

Chemical Reaction



Lipid Assets

The lipid content is crucial to the barrier function and, thus, is perhaps the decisive factor for the maintenance of youthful skin. **BY STEVE HERMAN**

LIPID: Any of a large class of organic substances, insoluble in water and typically greasy to the touch, including the fats, waxes, and sterols.

—Funk & Wagnalls Standard College Dictionary

FATS AND WAXES have a reputation as rather mundane cosmetic materials, while the public image of lipids tends to the exotic and technical. Cosmetic literature abounds with applications for lipids (from the Greek *lipos* for fat), a pervasiveness that demands the attention of every formulator. This family of ingredients contributes a crucial component to skin anatomy and physiology, and strongly warrants careful consideration in the construction of any modern treatment product.

Yet, as *Funk & Wagnalls* implies, lipids are not a small and easily categorized group of chemicals. With proteins and carbohydrates, lipids are components of all living cells. Lipids (and their key partner, water) may not seem to be ingredients vital to cutting-edge skin-care technology, but their proper balance and maintenance are the hallmarks of healthy skin.

Defining lipids by solubility is inadequate, as many have significant water solubility. One modern definition¹ is: "fatty acids and their derivatives, and substances related biosynthetically or functionally to these compounds." The definition includes cholesterol and plant sterols, waxes, phospholipids, and sphingolipids. Thirty years

ago, a simulation of skin lipids for cosmetic use might consist of a blend of common ingredients: synthetic triglycerides, triglyceride oil, hexadecyl stearate, spermaceti, squalane, palmitic acid, glyceryl monostearate, lanolin, and cholesterol USP. This concoction indicates the complex mix necessary to simulate lipid behavior. No single material can replicate all the attributes of skin lipids.

One of the simplest and clearly defined lipid groups is the triglycerols (or triglycerides), with the structure shown in Figure 1. Triglycerols are the primary source for a crucial array of cosmetic raw materials: They are hydrolyzed into glycerin and fatty acids, with the fatty acids and the corresponding alcohols incorporated into products as diverse as esters, surfactants, and conditioners. Phospholipids contain a phosphate functional group and have the general structure shown in Figure 2. Phospholipid bilayers, a variety of liquid crystal structures, are key components of all cell walls, providing a barrier to some materials and allowing the transport of others. These bilayers are essential to life.

Sphingolipids (Greek *spingos* for sphinx) were named for the

puzzle they provided for early investigators. They are derived from sphingosine (Figure 3), a long-chain unsaturated amino acid ($C_{18}H_{37}O_2N$). Sphingolipids are similar to phospholipids, having a polar head group and two hydrophobic hydrocarbon chains, one sphingosine and one a fatty acid. Ceramides are sphingolipids containing two acyl moieties. More complex sphingolipids, such as cerebrosides and gangliosides, are derived from ceramides. Glycosphingolipids are sphingolipids containing a carbohydrate.

Skin lipids arise from two sources. By far the largest quantity of lipids originates in the secretions of sebaceous glands, but this group may not be essential for healthy skin. The remaining lipids come from epidermal cells, undergoing constant modification by the evolution of the cells from the basal level to their eventual location in the cornified layer. Lipid leaflets frequently originate in membrane-coating granules termed Odland bodies. Lipids comprise 6 to 10 percent of healthy stratum corneum, where they are primarily found in intercellular spaces. The intercellular lipids, structured as lamellar liquid crystals, are a key component of >>>>

FIGURE 1: SIMPLE LIPIDS

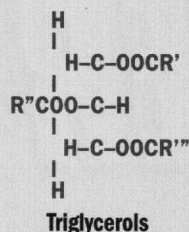


FIGURE 2: PHOSPHOLIPID STRUCTURE

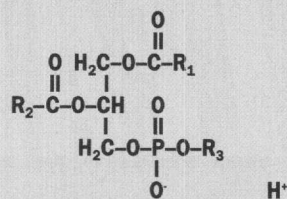
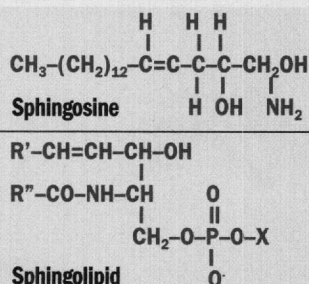


FIGURE 3: SPHINGOSINES & SPHINGOLIPIDS



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the skin's water barrier properties. There are many types of lipids, and some, such as ceramides, have been specifically identified for their value in skin treatment products. One analysis of the epidermal barrier² attributes 50 percent to ceramides, 20 percent to cholesterol sulfate, and 20 percent to free fatty acids.

The barrier function is less effective in older individuals. In addition, solvents and detergents compromise the barrier: Simple washing with soap significantly defats the skin. As the barrier function deteriorates, the skin becomes irritated and rough. The lipid content is more crucial to the barrier function than the thickness of the stratum corneum and, thus, is perhaps the decisive factor for the maintenance of youthful (if not actually young) skin. It seems logical to replace the lipids using treatment cosmetics, but care should be taken to ensure that the lipids chosen contribute to bilayer formation. Including cholesterol and free fatty acids is simple, but

complications arise when formulating with ceramides. Ceramides are highly hydrophobic and tend to crystallize in emulsions. Emulsifiers based on liquid crystal formation can be useful, but problems can still arise upon storage. The incorporation of ceramides into liposomal structures also can be useful for formulators.

Nonpolar lipids are of no use in setting up liquid crystal barrier structures. In addition, the interaction of emulsion formulations with the lipids in the skin, and the penetration of the lipids into the stratum corneum, will affect the efficacy of the product. Thus, creating a product that will truly restore the barrier function of the skin is a complex task.

Spreading of the lipids on the skin is necessary for the product's effectiveness, and must be specifically engineered to promote the desired performance.³ The availability of chemistry with branch chains, unsaturation, cyclic, and substituted structures makes the range of properties virtually endless. Slow-spreading lipids are more useful in locally applied decorative cosmetics, while rapidly spreading lipids are more appropriate for day creams and body lotions. Among common ingredients, castor oil spreads very slowly; oleyl alcohol represents average spreading; and isoheptadecane spreads very rapidly. The fundamental determinants of the spreading rate appear to be molecular weight, the degree of branching, and the presence of functional groups. The most obvious factor is molecular

weight: The higher the weight, the slower the spreading. Esters spread more rapidly than hydrocarbons of the same molecular weight. Branching, especially multiple branching, typically speeds spreading. Emulsion type (o/w, w/o) also has profound importance in controlling the application rate of oils. In addition, each individual's skin uniquely influences the spreading rate.

The role of lipids in the preservation of an effective skin barrier via lamellar structures highlights the crucial importance of fatty chemistry in the life sciences. Knowledge of the basic principles of skin physiology, especially of the intercellular matrix, is necessary for the creation of functional skin treatment products. The practical formulator also must be aware of parameters such as emulsion type and spreading efficiency of emollients to arrive at an optimum system for delivering genuine benefits to the consumer. **GCI**

References:

- For a thorough introduction to lipids, see Rieger, Martin M., "Skin Lipids and Their Importance to Cosmetic Science," *C&T*, Vol. 102, July 1987.
1. www.lipid.co.uk/infoces/Lipids/whatlip/index.htm
 2. www.cosmetic-register.com/cwjournal/798/role_of_ceramides_in_the_barrier.htm
 3. Zeider, U., "On the Spreading of Lipids on the Skin," translation of a German language article published in *Fette-Seifen-Anstrichmittel*, 87/No.10, p. 403, 1985.

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