by Michael J. Fevola, PhD

Glycerin

Michael J. Fevola, PhD, is a manager in the New Technologies group at Johnson & Johnson Consumer and Personal Products Worldwide in Skillman, NJ, where he leads R&D in polymer and surface chemistry. Fevola has authored 12 peer-reviewed articles and book chapters, is an inventor on seven US patents and is a member of the Personal Care Products Council's International Nomenclature Committee and the Society of Cosmetic Chemists' Committee on Scientific Affairs.

Author's Note: Glycerin is a unique and versatile chemical with numerous applications; to adequately cover all of the aspects of this compound in a short column would be impossible. Therefore, this column will highlight some key facts about glycerin, but interested readers are encouraged to pursue further, more comprehensive reading on the ingredient.[1]

Next to water, glycerin is the most common ingredient employed in the formulation of cosmetics, personal care products and over-the-counter (OTC) drugs, and the manufacturers of these products have been the leading consumers of refined glycerin for more than two decades.[2–4] According to the US Food and Drug Administration's (FDA) Voluntary Cosmetic Registration Program (VCRP), the use of glycerin has been documented in 11,972 cosmetic products, second to water, which was reported in 26,241 cosmetic products.[5–6]

Glycerin's long history of use and outstanding safety profile make it one of the most trusted chemicals in the industry; indeed, the FDA recognizes glycerin as a Generally Regarded As Safe (GRAS) ingredient, and glycerin derived from natural sources is listed as exempt from REACH in Annex V(9). In addition to being a critical excipient in the formulation of cosmetics and OTC drugs, glycerin may also be employed as an active ingredient in anorectal, laxative, oral health, ophthalmic and skin protectant drug products when used according to the FDA's US OTC monographs for these categories.[7–8]

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Chemistry and Manufacture

Before discussing the chemistry of glycerin, it is first important to differentiate between the terms *glycerol* and *glycerin*. Glycerol refers to the pure chemical compound 1,2,3-propanetriol shown in **Figure 1**. It is a trihydric alcohol with the chemical formula $C_3H_8O_3$, corresponding to a molecular weight of 92.10 g/mol. Conversely, glycerin refers to purified commercial products containing ≥ 95% glycerol with the remainder comprising water and trace impurities. The *International Nomenclature of Cosmetic Ingredients (INCI) Dictionary* and the *United States Pharmacopeia (USP)* both refer to this ingredient as glycerin.[5, 9]

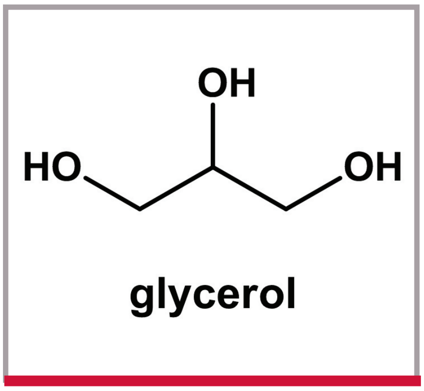

Figure 1. ***Chemical structure of glycerol***

Glycerol is a naturally occurring compound, but it is rarely found in nature in its free form.[2] Instead, it occurs in animal and vegetable fats and oils in the form of triglycerides, i.e. esters derived from glycerol and three fatty acids. Glycerol is also a key structural element of phosphoglycerides, a class of lipids that are the main component of biological membranes. A notable phosphoglyceride is phosphodityl choline, the primary constituent of lecithin, which is a naturally occurring emulsifier commonly used in food, drug and cosmetic applications.

Natural glycerin: The majority of the world's glycerin supply currently is a coproduct from the splitting of fats and oils to synthesize fatty acids, soaps and biodiesel, i.e. fatty acid methyl esters.[2, 4] **Figure 2** illustrates the key chemical reactions used to synthesize these oleochemical products from natural triglyceride feedstocks. Each reaction yields crude glycerin in aqueous solutions of varying glycerol content. The reactions include: hydrolysis under high temperature and pressure to produce free fatty acids and sweetwater (10–20% glycerol); saponification with sodium hydroxide (NaOH) to yield sodium soaps and spent lye (10–25% glycerol); and base-catalyzed transesterification with methanol (CH_3OH) to yield fatty acid methyl esters and biocrude glycerin (25–80% glycerol).

Following separation from the other coproducts produced via the above reactions, each of these crude glycerin solutions must undergo extensive isolation and purification to yield refined glycerin. The initial isolation processes include neutralization of any free caustic

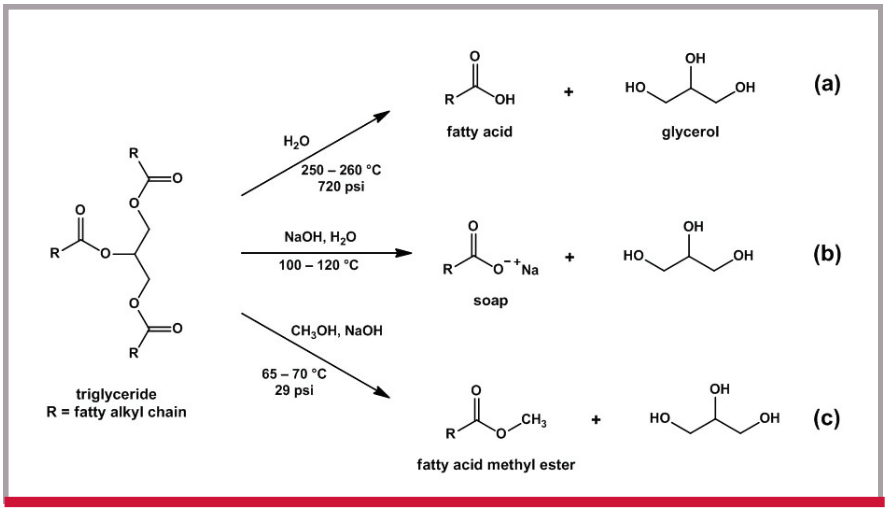

Figure 2. Key chemical reactions of natural fats and oils (triglycerides) that yield glycerol as a coproduct, a) hydrolysis to free fatty acids, b) saponification to soap and c) transesterification to fatty acid methyl esters.

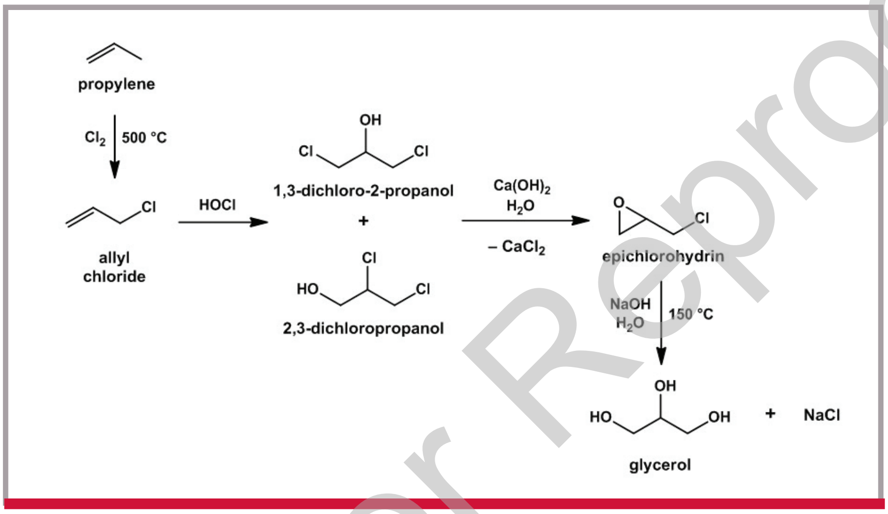

Figure 3. Synthesis of glycerol from propylene via the epichlorohydrin route.

(for spent lye and biocrude sources); separation of impurities such as unreacted fats/oils, residual fatty acids/soaps, methanol (for biocrude sources), salts and other organic matter; and concentration via evaporation of water. This concentrated crude glycerin containing approx. 80–88% glycerol is then further refined via vacuum distillation, bleaching and deodorization processes to yield the high purity glycerin (≥ 95% glycerol) required for food, drug and cosmetic applications. Refined glycerin typically costs two to three times the price of concentrated crude glycerin due to these additional processing operations.[10] Because glycerin is a coproduct of oleochemical production, its pricing is sensitive to oleochemical market driving forces, such as the supply of vegetable oil feedstocks and the demand for biodiesel. Consequently, glycerin pricing tends to be volatile.[10–11]

Synthetic glycerin: Glycerin may also be produced synthetically from the petrochemical feedstock propylene,[1] though production and usage of synthetic glycerin has experienced a significant decline due to the excess supply of oleochemical glycerin, e.g. from biodiesel production, and the market preference for naturally derived ingredients. A variety of elaborate synthetic routes for the manufacture of glycerol from propylene gas have been developed, yet the simplest and most important commercial process remains the base-catalyzed hydrolysis of epichlorohydrin.[12] **Figure 3** shows the synthesis of epichlorohydrin from propylene, followed by hydrolysis to glycerol.

Properties

High-purity, USP-grade glycerin is a clear, colorless, odorless, sweet-tasting fluid.[2, 3] Glycerin is hygroscopic, and the USP grade may contain up to 5% w/w water.[9] On an anhydrous basis, the *USP* specifies that glycerin should assay for 99–101% glycerol and may contain only trace levels of organic and inorganic impurities. In response to episodes of glycerin adulteration with diethyleneglycol (DEG), a toxic compound, the *USP* monograph for glycerin was updated in 2008 to include assays for ethylene glycol and DEG;[13] it specifies limits of no more than 0.1% for either contaminant. Glycerin is considered nontoxic and nonirritating, although anhydrous glycerin applied to the skin can have a drying effect due to its extremely hygroscopic character.

Anhydrous glycerol is a viscous Newtonian fluid with a viscosity of 945 cP and a density of 1.26 g/mL at 25° C; both the viscosity and density of glycerin decrease with increasing water content.[14] Glycerol is nonvolatile, completely miscible with water and other highly polar solvents, such as short chain alcohols and glycols, and it exhibits ample hydrogen bonding ability due to its three hydroxyl groups. This hydrogen bonding ability is responsible for glycerol's negative enthalpy of hydration (ΔH = -2.8 kJ/mol); thus, of the process of diluting glycerol with water is exothermic and can release considerable amounts of heat.[15]

Technology and Applications

Glycerin is among the most basic conditioning agents for skin and hair care applications. In cosmetic applications, glycerin is best known for its function as a humectant in products designed to deliver and retain moisture in the skin. Its outstanding ability to penetrate into the stratum corneum and bind water make it the benchmark against which all other humectants are evaluated. In cleansing applications, the addition of glycerin to bar soaps provides improved skin feel and softness,[16] and glycerin has been reported to help reduce the penetration of damaging surfactants such as sodium dodecyl sulfate into the skin.[17–19]

Glycerin is also a critical starting material used to manufacture many classes of cosmetic ingredients, such as glyceryl ethers, polyglycerols, glyceryl esters, polyglyceryl esters, alkoxylated glyceryl esters, polyesters, etc. In the future, glycerin is anticipated to become a feedstock of even greater importance for the synthesis of bioderived chemicals and ingredients. The prospect of continued oversupply of crude glycerin due to the ever-increasing global demand for oleochemicals such as fatty acids, fatty alcohol and biodiesel, has led to widespread R&D efforts to develop chemical processes that use glycerin as a renewable alternative to petrochemical feedstocks for the production of basic chemicals such as synthesis gas, propylene glycol, epichlorohydrin, glycidol and acrylic acid.[20, 21] One notable example is Solvay's proprietary Epicerol process, which converts glycerol to epichlorohydrin by reversing the last reaction step shown in **Figure 3** via catalytic reaction with hydrochloric acid. The development of such glycerin-based analogs for basic chemicals that were previously only obtainable from petrochemical sources offers the potential to create a new generation of sustainable personal care ingredients utilizing the proven chemistries that exist today.

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Send e-mail to CT_author@allured.com.

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