# The art and the science

# Fragrance

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Perfumes are pervasive in modern life. Blends of pleasing odorous chemicals are encountered in expensive designer fragrances, cosmetic and household products, and many other consumer goods.

Most natural fragrances come from plants. Perfume is usually associated with flowers, but many other parts of the plant can be utilized (Table 1).

By contrast, the animal kingdom provides only four products, but these are essential fixatives. Castoreum comes from the secretion of beavers' sex glands. Musk is a secretion from the abdominal pouches of male musk deer native to the Himalayas. The animals are killed to procure these products. Ambergris originates in the stomach or intestine of the cachalot, or sperm, whale and is expelled when the animal is irritated. It thus can be harvested from the sea, but it cannot be localized in any particular area. Civet is a glandular secretion of the civet cat, usually the male. It can be obtained without harming the animal. All of these products are either unavailable in unadulterated form or are in short and unreliable supply. Thus modern perfumers use synthetic substitutes.

## Isolation

One of the traditional methods to obtain odorous components from natural plant sources was enfleurage. A sheet of glass was spread with lard, flower petals were pressed into it, and in a few days the fragrance material was extracted into the fat. The fat–fragrance mixture, called *pommade*, was then treated with alcohol to obtain a pure fragrance concentrate called the absolute. Although of historical interest, this method is now obsolete (2).

The active components of citrus products are commonly obtained by expressing the oil mechanically from the outer layer of the fruit. These products are often referred to as "cold pressed." An exception is lime oil, which can be distilled.

Extraction with solvents is an important technology. The ideal solvent has a low boiling point so that the delicate components are not destroyed by heat. The solvent must also be selective, removing primarily odorous substances. Petroleum ether is a typical solvent, but for particularly sensitive extractions liquefied carbon dioxide can be used. It is the least destructive because of its low boiling point, and it enables the isolation of



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### "All the perfumes of Arabia"

Perfumes are mixtures of odorous substances that are usually liquids. The Latin *per fumum* translates literally as "by smoke." This reflects the fact that ancient fragrant materials were generally solids that were burned to release the aroma. Egypt, India, China, and parts of America were early centers of perfumery, and the Hebrews likely learned of perfumery during their exile in Egypt. The New Testament presents the most famous of all ancient references to the extreme value of odorous substances:

> "And when they were come into the house, they saw the young child with Mary his mother, and fell down, and worshipped him; and when they had opened their treasures, they presented unto him gifts; gold, and frankincense, and myrrh" (Matthew 2:11).

Ancient uses of perfumes included embalming and medicine, but the most important application was in religious rites. The burning of incense may have replaced animal sacrifice as an offering to the gods. The Greeks and Romans used fragrances so extensively for secular purposes that at various times in Athens and Rome their use was forbidden.

After the fall of Rome the Arabs maintained the knowledge of fragrance. The capture of Constantinople by Venice in 1204 restored trade in aromatics to Europe. The dominance of the Venetian Empire made Italy the center of perfumery for centuries. Technological advances in distillation made it possible to provide the materials as concentrated liquids rather than as a large bulk of roots, flowers, barks, and other unwieldy substances, and this greatly expedited their transport by sea.

The growing power of the French monarchy and the French love of luxury shifted the center of perfumery to France, particularly the area around Grasse near the Riviera. In Grasse the climate supported aromatic plants from many geographical regions. Proximity to technical knowledge from Moorish Spain and access to Mediterranean trade routes made Grasse an ideal perfume center, and it remains so to this day *(1)*.

The rise of the chemical industry in nineteenth-century Germany provided solvents that greatly improved the methods for extracting fragrance from natural sources. Later, synthetic chemicals revolutionized the creative potential of perfumers. The numerous synthetic products of the past hundred years form the basis of most modern perfumes.

# Chemistry

***Table 1.* Sources of perfumes**

| Plant part | Plant |
|---|---|
| Blossoms | Rose |
| Fruits | Coriander |
| Stems and leaves | Geranium |
| Seeds | Cardamom |
| Roots | Angelica |
| Wood | Sandalwood |
| Peels | Orange |
| Herbs | Tarragon |
| Resins | Olibanum |
| Bark | Cinnamon |
| Needles | Spruce |

otherwise unobtainable products such as lilac and lily of the valley.

The initial product of solvent extraction is a waxlike substance called the essence concrete. Extraction of concrete with ethanol yields the alcohol-soluble component known as the absolute, which is the purest and most expensive natural odorous product.

### Distillations

Steam distillation takes two forms. In the direct method a still is filled with the material to be treated. Steam is introduced at the base, and the volatile elements mix with the vapor. In the indirect method, the still is initially filled with the raw material and water, and brought to a boil so that the volatile elements escape with the steam. The vapor is then condensed, after which it separates into water and essential oil. Finally, continuous

*Table 2.* **Esters of benzyl alcohol**

| Ester | Odor |
|---|---|
| Acetate | Floral |
| Propionate | Fruity |
| Butyrate | Fruity |
| Isovalerate | Fruity |
| Benzoate | None |
| Phenyl acetate | Floral |
| Salicylate | None |
| Cinnamate | Balsamic |

*Table 3.* **Terpenes**

| *n* | Name | Formula |
|---|---|---|
| 2 | Monoterpene | $C_{10}H_{16}$ |
| 3 | Sesquiterpene | $C_{15}H_{24}$ |
| 4 | Diterpene | $C_{20}H_{32}$ |
| 5 | Triterpene | $C_{30}H_{48}$ |
| 6 | Tetraterpene | $C_{40}H_{64}$ |

separation occurs in the "Florentine flask," which functions like a separatory funnel.

Vacuum distillation modifies essential oils, produced by steam distillation, to improve concentration and solubility. This dry process is used to separate the oil into its components. The higher the vacuum employed, the lower the boiling point and thus less degradation of the oil.

Molecular distillation is used for the most difficult problems, such as substances with very high boiling points. The vacuum used is very high, and the distance from evaporator to condenser is extremely small. This method is often used to lighten the color of dark extracts.

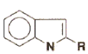
### Chemical structure and odor

Historically, organic compounds were categorized as aliphatic (fatty) or aromatic (fragrant). This early division points to the importance of aromatic compounds in perfumery (3). Many esters have characteristic pleasing odors. For example, Table 2 lists some esters of benzyl alcohol, $C_6H_5CH_2OH$.

This range for only one family of esters hints at the enormous number of materials that can be created from a relatively limited number of synthetic routes. (For syntheses of perfumery materials see reference 7.) Important compounds for developing modern fragrances include aromatic aldehydes, ketones, heterocycles, and terpenes (4).

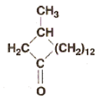
Not every odorant blended into a perfume has a pleasing odor when pure. For example, indole and its derivatives form two of the most foul odors used in perfumery.

**Indole** R = H
**Skatole** R = $CH_3$

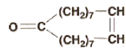



It might seem strange that a material with a very disagreeable odor would be used in perfume, but a mixture exclusively composed of pleasant ingredients would be excessively sweet and have no interesting character.

Two acyclic compounds used in perfumery are muscone and civetone. Muscone and civetone are the active components in glandular secretions from the male musk deer and civet cat, respectively. Because sources are limited, synthetic routes to these compounds are important to ensure a reliable supply for perfumers.

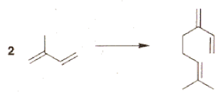



**Muscone**




**Civetone**

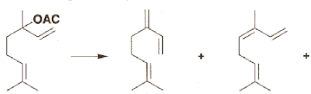
Natural terpenes have the molecular formula $(C_5H_8)_n$ (5) and are regarded as derivatives of isoprene units joined head-to-tail.



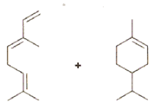

**Isoprene** **Monoterpene**

They are classified according to the number of terpene units (Table 3). Mono- and sesquiterpenes, the chief components of essential oils, are obtained by steam distillation.

The synthesis and reactions of terpenes generally result in mixtures, e.g., heating of linalool acetate yields (6):




**β-Myrcene** 43% **Cis-ocimene** 20%




***Trans*-ocimene** 35% **Dipentene** 2%

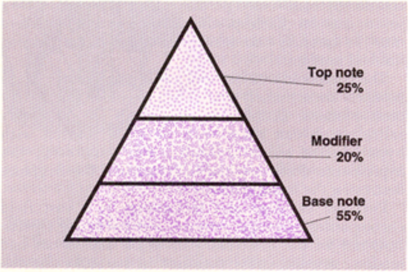



***Figure 1.*** **The perfumer's triangle.**

The ring structures of terpenes can easily be opened or closed under changing conditions of temperature or pH. They are also easily oxidized. This helps to explain the instability of perfume oils in different environments.

### Sense of smell

Olfaction is the study of smell from a physiological perspective. One of the classic theories of odor reception is the lock-and-key model that assumes odor receptors to have a three-dimensional configuration precisely accommodating specific odor molecules. When the molecule fits into the receptor, a pulse in the olfactory bulb transmits a message to the brain. Although some correlations have been found, predictions with this model lead to many discrepancies.

Recent research has apparently identified individual odor-receptor genes (*5*). Whereas the human eye has only three types of receptors to identify the primary colors, as many as a thousand genes may be involved in odor recognition.

### Compounding

The creative process in perfumery has evolved over the years. Until early in this century, creation was generally done by trial and error, with perfumers haphazardly looking at numerous mixtures and hoping to discover a pleasing blend. The availability of new synthetics opened a vast realm of possibilities, necessitating a more systematic approach. One of the pioneers of modern perfumery, Jean Carles, elucidated the new technique in a classic series of papers (*6*).

Carles began by creating accords, combinations of single odors that blend to produce new fragrance effects. The number of ingredients in an accord may run from two to several hundred. The basis of combining accords is volatility. The perfumer must first study individual raw materials to discover which are highly volatile and which, by contrast, are tenacious.

The composition of a perfume consists of a top note, middle note, and bottom note. The top note is the most volatile, least tenacious material, and provides most of the immediate impact of the fragrance. The middle note (modifiers) is somewhat less volatile and dominates after the top note evaporates. The bottom note (base note) is very tenacious and lasts long after the other components have faded.

A perfume constructed in this way can be likened to a triangle (Figure 1). Carles considered the bottom notes to be the basis of fragrance character, and he built from there. An example given by Carles is the creation of Chypre. Chypre is a fantasy creation launched by Coty in 1917 and is a classic fragrance type. Oakmoss is the basic odor group, and Carles began by modifying the basic odor with ambergris. He tested simple ratios of oakmoss–ambergris ranging from 9:1 to 5:5. He selected the 6:4 ratio for further study. Naturally, at this point we are not describing an exact science but the perfumer's personal art.

Carles chose to add a musk note to the oakmoss–ambergris mixture:

| | |
|---|---|
| Oakmoss | 6 |
| Ambergris | 4 |
| Musk ketone | 1 |

This simple accord of three ingredients became the elemental bottom note. He then modified it with a floral and animal note, which blended with his initial accord:

| | | |
|---|---|---|
| Modifiers | Absolute rose | 3 |
| | Absolute civet | 1 |
| Base note | Oakmoss | 6 |
| | Ambergris | 4 |
| | Musk ketone | 1 |

Absolute rose and absolute civet are the terms for the purest alcohol-soluble natural product. The civet is so strong an odor that it is actually used as a 10% solution.

The volatile top notes now to be added allowed the perfumer more freedom and fantasy. A citrus accord provided sparkle and formed a rounded mixture:

| | | |
|---|---|---|
| Top note | Sweet orange | 4 |
| | Bergamot | 1 |
| Modifiers | Absolute rose | 3 |
| | Absolute civet | 1 |
| Base note | Oakmoss | 6 |
| | Ambergris | 4 |
| | Musk ketone | 1 |

Each separate accord can now be similarly elaborated. A modern sophisticated fragrance can easily grow to several hundred ingredients, but the process remains fundamentally like the creation of this simple prototype.

### Fragrances are everywhere

No consumer uses "pure" perfume. What's purchased to be used as perfume is often an alcoholic or hydroalcoholic (water–alcohol) solution such as cologne or aftershave. Most personal care products contain perfume, either incidentally as a mild mask for other odors in the product or as an important element in marketing. For example, in products as similar as the many competing shampoos, fragrance becomes a highly significant differentiating factor. Some fragrances have become closely identified with product categories, such as the classic Johnson & Johnson fragrance of baby powder. Similarly, lemon oil is associated with cleaning and pine oil with disinfecting.

Hydroalcoholics are the most expensive fragrance products. Typical oil concentrations are 20–30% for perfume, 8–15% for cologne, and 1–3% for aftershave. The alcohol provides valuable lift for fragrance, the pure oil having much less sparkle (accentuation of the top note) than the solution. Consequently, raising the oil level does not necessarily improve the overall impact.

Alcohol often knocks waxy and resinous products out of solution and, with increasing amounts of water in a hydroalcoholic, more insolubilities result. The most common manufacturing procedure is to age, chill, and filter the solution. As the perfume solution ages it subtly changes character as some ingredients react with the ethanol. An example is an aldehyde converting to a hemiacetal.

Although hydroalcoholics are the simplest systems, problems can still arise. Antioxidants and UV absorbers may be needed for stability, and some of the certified colors often used can fade severely, particularly azo dyes.

Most cosmetics are emulsions, usually oil in water. The fragrance is generally added during the cooling phase to avoid excess exposure to heat. The level of perfume oil in emulsions is typically low, commonly 0.1–0.5%. Even at these percentages the perfume can affect emulsion stability, cause color changes, and trigger viscosity loss. Stability testing at ambient and elevated temperatures is essential to ensure a satisfactory product. When problems develop, an individual study of all the raw materials in the fragrance may be required to pinpoint the difficulty.

Products that contain a high concentration of water may need a water-soluble fragrance. This is almost invariably accomplished by mixing the oil with a surface-active agent such as polysorbate 20 or octoxynol-9. Many products have specific complications: For example, antiperspirants have a low pH and reactive ingredients and thioglycolate-based permanent wave solutions have a severe malodor. Each specific perfume oil and ingredient must be carefully coordinated for a stable and pleasing finished product.

The household area has additional complications. Many products are extremely acidic or basic, which can destroy most odorants. Disinfecting compounds use quaternary salts, which can react with perfume; bleach with hypochlorite poses a double dilemma, with the hypochlorite destroying the fragrance and the fragrance destroying the hypochlorite.

Perfume creation and technology is a vast field encompassing technical, creative, and marketing aspects. It is one of the few realms in which ancient art and modern science come together in harmony for the purpose of bringing pleasure to our lives.

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### Additional reading


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**Scientific creativity: "the succession of daringly playful fantasy and relentlessly realistic criticism." Sigmund Freud**