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Guest Articles

Chemistry of Perfumes

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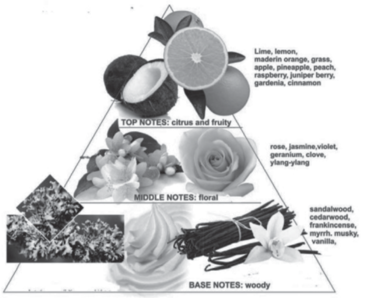
Perfumes or fragrances are the fusion of science and art: where chemists become creators and molecules make memories. Fragrances are unique. They are designed with care, passion and ingenuity. They give pleasure to billions of people around the world, who use and enjoy fragrances every day - from a fresh-smelling shampoo to freshly-laundered clothing. The word *perfume* derives from the Latin "*per-fumum*" meaning *through smoke*. The art of making perfumes "*perfumery*" has begun for more than 4,000 years - from ancient Egyptians, through the Persians, Greeks and Roman Empires and up to the modern day. Scents or the fragrances inspire a range of positive emotions, such as joy, pleasure, cleanliness, attraction, expression of status and for spiritual faiths.

The first perfume was the fragrant flower and continued to be in the present day. The modern perfume was made in 1370 at the command of Queen Elizabeth of Hungary and was known as "*Hungary Water*". Since then many perfumery arts have been developed. Fragrances are chemical compounds with a pleasant, sweet smell. By the 18th century, aromatic plants were being grown in the Grasse region of France to provide the growing perfume industry with raw materials. At present, the fragrance industry in France and England is most extensive and rule the markets in the world. Especially Paris remains the centre of the European perfume design and trade by furnishing the best raw materials, the finest essential oils. Givaudan, Firmenich, Symrise and IFF: International Flavours and Fragrances are the world largest and top ranked companies in the flavour and fragrance industry. The world-famous perfumes; *Angel by Thierry Mugler* from Firmenich, *One Million by Paco Rabanne* from Givaudan and *La Vie est Belle by Lancome* from IFF are few examples for their leading products in the international market.

The essential oils used in perfumes are classified according to their volatility, or the rate of diffusion into the air; hence, each essential oil is expected to have three *notes*. The *note* is an ingredient with one characteristic smell.



Top notes come out first (very volatile): first noticeable smell from a perfume last for few minutes to 30 minutes or less. They are often tangy or citrus-like smells that are easy to smell (*e.g.*: bergamot, juniper berry, cedar wood, lavender, geranium, gardenia, cinnamon, pepper, thyme).

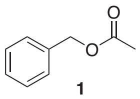
Middle notes often aromatic flowers: they may last for about an hour (*e.g.*: clove, ylang-ylang, lavender, jasmine, rose, pineapple, raspberry and geranium).

Base notes often woody fragrances, last longest or least volatile: they provide an enduring fragrance for longer time (*e.g.*: frankincense, myrrh, sandalwood, chocolate and vanilla).

Combination of two or more *notes* creates a new smell, which is different from each *note*. There are more than thousands of raw materials could be used as notes. Therefore, there is a possibility of generating infinite number of smells! For example, ***Fougère*** is one of the main families in perfumes. They are made of mixtures of *notes*: scents of lavender flowers, oakmoss (from lichens), bergamot (from citrus), coumarin (scent of newly-mown hay).

Most substances used in perfumery industry are derived from plants, animals, microorganisms, and by chemical synthesis. As in the natural sources contain many ingredients, it is a generally complex mixture. The use of synthetic chemicals started from 19th century with the development of organic chemistry. Synthetic molecules are less expensive to prepare, rather than isolating alternatives from the natural substances. Most natural substances may degrade at different acidic, basic, neutral and oxidizing media by changing their odour and colour. Many naturally occurring compounds are also not stable in bleach, laundry powders and soaps. Therefore, synthetic chemists developed synthetic molecules that can withstand for these natural products. As a result, by now, a wider range of consumer products contain durable perfumes.

The pleasant and finest odour of roses or jasmines is particularly from their flowers. But all the flowers of the plants do not contain the active ingredient. Yet it is not the blossoms alone; in some plants the fragrant substances are present in every part (pines and mints), only in the fruits (nutmeg, vanilla), only the rinds of the fruits (lemon, oranges), and some plants are entirely odourless but their roots stock the fragrant substances. It is found that benzyl acetate (34%, **1**), benzyl benzoate (24%, **2**), linalool (8%, **3**), benzyl alcohol (5%, **4**) and *cis*-jasmone (3.5%, **5**) account for the *base note* fragrance of jasmine. The major ester compounds, benzyl acetate and benzyl benzoate could be synthesised easily by esterification reactions. Due to its commercial viability, jasmine flavoured incense sticks, perfumes, deodorants, toilet soaps and other cosmetic products are commonly available.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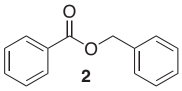
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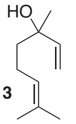
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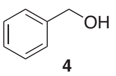
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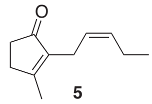
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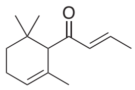
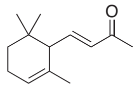
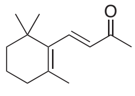
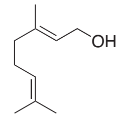
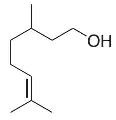
Similarly, violet flower oil was the most expensive of all essential oils and it is still economic to produce. To produce one kilogram of violet oil; 33,000 kg of violet blossoms are needed. As an alternate some industries use violet leaf as a substitute, but the smell is not quite same as that of the flower. In 1893, ionoes were synthesised which revolutionized perfume industry. Today almost all perfumes include them as they blend well with other perfumery materials. The damascones are a group of ionones and they are components of rose oils and have very intense fruity-floral smell. Rose notes are now available as inexpensive synthetics such as geraniol, citronellol, and 2-phenylethanol.

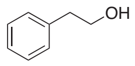

Damascone


α-Ionone

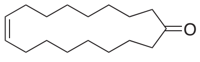

β-Ionone


Geraniol

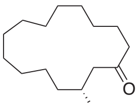

Citronellol


2-Phenylethanol

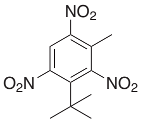
Musk is a glandular secretion from animals especially from male Musk deer which is extensively used in perfumery in 19th century. Till today natural musk is one of the most expensive animal products in the world. Not only the musk deer, there are other animals that priced for perfumery industry; such as, Civets (cat like animal with a long tail, yellow paste like faecal is used in perfumery industry). Macrocyclic muscone and civetones are the main fragrant compounds of musk and civets. During 1888, while searching for explosives, Albert Baur discovered pleasant musky smell in the product "musk Baur" formed with trinitrotoluene with *tert*-butyl halides. Later he developed musk ketone which was a major perfumery ingredient. Subsequently many derivatives were prepared using musk synthetics, and famous musk perfumes are now available in the market (*e.g.* Celestolide by IFF and Versalide by Givaudan).



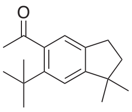
Civetone



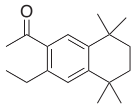
Muscone



musk Baur

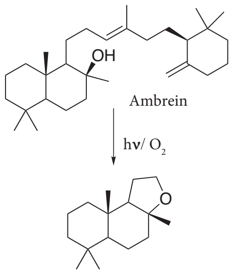


Celestolide
IFF



Versalide
Givaudan

Ambergris (a waxy substance found in the intestines in sperm whales and expel as a faecal matter) is one of the rarest and high valued perfumery ingredients. The formation of Ambergris is due to the reaction of sunlight, waves and oxygen in air. It favours the conversion of odourless Ambrein to Ambrox (Ambergris).

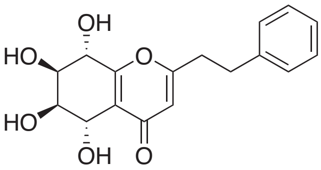


Ambrox (ambergris)

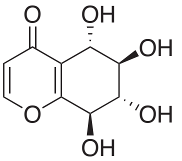
Other examples include Castoreum, the fluid from castor sacs of American beaver; and Hyraceum, rocklike excreta of Rock hyrax which releases a dark oil with intense and complex scent.

Agarwood is a resinous product produced in the heartwood of *Aquilaria, Gyrinops, Aetoxylon* and *Gonystylus* species. Once the heartwood of these species is infected with the fungi or bacteria as a defence mechanism, the dark, highly fragrant and economically valued oleoresins are produced. Agarwood resin is also found in Walla Patta tree, thus, illicit cutting and smuggling of these trees is being reported in Sri Lanka.

Agarotetrol and isoagarotetrol are the common chromones which are the important contributors to the sweet, fruity and long-lasting scent of agarwood. These two natural compounds are considered as potential marker compounds to grade the agarwood products.



Agarotetrol



Isoagarotetrol

The common techniques used for identification and characterisation of active components of fragrances are GC and LC-MS, which helped the synthesis of these valuable organic molecules. As a result, search for new *notes* and thereby *accords* become easier. Similarly, now many synthetics are available, which mimics the natural behaviour of fragrant substances. Therefore, synthetic chemistry brings more creativity to perfume industry and provides affordable and safer ingredients to discover unique eternal fragrances.

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Student Corner

Student Corner

Isomerism in Coordination Compounds

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Isomers (compounds with the same chemical formula) can be broadly classified into (i) **stereoisomers** (*e.g.* geometrical and optical) with the same connectivity but having different spatial arrangements and (ii) **structural isomers** with different connections between atoms. We are quite familiar with the geometrical (*cis* and *trans*) and optical isomers (*e.g.* enantiomers) of organic molecules where the valency of carbon is **four**. Coordination compounds can form several different types of isomers because metal centres, often, can have coordination numbers higher than four and can adopt different geometries. The following are the common structural isomers of coordination compounds: **ionization**, **hydrate**, **linkage** and **coordination**.

Ionization isomers

Ionization isomers have the same **empirical formula** but differ in the **coordinated anion(s)** thus, yielding different ions **when dissolved in a solution**. Furthermore, ionization isomerism is shown by salts, often involves the exchange of an **anionic ligand** (*e.g.* halide, sulphate, *etc*) between the complex ion (**coordination-sphere**) and the remainder of the salt (**ionization-sphere).** For example, $[CoBr(NH_3)_5]SO_4$ and $[Co(SO_4)(NH_3)_5]Br$ are such isomers. They have the same **chemical composition**, $CoBrSO_4(NH_3)_5$, but differ in ions present in an aqueous solution. In water, $[CoBr(NH_3)_5]SO_4$ produces sulphate ions whilst $[Co(SO_4)(NH_3)_5]Br$ gives bromide ions.

Hydrate isomers

This is analogous to ionization isomerism except that **water** molecule(s) (a **neutral ligand**) replaces the **ionic ligand**, bromide. For example, there are **four** different **octahedral** Cr(III) compounds with the **composition** $CrBr_3{\bullet}6H_2O$. They are given below.

Compound	No. of Br^- ions
$[Cr(H_2O)_6]Br_3$	3
$[CrBr(H_2O)_5]Br_2.H_2O$	2
$[CrBr_2(H_2O)_4]Br.2H_2O$	1
$[CrBr_3(H_2O)_3].3H_2O$	0

Linkage isomers

Some ligands can bind in **more than one way** hence they are called **ambidentate** ligands (*e.g.* NCS and SCN; thiocyanate and isothiocyanate). Complexation of these ligands can result in isomeric compounds, known as **linkage isomers**, with different modes of bonding to the metal centre. For example, the coordination compound with the empirical formula $MnNCS(CO)_5$ shows two linkage isomers $[MnNCS(CO)_5]$ with a Mn-N bond and $[MnSCN(CO)_5]$ with a Mn-S bond. The NO_2 ligand is also an ambidentate ligand and can use either N or O as the donor atom.

Coordination isomers

When both the **cation** and the **anion** are of complex ions of two different metal centres (*e.g.* Co and Cr), the distribution of ligands can vary between the two metal centres giving rise to isomers. This isomerism can be considered as an extreme case of ionization isomerism. *e.g.* $[Co(NH_3)_6][CrBr_6]$, $[Cr(NH_3)_6][CoBr_6]$ are **coordination isomers** with the same empirical formula, $CoCrBr_6(NH_3)_6$.

Geometric isomers

Geometric isomers (or *cis*- and t*rans*- isomers) occur when the relative positions of ligands in a **disubstituted**