Glycols in skin care preparations and dermatics

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Glycols are widely used as cosmetic additives or active agents in skin care preparations and dermatics. They ensure that preparations are microbiologically safe, have excellent haptic features and improve the skin moisture. Their specific features are described in the following.

Glycols are related to ethyl alcohol. Chemically speaking, glycols are distinguished from ethyl alcohol and other alcohols such as isopropyl-, propyl-, or the long-chain cetyl alcohol by the number of alcoholic hydroxyl groups (OH). While ethyl alcohol alias ethanol has one OH-group, ethylene glycol alias ethanediol has two OH-groups. The longer-chained glycols are structured in analogy: propylene glycol, butylene glycol, pentylene glycol, hexylene glycol etc.
The fact that these compounds have a sweetish taste is responsible for their name which is derived from the Greek language and means sweet. Chemically related to glycols are glycerin alias propantriol with 3, monosaccharides such as glucose with 5 and sugar alcohols such as sorbitol (E 420) alias hexanhexol with 6 hydroxyl groups.

Antimicrobial activity

A typical feature of glycols is their inhibition of microbial activities when they reach the minimal inhibitory concentration (MIC) – similar to ethyl alcohol. As a consequence of this, the yeasts die off after a certain alcohol concentration has been reached during the fermentation of grape juice into wine. For the preservation of cosmetic products glycols often are preferred to alcohol since the smell of alcohol is not wanted and it also tends to evaporate. This evaporation after frequent openings of the containers of aqueous alcoholic products involves that the concentration can fall below the MIC and the product hence becomes microbiologically unstable and spoils. Since all glycols are non-volatile this problem can be excluded.

Propylene glycol

By far the most frequently used type of glycol is propylene glycol. Every once in a while there have been reports on allergic reactions that still today are circulated although said reactions obviously were due to contaminations. In this context it should be recalled that the propylene synthesis occurs via propylene oxide and that accordingly various ethers can occur as by-products and residual traces of propylene oxide after reaction with water. The University Dermatological Clinic Karlsruhe could prove that the high purity of today's propylene glycol does not involve any risk of sensitization even at intense usage. Other data also are favorable such as the reports on the tolerance which show very low toxicity and there is no evidence for MCT potential (M = mutagenic, C = carcinogenic, T = teratogenic). This distinguishes propylene glycol from the Cosmetic Regulation-licensed preservatives that all, without exception, have allergenic potential even if they can be added in considerably lower concentrations.
Propylene glycol is licensed as a food additive (E 1520) and also serves as additive in tobacco products and E-cigarettes. In these products as well as for the use in cosmetic products the water-binding and solvent features are in focus ("botanicals"). Since propylene glycol has very similar properties but is less expensive than tax paid ethyl alcohol and furthermore is an alternative for inexpensive denatured alcohol (alcohol denat.) with added phthalic acid esters, it is a popular solvent for plant extracts.

The above mentioned ethylene glycol is used for the frost protection in engine coolants of cars and the production of artificial fog in movies and TV. Ethylene glycol is rarely used in cosmetic products. Its main metabolite in the human body is oxalic acid which is known from rhubarb (alias pie plant) and licensed up to 5% in professional hair care products; it also is known for its kidney-damaging effects. A further metabolite of ethylene glycol is glycolic acid which belongs to the alpha hydroxy acids (AHA); in the form of its sodium and potassium salts it is a component of moisturizing creams. Multi-faceted metabolites form during degradation of higher molecular glycols such as pentylene glycol (see below).

Moisturizers

Glycols and particularly propylene glycol, butylene glycol and pentylene glycol have hygroscopic features or in other words, they absorb water and retain it through hydrogen bridges. Glycerin-containing cosmetic products improve the skin moisture. The water retention is particularly pronounced in the related natural glycerin of the skin (component of the natural moisturizing factor [NMF]). Again and again there have been speculations that the glycerin-bound water is no longer available for the skin and that the skin will further dehydrate in this way; this, however, could not be proved even in the case of high glycerin concentrations. It should be mentioned though that the strong hydrophilic compounds are easily washed out with skin cleansing. Highly dosed glycerin creams hence have an excellent moisturizing effect after application, however if the glycerin has been largely washed out after a subsequent skin cleansing, the skin feels rather dehydrated. This effect can largely be neutralized by lowering the glycerin percentage and increasing the lipid concentration in the product. By the way: If the compensation of the concentrations of water-soluble substances is disturbed, there is a risk of irritation in the form of a light burning sensation after the application of aqueous skin care preparations and particularly oil-in-water emulsions; this condition is particularly frequent in the case of rosacea-prone skin and perioral dermatitis. The lower the molecular weight and the higher the concentration of the substances dissolved in the water phase, the stronger the reaction. A typical example is urea that also is a component of the above mentioned NMF.

Besides propylene glycol, glycerin is the most popular substance in skin care preparations. It forms in the skin, among others, during the enzymatic degradation of natural lipids and oils with triglycerides as their main component – in triglycerides glycerin is esterified with three fatty acids. Hence glycerin can be produced by saponification of natural oils or alternatively in a biotechnological process with the help of yeasts. A further alternative is the chemical synthesis based on propene via several intermediate stages. In contrast to the opinion of some spiritual-oriented supporters of natural substances, it can be argued that there is no difference between herbal, biotechnological or synthetic glycerin. What matters is that there are no impurities in the product. Glucoside is a compound of glycerin with glucose (dextrose, grape sugar) with similar affinity to water. Moreover, the natural substance is alleged to stimulate the aquaporin-3 of cells. Aquaporins are membrane proteins and regulate the water supply in cells.

Multifarious applications

Diglycerides with their two fatty acids and monoglycerides with one fatty acid linked to the glycerin are intermediate stages in the saponification of triglycerides into glycerin and free fatty acids. They belong to the first known emulsifiers and are convenient insofar as they are absolutely physiological, or in other words, they can be degraded and metabolized without any problems. A disadvantage is that their emulsions are prone to chemical and physical destabilization during storage involving changes of the consistency. Monoesters of ethylene glycol ("glycolic ester“) or in other words compounds of ethylene glycol with a fatty acid, have similar characteristics.

In terms of their structure, sugar alcohols are closely related to glycols and glycerin and can also effectively retain water. There is a difference though: sugar alcohols are not liquid but solid substances. The above mentioned sorbitol (sorbite) is the most important representative: it has a sweetish taste and hence is used as a sugar substitute. Sorbitol is a common plant component. Its industrial production is based on starch which first is cleaved into glucose and then reduced. Similar substances are mannitol (mannite) which is an ingredient of algae, dune-, and tideland plants, the natural inositol of the human body as well as xylitol (xylite) and maltitol.

Similar to glycols, sugar alcohols only have antimicrobial effects after a certain threshold concentration is reached. Hence ethanol, glycols, glycerin and sugar alcohols (predominantly sorbitol) can be combined as desired and used for preservative-free skin care preparations, as already described in the context of propylene glycol. The individual components of the mixtures can be used in lower doses than required for a single substance. Sensitizations as known from preservatives are practically excluded. As a matter of fact, also the closely related monosaccharides with their five alcoholic hydroxyl groups could be included here. Due to their stickiness they are less frequently used though – examples are preparations with honey additives.

Polyethylene glycols (PEGs)

In conclusion, also the polyethylene glycols (PEG) should be mentioned. They contain two hydroxyl groups that, however, are linked at the end of a long chain instead of the side-by-side linkage as in most of the glycols. PEGs

are formed by linkage of ethylene glycol molecules with elimination of water. Two molecules of ethylene glycol thus form diethylene glycol which has an ambiguous reputation after some wine growers used it years ago to round out the taste of certain wines. Diethylene glycol plus an additional ethylene glycol molecule forms triethylene glycol and so on up to the formation of polyethylene glycol (the term poly means many). Polyethylene glycols are synthetically processed from ethylene oxide (EO) and water. In contrast to the glycols, polyethylene glycols are not degraded in the body. Due to their high molecular weight they are not resorbed either. PEGs are water-soluble and retain water – although comparatively less than the low molecular glycols. Being filming agents, they influence the transepidermal water loss (TEWL) or in other words, they retard the water evaporation from the skin. PEGs smooth the skin surface and are used to control the consistency in cosmetic products. They have no antimicrobial activity.
Chemical bonding of long-chain alcohols to PEGs forms typical emulsifiers which can be identified in the INCI by their suffix "eth". The parenthesized number following the term indicates the number of EO groups. Thus the INCI term laureth-10 refers to a C_{12} alcohol linked with 10 EO units. By sulphating the end of chain, laureth sulphate forms which is a strong anionic emulsifier. The longer the PEG chains in emulsifiers, the lower the irritation potential of the emulsifiers. Typical feature of all the PEG compounds and particularly of emulsifiers is a high wash out effect as they are not degraded in the skin and in the presence of water, i.e. during skin cleansing, they again emulsify lipids and transport them out of the skin.
In the presence of UV radiation PEGs are sensitive to oxygen. The associated formation of peroxides usually can be impeded by adding antioxidants. Otherwise the peroxides on the skin will cause inflammatory irritations ("Mallorca acne").

Degradation of glycols

The biodegradation of glycols in humans is shown in the following figure using the example of pentylene glycol.

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