The Detailed Analysis of Essential Oils Leads to the Understanding of their Properties[a]

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Essential oils are valuable natural products used as raw materials in many fields, including perfumes, cosmetics, aromatherapy and phytotherapy, spices, and nutrition. Essential oils are complex mixtures comprised of, in some cases, more than 250 single compounds. Each of these constituents contribute to the beneficial or adverse effects of these essential oils. Therefore, the intimate knowledge of essential oil composition allows for a better and specially directed application. For example, an essential oil with a high content of a relaxant cannot be applied for activating purposes. An essential oil containing furocoumarines cannot be used as perfume material for suncreens. As a natural product, essential oil composition depends on climate, soil, harvesting time, method of production and similar factors. The different chirality of main constituents governs the uses of essential oils and should be considered as well.

A series of factors influencing the composition of essential oils are discussed under the general topic of cosmetology applications. Because essential oils are naturally occurring fragrance mixtures, the question is, why are fragrances used in cosmetic products? To answer this, we must answer the following:

- One must not forget that many cosmetic raw materials possess an odor that cannot be described as pleasant, sometimes smelling outright disagreeable. Because of this, one main goal of any fragrance addition to a cosmetic product is to conceal, to mask a bad smell or a malodor inherent to ingredients.
- The application discipline of a cosmetic product is often increased by a pleasant fragrance. This is beneficial to both partners: the user, who gains efficacy by following the recommended application schedule, and the producer, who can sell more of his product.
- The germicidal properties of essential oils should be considered. This is especially true in creams. Due to their content of water and organic compounds, they offer excellent growing conditions for bacteria and fungi. Dry powders, on the other hand, offer an unfavorable environment to these organisms. With each finger touch to the cosmetic product in an opened jar, the user inserts about 10,000 new germs. Repeated contamination to the cosmetic product by such a method is a fact. However, fragrance compounds, and particularly those containing terpenic alcohols, do not only support preservatives in their function, but also kill germs, or at least stop their growth. Therefore, the safety for the user as well as the extended usefulness of the cosmetic product is guaranteed.
- A pleasant fragrance creates or restores the self confidence of the user. Who does not want to feel clean, good-smelling and, therefore, appreciated and attractive?
- A deliberately chosen fragrance stresses advertising statements (eg. a fresh odor creates the illusion of an ocean breeze, supporting the feeling of freshness, freedom and cleanliness).
- Essential oils and single-fragrance compounds are added to a cosmetic product in order to create a characteristic matchless aroma profile.

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Aspects of Essential Oils

Essential oils are naturally occurring mixtures of many volatile compounds with the common property of emanating a scent. Some essential oils consist of only a few volatiles while the analysis of others shows more than 200 (eg. rose oil contains up to 270 single constituents). Each constituent possesses a distinct molecular formula, certain molecular weight (roughly between 100 and 300 amu) and, therefore, certain physicochemical properties, like polarity, electron density, and optical activity, among others. By means of these properties, fragrances are used in medical and/or cosmetic treatments.

Fragrance compounds can act in a pharmacological capacity beyond their abilities to evoke emotions. Because of their lipophilicy, they penetrate the skin (the absorption through the nasal mucosa is as fast as an intravenous injection) and demonstrate a high affinity to adipose tissues and central nervous system. It is known that they can pass the blood-brain barrier due to the discovery of traces in brain tissue of animals, as experiments have shown. The staying power of these chemicals can be as high as about 58 h beyond original exposure. The application of single-fragrance compounds as well as of essential oil has to be done carefully, considering all toxicological and pharmacological data.

The Roots of Oil Character

The most important tool for considering the proper application of an essential oil is detailed analysis via a capillary GC. The composition of an essential oil is dependent on such characteristics as the geographic character from which the plant is obtained, seasonal variations and climate, production techniques, and purity.

Certain geographic places very often bring forth specific species of essential oil-producing plants, Therefore, the same plant from different geographic origins produces varying constituents of the essential oil in either the concentration pattern or the lack of certain volatiles. Chamomile oil from Morocco is not the same as the English or German versions, though the material is always obtained from the flowers of *Matricaria chamomilla* L (*Matricaria recutita* L.) (Asteraceae). The GC's of their essential oils are distinctly different from one another. In the essential oil of *Artemisia laciniata* (Asteracea) from the Himalayan region near Srinagar, Kashmir, altitude is responsible for differences in the composition of oils. The essential oil of a plant grown at an altitude of about 1800 m above sea level, contains no piperitone, while the essential oil from *Artemisia laciniata* grown in the same region at 2700 m above sea level shows this terpene ketone as the main compound. The camphor concentration in the first essential oil is about ten times higher than in the second. Artemisia ketone can be found in a range of concentrations between 12% and one percent. These results, published some years ago by Weyerstahl and his team from the Technical University of Berlin, clearly demonstrate the influence of temperature, total amount of sunhours and UV light on the composition of an essential oil.

Seasonal variations and the time of harvesting also show a great influence on the composition of essential oils. The content of geranial in the essential oil of the flowers of *Dracocephalum moldavica* (Lamiaceae), an aromatic plant of Asia and Eastern Europe used for its antibacterial, antiviral, antispasmodic and culinary qualities, increases from about 18% (early flowering stage) to 35% (full senescens stage). The differences in flowering stages also affects the concentration of its corresponding alcohol, geraniol, which decreases from about 17% to five percent, respectively. Depending on the length of sunlight (UVB), the concentration of menthol in the essential oil of *Mentha piperita* (lamiaceae) declines from 48% to 10%, while the content of menthofurane rises from 9% to 20%, thus giving evidence of a type of aging.

Oil composition is also affected by variations in production techniques. Essential oil qualities vary if obtained by hydrodistillation (the plant material is heated in two to three times its weight of water with indirect steam from outside the still) as opposed to steam distillation (the plant material is extracted by direct steam, produced in the still, or by indirect steam, produced outside and fed into the still), hydrodiffusion (low-pressure steam (<0.1 bar) replaces the volatiles from the intact plant material by osmotic action) or CO_2 extraction. For example, as was shown by Boelens some years ago, the chemical composition of the essential oil of the flowers of *Rosa damascena* (rosaceae) is very different depending on the production technique. In an essential oil sample obtained by hydrodistillation, the main compounds are citronellol (30%) and geraniol (18%). In the CO_2-extraction, 2-phenylethanol (67%) was found as the main constituent. The concentration of the very potent trace- and character-impact compound β-damascenone is about three times higher in the essential oil obtained by hydrodistillation. The resultant oil varies if the distillation still for the production of the essential oil is totally or partly filled, or if the distillation process is performed in a glassware-equipment or copper still, as has been reported on different compositions of geranium oils from *Pelargonium graveolens* (geraniceae) of France's Réunion Islands.

Safety Concerns

An important factor in this industry is the use of solvents and pesticides because developing countries, where environmental considerations still do not play the same role as in the industrialized world, represent about 55% of total global essential oil production. For example, as has been shown by Schilcher and his team at the Free University of Berlin, in 72 samples of approximately 110 commercially available essential oil samples, 34 different essential oil organochlorine pesticide residues were found. DDT, long forbidden in the industrialized world, was located often. Also detected were lindane, α-endosulfane and hexachlorocyclohexane. All of these can create serious health and safety problems if such tainted essential oils are used in cosmetics.

Even if the detected amount is too small for a toxic reaction after a single application, the danger of accumulation in adipose tissues exists, especially upon repeated cosmetic- and perfume-product applications. In nonsense applications such as aromatherapy-massage wherein essential oils are applied on cellulite, the skin often acts as a reservoir for topically applied chemicals.

The Life Span of Essential Oils as Perfume Constituents in Cosmetic Products

Perfumed rinse-off products, like shampoos, can be used without a great fear of toxicity. However, this attitude is not valid with regard to creams, lotions, lipsticks, etc., which are used on large skin areas, have a prolonged contact with the skin or are applied to mucus membranes. In all cases, the absorption through the skin has to be considered. Normally, the perfume concentration in most of cosmetic products ranks between 0.5% and two percent, thus being too small for any toxicity risk from essential oil-constituents, with the exception of some more or less toxic terpenic ketones, such as thujone or pulegone. However, none can ignore the cumulative effect of the lipophilic fragrance compounds in adipose tissues (e.g. cutaneous reservoir), diverse organs of the body or its misuse in the form of repeated high-quantity applications.

The cosmetic chemist also has to consider biochemical interactions of the essential oil constituents with the skin. This includes oxidations, de-acetalizations and ester cleavages, which often occur on moist skin (e.g. in the axilla), thus furnishing an altered perfume composition. Esteras of the skin cleave phenylethyl acetate to phenyl ethyl alcohol and acetic acid, which may, in some cases, cause skin irritations, changing the odor of cosmetic products. Another good example is d-limonene, which hardly shows a sensitizing capacity. However, because of its easily formed oxidation products, it can be compared to common allergens such as formaldehyde. The volatilities of each single compound in the essential oil is different, thus aiding longer skin contact for low-volatile compounds (e.g. 1 h after the application of benzyl acetate to the skin, this fragrance compound shows a tripled skin-life over that of limonene and cis-jasmone; at times, this can increase up to 20-fold longer). Substances with a somewhat higher toxicity potential should not remain too long on the skin.

Another fact that clearly shows the importance of a detailed analysis of an essential oil sample is the danger of phototoxicity and dermal sensitization. Furocoumarines are well known to cause the *Berloque*-dermatitis, when such a treated skin area is exposed to sunlight. This is also true with cinnamic derivatives, oak moss and balms. The fact that fragrance compounds may, in some cases, cause dermal sensitization should not discredit their careful use. Sesquiterpene hydrocarbons and cinnamic derivatives are known to possess a high sensitization potential.

Chirality, a molecular property, is frequently encountered in natural products in mono- and sesquiterpene compounds of essential oils. The absorption rate of an enantiomeric pair of such fragrance compounds is different, as has been shown using (+)- and (–)-carvone, or (+)- and (–)-limonene in human experiments. (+)-Carvone and (+)-limonene have been found to have a longer plasma life than their enantiomers, which get metabolized more quickly (on the other hand, the concentration of their corresponding metabolites in the urine is higher).

Conclusion

It is evident that essential oils are mixtures of volatile compounds and not esoteric miracles. Because of the molecular attributes of each single essential oil constituent, the perfumer is able to create perfumes for cosmetic products in safe ways while carefully considering the harmful properties of some fragrance ingredients and using the guidelines of the International Fragrance Association. Considering all the afore-mentioned differences in essential oil composition, it is clear that only a detailed knowledge of the constituents of an essential oil will lead to a proper use in cosmetics by perfumers and cosmetic chemists. However, such a detailed knowledge can only be obtained by means of a carefully performed capillary-GC. Therefore, each essential oil charge should be provided with such a precise chromatogramm. A careful quality-control testing of each sample, dealing with the residue, authenticity of the main compounds by chiral determination and concentration pattern is a must. Each batch should be labelled properly. Regarding essential oils as harmless because they are natural is as stupid as it is irresponsible.

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