

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 component 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 ninth century A.D. by the Arabs, the production and application of these concoctions remained essentially unchanged for centuries. Systematic development began in the thirteenth century, when pharmacies started to prepare the 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 sixteenth and seventeenth centuries.

Another important step in the history of natural fragrance materials occurred in the first half of the nineteenth 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 Pélégot 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 was introduced 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, 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. With the development of modern analytical techniques, however, it became possible 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 require 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, similar to 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 molecules with olfactory and taste receptors is processed in defined cerebral areas, resulting in perception. During the past 15 years, much research was done concerning sensory perception, and the results have been published in, for example, [2–23].

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 are essential for the creation of a perfume.

1.4

Natural, Nature-Identical, and Artificial Products

Natural compounds are obtained directly from natural sources by physical or biotechnological (enzymatic, microbial) procedures. As a result of the rapid development and expansion of biotechnology in the past two decades, far more than 100 natural flavoring substances are available from biocatalytic processes today [24–26]. *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 [27]. 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. A considerable proportion of compounds used in fragrances are those identified as components of natural products, for example, constituents of essential oils or resins. The fragrance characteristics of artificial compounds nearly always mimic those of natural products.

1.5

Sensory Properties and Chemical 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), for example, are compounds with similar odors but totally different structures [28, 29]. Small changes in the 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 odors of still unknown compounds [30–52].

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 about 200 occur relatively frequently; masses over 300 are an exception.

Since fragrance materials differ in volatility, the odor of a perfume composition changes during evaporation and is divided into the top note, the middle note 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 [53].

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 materials 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 [54, 55].

1.8

Sensory Properties

The sensory properties of single aroma chemicals are extremely difficult to describe unequivocally. 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 a classification is always subjective, sensory properties can be described by adjectives such as flowery, fruity, woody, hay-like, which relate the fragrances or flavors to natural or other known products with similar sensory impressions [56]. However, such terms are not strictly defined and run into each other. In most cases, sensory properties of one and the same material can only be described by using more than one term.

1.8.1

Fragrance Ingredients

In accordance with the evolution of its fragrance properties, a perfume composition can formally be divided into three categories: top note, heart note (body; bouquet), and base note (fond).

In classic perfumes of feminine and masculine types, the heart note consists of fragrance materials with a floral character. It is enveloped by materials that are perceived immediately (top notes) and materials that are perceived mainly in the dry-out and impart tenacity to the composition (base notes). In a striking illustration of a “fragrance circle,” a circular central body is ringed by segments of top notes in the upper part and by base notes in the lower part [57]. The segments contain the most important fragrance categories that determine the character of a perfume.

Typical top notes are as follows:

| | |
|-------------------|---|
| Citrus | Fresh, stimulating odor of citrus fruits such as lemon, lime, orange, bergamot |
| Aldehydic | Odor note of the long-chained fatty aldehydes: fatty-sweaty, ironed laundry, metallic, fresh seawater, ozone-like, marine fragrances |
| Fruity | Light fruity notes: typical notes of aliphatic esters: found, for example, in odors of apples, pears, melons Dark (heavy, sweet) fruity notes: found, for example, in odors of strawberries, raspberries, lactone odor of peaches and coconuts |
| Green | Typical odor of green vegetation: green leaves and freshly cut grass |
| Herbaceous/Herbal | Odor of green herbs and spices, for example, sage, mint, eucalyptus; camphoraceous such as rosemary; coniferous such as fir needles; earthy agrestic |

Examples of floral notes (heart notes; body) are as follows:

| | |
|----------------------|-----------------------------|
| Floral light | Rose |
| Floral green, clean | Lily of the Valley (muguet) |
| Floral fresh, herbal | Geranium, lavender |
| Floral fruity | For example, damascones |

| | |
|------------------------|--|
| Floral heavy | Narcotic flower fragrances such as jasmine, tuberose |
| Floral woody (powdery) | For example, methylionones |

Typical base notes are as follows:

| | |
|-------------------|---|
| Aromatic | Sweet aromatic to aromatic spicy odors, for example, of honey, almond, aniseed, woodruff, nutmeg, clove. This segment also contains the so-called gourmand notes having pronounced culinary properties, for example, vanilla, tonka, lovage |
| Balsamic | Heavy sweet odors, such as chocolate and vanilla, cinnamon with resinous elements |
| Moss | Dry, algae-like, tar-like, phenolic, oak moss |
| Leather, animalic | Odor of cresol, isobutyl quinoline, and so on; fecal such as indole |
| Musk | Warm soft odor reminding of freshly washed and ironed laundry, often with skin-like and animalic-erogenous facets |
| Amber | Warm, slightly earthy-camphoraceous woody note, reminding natural ambergris, represented typically by amber oxide |
| Wood | Clear cool radiant odor found in natural materials such as cedarwood (pencil note), patchouli, sandalwood, and vetiver |

In addition to these generic properties, a number of specific terms are used to characterize fragrance material more in detail, for example, fatty, waxy, burnt, phenolic, fishy, sulfurous, musty, medicinal, [57].

1.8.2

Flavoring Substances

Sensory properties of flavoring substances can simply be illustrated when arranged in segments of a circle, “flavor wheel” [58], containing the following descriptors:

Green, grassy; herbaceous; spicy; fruity, ester-like; tropical; blackcurrant; vegetable; nutty; caramel; smoky; roast, burnt; beefy; pork, lamb, chicken; savory, bouillon; fatty; rancid, cheesy; mushroom, earthy; truffle; garlic; onion.