption. Alcohols, aldehydes, ketones, esters, and lactones are classes of compounds that are represented most frequently in natural and artificial fragrances.

Nature-identical aroma substances are, with very few exceptions, the only synthetic compounds used in flavors besides natural products. The primary functions of the olfactory and taste receptors, as well as their evolutionary development, may explain why artificial flavor substances are far less important. The majority of compounds used in fragrances are those identified as components of natural products, e.g., constituents of essential oils or resins. The fragrance characteristics of artificial compounds nearly always mimic those of natural products.

1.5 Organoleptic Properties and Structure

Similarity between odors arises because dissimilar substances or mixtures of compounds may interact with receptors to create similar sensory impressions in the sensory centers of the brain. The group of musk fragrances (comprising macrocyclic ketones and esters as well as aromatic nitro compounds and polycyclic aromatics) are, for example, compounds with similar odors but totally different structures [5], [6]. Small changes in structure (e.g., the introduction of one or more double bonds in aliphatic alcohols or aldehydes) may, however, alter a sensory impression or intensify an odor by several orders of magnitude. Increasing knowledge of the structure and functioning of olfactory receptors provides a better scientific basis for the correlation of odor and structure in fragrance and flavor substances, and facilitates the more accurate prediction of the odor of still unknown compounds [7].

1.6 Volatility

Fragrances must be volatile to be perceived. Therefore, in addition to the nature of the functional groups and the molecular structure of a compound, the molecular mass is also an important factor. Molecular masses of ca. 200 occur relatively frequently; masses over 300 are an exception.

Since fragrance compounds differ in volatility, the odor of a perfume composition changes during evaporation and is divided into the top note, the middle notes or body, and the end note or dry out, which consists mainly of less volatile compounds. Odor perception also depends largely on odor intensity. Therefore, the typical note is not determined only by the most volatile compounds.

In some cases, substances (fixatives) are added to perfumes to prevent the more volatile components from evaporating too rapidly [8].

1.7 Threshold Concentration

Due to the specificity of olfactory receptors, some compounds can be perceived in extremely low concentrations and significant differences in threshold concentrations are observed. The threshold concentration is defined as the lowest concentration at which a chemical compound can be distinguished with certainty from a blank under standard conditions.

For the compounds described in Chapter 2, threshold concentrations vary by a factor of 10^6–10^7. This explains why some fragrance and flavor compounds are manufactured in quantities of a few kilograms per year, others in quantities of several thousands of tons.

The relative contribution of a particular compound (its odor or flavor value) to the odor impression of a composition can be expressed as the ratio between the actual concentration of the compound and its threshold concentration [9], [9a].

1.8 Odor Description

The odors of single chemical compounds are extremely difficult to describe unequivocally. The odors of complex mixtures are often impossible to describe unless one of the components is so characteristic that it largely determines the odor or flavor of the composition. Although an objective classification is not possible, an odor can be described by adjectives such as flowery, fruity, woody, or hay-like, which relate the fragrances to natural or other known products with similar odors.

A few terms used to describe odors are listed below:

Aldehydic	odor note of the long-chain fatty aldehydes, e.g., fatty-sweaty, ironed laundry, seawater
Animal(ic)	typical notes from the animal kingdom, e.g., musk, castoreum, skatol, civet, ambergris
Balsamic	heavy, sweet odors, e.g., cocoa, vanilla, cinnamon, Peru balsam
Camphoraceous	reminiscent of camphor
Citrus	fresh, stimulating odor of citrus fruits such as lemon or orange
Earthy	humus-like, reminiscent of humid earth
Fatty	reminiscent of animal fat and tallow
Floral, flowery	generic terms for odors of various flowers
Fruity	generic term for odors of various fruits
Green	typical odor of freshly cut grass and leaves
Herbaceous	noncharacteristic, complex odor of green herbs with, e.g., sage, minty, eucalyptus-like, or earthy nuances
Medicinal	odor reminiscent of disinfectants, e.g., phenol, lysol, methyl salicylate
Metallic	typical odor observed near metal surfaces, e.g., brass or steel
Minty	peppermint-like odor
Mossy	typical note reminiscent of forests and seaweed
Powdery	note associated with toilet powders (talcum), diffusively sweet
Resinous	aromatic odor of tree exudates
Spicy	generic term for odors of various spices
Waxy	odor resembling that of candle wax
Woody	generic term for the odor of wood, e.g., cedarwood, sandalwood

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2 Single Fragrance and Flavor Compounds

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

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

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, England
Dragoco	= DRAGOCO Gerberding & Co. AG, Germany
Firmenich	= Firmenich S.A., Switzerland
FR	= Fragrance Resources Inc., USA
Giv.-Roure	= Givaudan-Roure (International) S.A., Switzerland
H&R	= Haarmann & Reimer GmbH, Germany
Henkel	= Henkel KGaA, Germany
Hüls	= Chemische Werke Hüls, Germany
IFF	= International Flavors & Fragrances, USA
Kao	= Kao Corp., Japan
NZ	= Nippon Zeon Co., Ltd., Japan

PFW	= Polak's Frutal Works BV, Netherlands
Polarome	= Polarome Mfg. Co., Inc., USA
Quest	= Quest International, Netherlands
Rhône-Poulenc	= Rhône-Poulenc, France
Soda Aromatic	= Soda Aromatic Co., Japan
Takasago	= Takasago Perfumery Co., Japan

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 compounds are structurally related to the cyclic terpenes and are, therefore, discussed in Section 2.4 after the cyclic terpenes.

2.1.1 Hydrocarbons

Saturated and unsaturated aliphatic hydrocarbons with straight as well as branched chains occur abundantly in natural foodstuffs, but they contribute to the odor and taste only to a limited extent. The highly unsaturated hydrocarbons 1,3-*trans*-5-*cis*-undecatriene [*51447-08-6*] and 1,3-*trans*-5-*trans*-undecatriene [*19883-29-5*], however, contribute to the odor of galbanum oil [10].

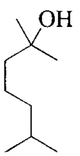
2.1.2 Alcohols

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 C_4–C_{10} alcohols, isoamyl alcohol). Unsaturated alcohols are most important (e.g., leaf alcohol with its intensely green odor) and may impart characteristic notes to compositions.

Naturally occurring fatty alcohols used in the fragrance industry are produced principally by reduction of the methyl esters of the corresponding carboxylic acids, which are obtained by transesterification of natural fats and oils with methanol. Industrial reduction processes include catalytic hydrogenation in the presence of copper–chromium oxide catalysts (Adkins catalysts) and reduction with sodium (Bouveault–Blanc reduction). 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*]
$CH_3(CH_2)_4CH(OH)CH_2CH_3$, $C_8H_{18}O$, M_r 130.23, $bp_{97.6\,kPa}$ 176–176.5 °C, d_4^{20} 0.8264, n_D^{20} 1.4252, may occur in its optically active form. It is a colorless liquid that has a mushroomy-earthy odor and occurs in mushrooms. 3-Octanol can be obtained by hydrogenation of 3-octanone; it is used in lavender compositions and for imparting mushroom-like odors.
FCT 1979 (**17**) p. 881.

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



$C_9H_{20}O$, M_r 144.26, $bp_{101.3\,kPa}$ 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 fresias. 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*]
$CH_3CH_2CH_2CH=CHCH_2OH$, $C_6H_{12}O$, M_r 100.16, $bp_{101.3\,kPa}$ 155 °C, d_4^{20} 0.8459, n_D^{20} 1.4382, occurs in many fruits and has a fruity, green odor, which is sweeter than that of the isomeric *cis*-3-hexen-1-ol and is, therefore, preferred in aroma compositions.
FCT 1974 (**12**) p. 911.

***cis*-3-Hexen-l-ol** [*928-96-1*], **leaf alcohol**
$CH_3CH_2CH=CHCH_2CH_2OH$, $C_6H_{12}O$, M_r 100.16, $bp_{101.3\,kPa}$ 156–157 °C, d_4^{20} 0.8459, 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*]
$CH_3(CH_2)_4CH(OH)CH{=}CH_2$, $C_8H_{16}O$, M_r 128.21, $bp_{94.6\,kPa}$ 175–175.2 °C, d_4^{20} 0.8383, n_D^{20} 1.4378, may occur in the optically active form. It is found, for example, in lavender oil and is a steam-volatile component of mushrooms. 1-Octen-3-ol is a liquid with an intense mushroom, forest-earthy odor that can be prepared by a Grignard reaction from vinylmagnesium bromide and hexanal. It is used in lavender compositions and in mushroom aromas.
FCT 1976 (**14**) p. 681.

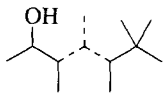
Trade Name. Matsutake alcohol (Takasago).

9-Decen-1-ol [*13019-22-2*]
$CH_2{=}CH(CH_2)_7CH_2OH$, $C_{10}H_{20}O$, M_r 157.27, $bp_{0.27\,kPa}$ 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 Name. Rosalva (IFF).

10-Undecen-1-ol [*112-43-6*]
$CH_2{=}CH(CH_2)_8CH_2OH$, $C_{11}H_{22}O$, M_r 170.29, $bp_{2.1\,kPa}$ 133 °C, d_4^{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 vetivert character. Synthesis starts from 2-methyl-2-butene (isoamylene) which is dimerized and the product acetylated to give the corresponding hepten-2-ones. 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, $bp_{1.5\,kPa}$ 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.

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 C_8–C_{13}, however, are used, singly or in combination, in nearly all perfume types and also in aromas. Their odor becomes weaker with increasing molecular mass, so that aldehydes $> C_{13}$ are not important as perfume ingredients.

In addition to the straight-chain saturated aldehydes, a number of branched-chain and unsaturated aliphatic aldehydes are important as fragrance and flavoring materials. The double unsaturated 2-*trans*-6-*cis*-nonadienal [*557-48-2*], 'violet leaf aldehyde' (the dominant component of cucumber aroma), is one of the most potent fragrance and flavoring substances; it is, therefore, only used in very small amounts. 2-*trans*,4-*trans*-Decadienal [*25152-84-5*] with its specifically fatty odor character is indispensible 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**
$CH_3(CH_2)_4CHO$, $C_6H_{12}O$, M_r 100.16, $bp_{101.3\,kPa}$ 128 °C, d_4^{20} 0.8139, n_D^{20} 1.4039, occurs, for example, in apple and strawberry aromas as well as in orange and lemon oil. It is a colorless liquid with a fatty-green odor and in low concentration is reminiscent of unripe fruit.

Hexanal is used in fruit flavors and, when highly diluted, in perfumery for obtaining fruity notes.
FCT 1973 (**11**) p. 111.

Octanal [*124-13-0*], **caprylaldehyde**
$CH_3(CH_2)_6CHO$, $C_8H_{16}O$, M_r 128.21, $bp_{101.3\,kPa}$ 171 °C, d_4^{20} 0.8211, n_D^{20} 1.4217, occurs in several citrus oils, e.g., orange oil. It is a colorless liquid with a pungent odor, which becomes citrus-like on dilution. Octanal is used in perfumery in low concentrations, in eau de cologne, and in artificial citrus oils.
FCT 1973 (**11**) p. 113.

Nonanal [*124-19-6*], **pelargonaldehyde**
$CH_3(CH_2)_7CHO$, $C_9H_{18}O$, M_r 142.24, $bp_{101.3\,kPa}$ 190–192 °C, d_4^{20} 0.8264, n_D^{20} 1.4273, occurs in citrus and rose oils. It is a colorless liquid with a fatty-roselike odor and is used in floral compositions, particularly those with rose characteristics.
FCT 1973 (**11**) p. 115.

Decanal [*112-31-2*], **caprinaldehyde**
$CH_3(CH_2)_8CHO$, $C_{10}H_{20}O$, M_r 156.27, $bp_{101.3\,kPa}$ 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*]
$CH_3(CH_2)_9CHO$, $C_{11}H_{22}O$, M_r 170.29, $bp_{2.4\,kPa}$ 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**
$CH_3(CH_2)_{10}CHO$, $C_{12}H_{24}O$, M_r 184.32, $bp_{13.3\,kPa}$ 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.

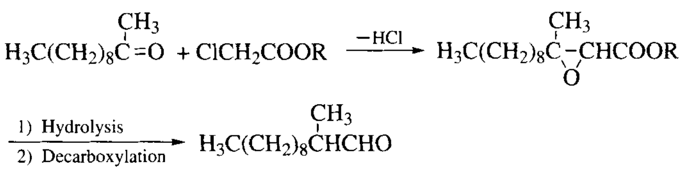
Tridecanal [*10486-19-8*]
$CH_3(CH_2)_{11}CHO$, $C_{13}H_{26}O$, M_r 198.34, $bp_{1.3\,kPa}$ 128 °C, d_4^{18} 0.8356, n_D^{18} 1.4384, occurs in lemon oil and has been identified as a volatile constituent of cucumber. It is a colorless liquid having a fatty-waxy, slightly citrus-like odor. Addition of tridecanal to fragrance compositions imparts fresh nuances in the top note as well as in the dry out.

2-Methyldecanal [*19009-56-4*], **methyloctylacetaldehyde**
$CH_3(CH_2)_7CH(CH_3)CHO$, $C_{11}H_{22}O$, M_r 170.29, $bp_{98.8\,kPa}$ 119–120 °C, d_4^{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**
$CH_3(CH_2)_8CH(CH_3)CHO$, $C_{12}H_{24}O$, M_r 184.32, $bp_{1.3\,kPa}$ 114 °C, d_4^{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].

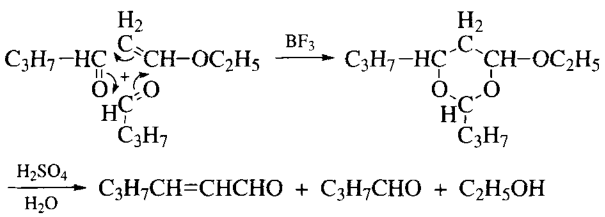
$$H_3C(CH_2)_7CH{=}CH_2 \xrightarrow{H_2,\,CO} H_3C(CH_2)_9CHO + H_3C(CH_2)_7\overset{CH_3}{\overset{|}{C}}HCHO$$

$$H_3C(CH_2)_9CHO \xrightarrow{HCHO} H_3C(CH_2)_8\overset{CH_2}{\overset{||}{C}}CHO \xrightarrow{H_2} H_3C(CH_2)_8\overset{CH_3}{\overset{|}{C}}HCHO$$

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**
$CH_3CH_2CH_2CH{=}CHCHO$, $C_6H_{10}O$, M_r 98.14, $bp_{101.3\,kPa}$ 146–147 °C, d_4^{20} 0.8491, n_D^{20} 1.4480, is the simplest straight-chain unsaturated aldehyde of interest for perfumes and flavors. It occurs in essential oils obtained from green leaves of many plants.

trans-2-Hexenal is a colorless, sharp, herbal-green smelling liquid with a slight acrolein-like pungency. Upon dilution, however, it smells pleasantly green and apple-like. The aldehyde can be synthesized by reacting butanal with vinyl ethyl ether in the presence of boron trifluoride, followed by hydrolysis of the reaction product with dilute sulfuric acid [17].



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

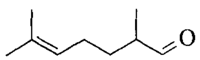
trans-2-Hexenal has an intense odor and is used in perfumes to obtain a green-leaf note, and in fruit flavors for green nuances.
FCT 1975 (**13**) p. 453.

***cis*-4-Heptenal** [*6728-31-0*]
$CH_3CH_2CH{=}CHCH_2CH_2CHO$, $C_7H_{12}O$, M_r 112.17, $bp_{1.33\,kPa}$ 41 °C, n_D^{20} 1.4343, is a widespread volatile trace constituent of food flavors. It is a colorless, oily

liquid with a powerful, fatty, somewhat fishy and, in high dilution, creamy odor. It can be prepared from 1-butyne (via lithium 1-butynide) and acrolein (which is converted into 2-bromopropionaldehyde dimethyl acetal). The resulting 4-heptynal dimethyl acetal is cleaved and the triple bond is hydrogenated catalytically to give *cis*-4-heptenal [19].

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

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



$C_9H_{16}O$, M_r 140.23, bp_{2kPa} 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.

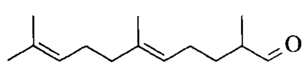
Trade Name. Melonal (Giv.-Roure).

10-Undecenal [*112-45-8*]

$CH_2=CH(CH_2)_8CHO$, $C_{11}H_{20}O$, M_r 168.28, $bp_{0.4\,kPa}$ 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*]

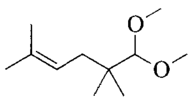


$C_{14}H_{24}O$, M_r 208.35, d_4^{20} 0.870–0.877, n_D^{20} 1.468–1.473, not found in nature, is a clear, colorless to pale yellowish liquid. It has an aldehydic-floral odor reminiscent of nerolidol, with fruity nuances. It can be prepared from geranylacetone (see p. 41) by Darzens reaction with ethyl 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, $bp_{1.6\,kPa}$ 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 Name. Methyl Pamplemousse (Giv.-Roure).

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**
$CH_3COCH(OH)CH_3$, $C_4H_8O_2$, M_r 88.11, $bp_{101.3\,kPa}$ 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**
$CH_3COCOCH_3$, $C_4H_6O_2$, 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.