On substances that release emotions – a tour across the world of perfumes

published in Kosmetische Praxis 2010 (5), 10-14

Scents and fragrances are part of our daily life to the point that we often have become oblivious of them. But we unknowingly react to them. Tiny chemical molecules signalize messages with major psychological effects.

The use of scents like lavender or rosemary can be traced back thousands of years. Back then and still today, they are used to enhance our wellbeing, for aromatherapy or for masking body odors. From the chemical point of view, we are dealing with the microcosm of a lot of different components that compose a scent or fragrance. Several factors are required so that our olfactory sense can register a scent.

- The substance needs to be volatile
- The base molecule has to be relatively small – generally assumed is a limit of about 300 Dalton
- The olfactory sense has to be conditioned to this substance

Perceiving a scent

The individual perception of a scent may be rather different. What may lead to positive emotions in the one person may as well be unbearable for the other or, another alternative is that the person may not even perceive the scent, an extreme case though. By the way, this is one of the reasons why more than 50 percent of the population will only exceptionally agree to a perfumed cosmetic product. On the other hand, there are molecules which can modify the olfactory scent. Just to mention an example: after a certain while, the rotten egg odor of toxic hydrogen sulfide is no longer perceived.
Scents appeal to the emotional level. According to Paul Jellinek, they have refreshing (anti-erogenous), stimulating, erogenous or narcotic effects. The professional perfumer uses the term “sensuous” for blendings between the main types “erogenous + narcotic” and the term “calming” for blendings between narcotic + anti-erogenous.

Natural or synthetic?

Natural vegetable scents originate from blossoms, fruits, leaves, barks, resins and roots. Among them are a lot of spice plants, grasses and mosses. Animal secretions like amber (from the digestive tract of sperm whales, musk (from the glands of the musk deer), civet (from the anal glands of the civet cat) and castoreum (from the glands of the beaver) are no longer used in perfumes. However, the number of synthetic odorants has largely increased. Many of the natural and particularly of the animal components have been chemically copied or replaced by other formulations.
It still is an extraordinary skill to compose different smelling substances into a scent or perfume. There are only few experts worldwide who master this specific craft. The different smelling substances belong to chemical compound classes with the following dominant functional groups:

- esters and lactones
- phenols and phenol ethers
- alcohols
- aldehydes und ketones
- acetals and ketals
- amines

Acids are rarely found. **Esters**, however, which form after release of water (“condensation”) from acids and alcohols, occur quite frequently. For the most part, esters have a completely different smell than the basic acids. Thus, butyric acids intensely reminds of rancid butter whereas the esters have a rather agreeable pineapple (ester with ethyl alcohol) or strawberry smell (ester with propyl alcohol).
Lactones are intramolecular esters from compounds with both acidic and alcoholic function which hence are able to condensate to a cyclic molecule. Ambrettolide obviously is one of the most prominent representatives of this group with 18 carbon atoms and a sweet erogenous note.
Phenols are aromatic compounds, analogous to alcohol. In this specific context, aromatic is rather used as a historical term and points to the benzene ring (“aromatic ring”) contained in the molecule. Phenol has an unpleasant penetrative drawing ink smell. It is often used in it as a preservative. **Phenolic ethers** form

from phenol and alcohol after release of water and are characterized by pleasant smells like anise oil for instance. The compound from phenol and methyl alcohol has a strong anise smell.

The intensely smelling esters rather result from short-chained **alcohols**. These have a characteristic individual smell like the isopropyl alcohol used in hair tonics among others, but as fragrance components they are of relatively small importance. Ethyl alcohol is an appropriate vehicle in perfumes and also used as a solvent. By contrast, due to their sweaty smell tiniest amounts of alcohols with longer chains are contained in perfumes as erogenous components. Alcohols with terpene structure such as geraniol (flowery-rose-like), nerol (rose-like) linalool (lily of the valley-like), citronellol (rose-like), menthol (cool, mint-like), terpineol (lilac-like), farnesol (lily of the valley-like), eucalyptol (camphor-like) are frequently found.

Aldehydes and **ketones** form by oxidation of alcohols. Besides the solvent properties of their low-molecular representatives (acetone, methyl ethyl ketone), they are characterized by their fresh and flowery notes. This particularly applies for representatives with terpene structure such as geranial (citral A, lemon-like), neral (citral B, lemon-like), carvone (caraway-like) citronellal (lemony), hydroxyl citronellal (flowery-sweet). Aldehydes are sensitive to atmospheric oxygen and that is why essential oils and perfumes that are rich in aldehydes can change their scent after extended storage.
Rather unpleasant rancid smells caused by aldehydes and ketones are formed during the autoxidation of unprotected, unsaturated acids like linoleic acid. Besides the saturated aldehydes pentanal, hexanal and heptanal, extremely smelling unsaturated aldehydes with 7-10 C-atoms are formed, among them 2-nonenal and 1-octen-3-on.
The increased chemical reactivity of aldehydes and ketones is not only the reason for their antimicrobial effect but also for their allergenic potential which is specifically pronounced in cinnamic aldehydes (cinnamal, amyl cinnamal, hexyl cinnamal). Aldehydes and ketones often have a stimulating effect.

Pleasant fragrance notes are generated by the reaction products of 2 molecules of an alcohol with an aldehyde or ketone molecule. **Acetals** and **ketals** are formed in this process while water is released. They also occur in natural environment and can easily be manufactured as synthetic substances, which is the reason why they are frequent components in perfume compositions. Glycosides also belong to the group of acetals and ketals and are widely spread in natural environment.

Hemiacetals and **hemiketals** are intermediate products. They form, if only one alcohol molecule bonds. Hemiacetals and hemiketals are rather instable and easily disintegrate into their base components. They can cause nuances in perfumes. If they form an intramolecular bonding they are more stable, as is the case with monosaccharides (simple sugars) for instance.

Amines remind of decomposition products of body secretions and their scents are ranging from fishy to fecal-like. Tiny dosages of the amines indol and skatol (3-methylindol) which have a rather fecal odor in their pure form though, are important components of perfumes as they unconsciously convey a feeling of physical proximity. Besides, tiniest amounts of them have a jasmine-like note and, as a matter of fact, they are components of the jasmine flower scent.

"Body notes"

Body odor can have attractive but also repulsive effects. On the one hand, it can be attributed to the components of specific **gland secretions** but on the other hand also to the **decomposition products** forming by microbial, oxidative or enzymatic processes. The decomposition products are particularly intense, if the **moisture** cannot escape due to occlusive clothing, shaved arm-pits or tight shoes as e.g. boots. These are ideal living conditions for **microorganisms**. Excessive hygiene may even deteriorate the problems with the result of barrier disorders which then facilitate the penetration of microorganisms.
Smell of perspiration in the **arm-pits** is primarily due to the presence of androstenone (decomposition product of testosterone), isovaleric acid und branched, partly unsaturated C_6-C_{11}-acids. It is an interesting fact that a relatively large percentage of people cannot perceive androstenone.
In normal circumstances, isovaleric acid dominates in the **foot area**. If specific bacteria have settled there, nasty smelling sulfurous compounds will form as for instance mercaptans, thioethers and thioesters. Bactericidal products and breathing shoes may be of help in this case.

Perfumes

Perfumes are composed of a multitude of scents which in turn consist of a variety of different components. Hence, there is a rather

complicated interaction between all the different components due to the fact that they can either react with each other or show individual instabilities. Already lightly acidic media may cause the cleavage of esters, acetals and ketals into their different components in the long term. Other compounds are oxidized by atmospheric oxygen and heavy metal traces. High storage temperatures may even accelerate the processes. Also the matrix has a significant influence here. There is a noticeable difference whether the smelling substances are mixed in an alcoholic solution, a watery emulsion of a skin care cream or a non-aqueous formulation. Hence, a great deal of experience is needed to create a new perfume or equip cosmetic preparations with fragrances. In general, perfumes contain

- a **top note**, which is rather volatile
- a **middle note**, which conveys the main sensory impression and
- a **base note** for the lasting effect.

Scents are frequently used to hide the inherent smell of cream components. Today, the variety of scents is larger than ever before. Even notes that remind us of food like caramel, chocolate, vanilla, gingerbread, specific fruit and crop varieties, still unthinkable in former times, enjoy great popularity.

Basically, it makes sense to keep skin care creams free of perfumes due to their allergenic potential, and then apply the perfume after the skin care creams. This reduces the risk of a penetration of allergenic components into the skin. Another effect: the perfume scent can fully unfold on the skin surface.
The following smelling substances have an allergenic potential and must be declared at the end of the INCI: Amyl Cinnamal, Benzyl Alcohol, Cinnamyl Alcohol, Citral, Eugenol, Hydroxycitronellal, Isoeugenol, Amylcinnamyl Alcohol, Benzyl Salicylate, Cinnamal, Coumarin, Geraniol, Hydroxyisohexyl 3-Cyclohexene Carboxaldehyde, Anise Alcohol, Benzyl Cinnamate, Farnesol, Butylphenyl Methylpropional, Linalool, Benzyl Benzoate, Citronellol, Hexyl Cinnamal, Limonene, Methyl 2-Octynoate, Alpha-Isomethyl Ionone, Evernia Prunastri Extract, Evernia Furfuracea Extract. The individual experience shows, however, that a lot of other components also may have sensitizing properties. Frequently they are oxidation products only formed during the use.

By the way: the pleasantly smelling **balsams** are viscous liquids gained from plant saps or resins. Examples are: benjamin, frankincense, myrrh and Peruvian balsam. Balms or balsams have been very precious in ancient times and already mentioned in the bible. Among other substances, they contain free acids and aromatic esters of the cinnamic and benzoic acids, frequently also different benzoic aldehydes like vanillin. Hence, they also can trigger allergies.

Dr. Hans Lautenschläger