Lipids that Act in a Cosmetic Pack

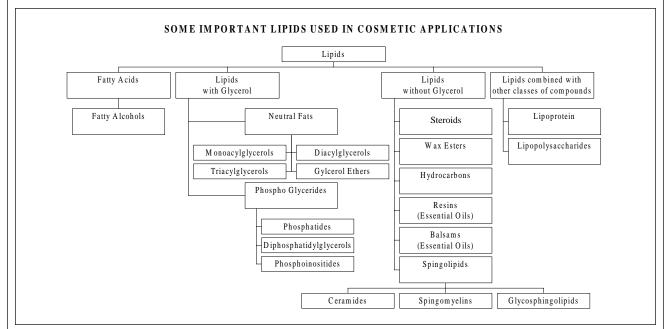
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ils and fats are a diverse group of essential constituents found in all living plants and animals. Although more than two and half lakh plants exist, only a minuscule proportion produces seeds that bear oil in sufficient quantities for commercial exploitation. Of all the vegetable oils commercially developed, a dozen of them actually contribute more than 90% of vegetable oil production for use. Animal and plant lipids have been traditionally used for more than a thousand years for human consumption as food and in the manufacture of non-food items for personal grooming and adornment. Now-a-days, plant fats and oils are also used in manufacturing chemical derivatives and oleochemicals.

The most important class of plant lipids used in cosmetic formulations are the triacylglycerol or triglycerides. Triacylglycerols have been used in personal care formulations, colour cosmetics and hairdressing products, for their cosmetic and pharmaceutical properties. Triglycerides, structurally, can be split to give one molecule of glycerol and three molecules of fatty acids. Fatty acids used in cosmetic products have varying chain lengths, which are all straight chain, containing an even number of carbon atoms. There are about 40 different fatty acids occurring in nature, the largest is the group containing 18 carbon atoms.

Natural oils and fats vary widely in their physical properties eventhough they consist of similar or same fatty acids. This is largely because individual fats and oils differ over a large range in the component fatty acid proportion. The structure of the individual triglyceride components may also vary. Moreover, the two factors are interdependent and are largely responsible to the overall effects observed in individual fats and oils.

A cosmetic formulation consists of a number of ingredients. Ingredients are generally selected to take advantage of their physical, rheological and functional properties, as diluents or even simply for marketing claims. Vegetable fats and oils, wax esters from lanolin and Jojoba oil, phospholipids, ether lipids, sphingolipids are some lipid classes that are becoming popular in many personal care products largely due to their skin conditioning, emolliency and emulsifying properties. Market dynamics indicates that the use of naturals and its derivatives in personal care products will only increase in times to come, making these actives easily available for regular use.



FATTY ACIDS

Fatty acids normally used in cosmetic preparations are naturally occurring straight chain monocarboxylic acid with an even number of carbon atoms. The fatty acid molecules are either saturated or unsaturated. Of the various fatty acids used, the most important ones are given below. Natural lipids used in cosmetic applications are generally in the form of fatty acid derivatives where the fatty acid is condensed to fatty alcohol or long chain derivatives:

Lauric acid	12 Carbon atoms
Myristic acid	14 Carbon atoms
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Palmitic acid	16 Carbon atoms
Stearic acid	18:0 Carbon atoms
Oleic acid	18:1 Carbon atoms
Linoleic acid	18:2 Carbon atoms
Linolenic acid	18:3 Carbon atoms
Ricinoleic acid	18:1 Carbon atoms

LIPIDS WITH GLYCEROL

Neutral fats and natural oils, fats and waxes were some of the earliest cosmetic ingredients to be used in cosmetic preparations. Fatty acid esters of glycerol that are distributed in plant and animal oils can be either liquid or solid in nature, depending on the chain length and their unsaturation. Triacylglycerols can have two or more fatty acid groups in each of the position or can also have the same fatty acid group.

$CH_2 - OH$	$CH_2 - OCO(CH_2)_{14}CH_3$
CH — OH	$CH - CO(CH_2)_{14}CH_3$
$CH_2 - OH$	$CH_2 - OCH(CH_2)_{14}CH_3$
Glycerol	Triacylglycerols

Triacylglycerols are insoluble in water but are soluble in most organic solvents. On hydrolysis, they produce glycerol and the combined fatty acids. Triacylglycerols lipid rich natural oils have a beneficial effect on skin with a good water barrier, reducing trans-epidermal water loss (TEWL). TEWL from our skin leads to dry skin that can be corrected by use of cosmetic application containing oil rich in essential fatty acids.

Natural oils

emmolliency in creams and lotions. Oils are also used as carrier of other ingredients to be delivered to skin in a cosmetic formulation. Some natural fats are prone to oxidation due to the presence of unsaturated bonds. This is more if the neutral fat breaks down during processing and manufacture. Oxidation products like aldehydes; peroxides, etc. interact with the fragrance and other active material giving rise to coloration and rancidity. Super refining of these oils removes these oxidation products for use in cosmetic applications without any problems.

Essential fatty acids

Essential fatty acids metabolised in our body are required for an unimpaired condition of the epidermis. Essential fatty acid deficiency can be due to poor diet, diseases like psoriasis, atrophic eczema, skin dermatitis, dry skin caused due to ageing, modern lifestyles and use of harsh soaps and detergents. Human body cannot synthesise essential fatty acids repeatedly at short intervals and they have to be supplemented, either by diet or by topical application. Naturally occurring oils that have triacyglycerol lipids include cocoa butter, shea butter, babassu, almond, sesame, shorea butter, mango seed oil, and these are often used in cosmetic formulation. However, all these oils are often expensive and difficult to use in mass market cosmetic formulations. The best way to get around the situation is to use alternative fat derivatives that are less expensive, but equally functional. The simplest method to do this would be the use of hydrogenated and fractionated fat additives.

Hydrogenated & fractionated fat additives

Hydrogenation is a simple process by which the properties of vegetable oils can be altered. During hydrogenation, the unsaturated form of the fatty acid in the vegetable oil is converted to their saturated form. Hydrogenation is an inexpensive way for changing the property of a specific oil, as the degree of hydrogenation can be adjusted and controlled according to our requirements. Hydrogenated fat can also be fractionated further into different fraction (stearin fraction, olien fraction, etc). The degree of fractionation and the technique used generally determines the property of the obtained fat fraction.

Although any vegetable oil or fat is suitable for Natural oils of plant origin provide very good | hydrogenation and subsequent fractionation, generally

inexpensive oils that are abundantly available are only used as starting material for this purpose. Some typical vegetable oils used for this purpose include, coconut oil, soybean oil, rapeseed oil, palm kernel oil, etc. An important factor that cannot be ignored is that all these fats are used in a cosmetic formulation with additives like hydrocarbon, actives, emulsifiers, etc., that may significantly influence the performance properties and behaviours of the finished product.

Glycerol ethers

Glycerol ethers are also known as alkyl glycerol or ethyl lipids. Shark liver oils contain large amounts of glycerol ethers when compared to their availability in human tissues. They are generally found as esterified fatty acids. Batyl alcohol that is widely found in animal tissue is a typical glycerol ether.

Natural glycerol ethers, due to its scarcity, are used in a minor proportion in cosmetic applications. Semisynthetic materials that have been prepared have become available for use in the recent past. Anti fungal and anti bacterial activity, UV protection and skin conditioning are some therapeutic benefits credited to its use in cosmetic applications.

CH_2 -O- $CH_2(CH_2)_{16}CH_3$	$CH_2-O-CH_2(CH_2)_{16}CH_3$
$CH-O-CO(CH_2)m CH_3$	CH-OH
 CH ₂ -O-CO(CH ₂)n CH ₃	CH ₂ -OH
Ether lipid	Batyl alcohol

Phosphoglycerides

Phosphoglycerides are an important group of lipids found in almost all-living cells. The basic difference between phosphoglycerides and other glycerol compounds is the presence of one hydroxyl group esterified to phosphoric acid. Phosphoglycerides on hydrolysis give fatty acids, glycerol and phosphate. Phospholipids are both hydrophilic and hydrophobic in nature.

This amphipathic property enables phosphoglycerides help in linking both the polar and non-polar molecules — an essential requirement in cell membrane functioning. Phosphoglycerides include phosphatidylcholin (lecithin), phosphatidyl eth-

CH ₂ – COOR	CH ₂ – COOR	CH ₂ – COOR
KCOO-CH O	 R/COO – CH O	RCOO-CH O
∥ CH ₂ − O− P− OH	∥ CH→ O−P−X	 CH ₂ − O−P−O−CH ₂ CH ₂ − N ⁺ (CH ₃) 3
Phosphatidic Acid	Phoenhatida	Lecithin
Phosphaudic Acid	Phosphatide	Lecitinii

anolamine, phosphatidyl serine, etc. — all derivatives of phosphatidic acid.

LIPIDS WITHOUT GLYCEROL Sphingolipids

It consists of amino alcohol like sphingosine, Nacylated by fatty acid. The parent compound is ceramide. Ceramides are found in plant and animal tissues.

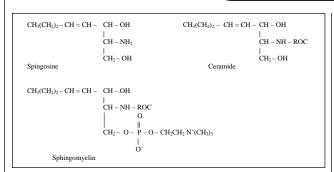
Water loss in human skin is controlled by a fivemicron thick lipid structure present at the base of the stratum corneum. The lipid structure, which acts as a water barrier, is made up of ceramides that are a mixture of complex sphingolipids. Two important ceramide structures are spingosine, N-acylated with long chain saturated fatty acid ($C_{16} - C_{30}$) and a linoleate bearing esters linked to spingosine with long chain hydroxyacid.

When there is a fatty acid deficiency in human body, due to poor diet or disease, the linoleate is replaced by oleate. This replacement causes the lipid bilayer to change in its physical structure, resulting in the skin becoming permeable to water. Thus to maintain proper water balance in the skin the stability of the linoleaterich ceramides bilayer is very important. Although ceramides are found in plant and animal tissues, it is not available in large amounts.

	ОН	RCO = Linoleate	
R - COO(CH ₂) ₂₉ - CON	H-CH - CH - R'	$R^{\prime}=CH_3CH_2CH=CH_2\!-\!$	
	CH ₂ OH		
Linoleate based Ceramide			

However, synthetic ceramides, derived from natural intermediates is now available as functional alternatives.

Complex sphingolipids are compounds formed by the esterification of the primary hydroxyl group of simple ceramides. Some common examples are Spingomyelin, Glucosphingolipid, Cerebroside, and Ganglioside.



WAX ESTERS

Wax esters have been traditionally used in cosmetic formulations. The important ones are esters obtained from living animals like Spermaceti (Whales), Lanolin (Sheep)¹, Orange roughy oil (Deep-Sea fish, *Hoplostethus atlanticus*) and from vegetable sources like Jojoba oil. Wax esters obtained in nature are mixtures of long chain fatty esters with the carbon chain length between 20 and 40. They are resistant to hydrolysis and are often found in nature as water repellent coating on plant and animal surfaces. When fatty acid is esterified to obtain an aliphatic primary alcohol, it is termed as a wax ester. Wax esters can be either solid or liquid in nature. Nowadays wax esters from whale spermaceti has been completely replaced by hydrogenated Jojoba oil that possesses very similar composition as spermaceti. Jojoba oil is a vegetable oil and renewable. Orange roughy oil is a by-product obtained from marine food industry. However, the largest source of wax esters is woolgrease refined to get lanolin that contains important lipids and cholesterol esters occurring in human skin.

O

$$\parallel$$

 $CH_3(CH)_p - C - O - (CH)_qCH_3$
Wax Ester

Natural lipids that are complementary to human skin lipids are very important in formulating cosmetics. Traditionally we know that lipids help in correcting imperfect skin condition and maintain it in order. With skincare product market on an increase, use of lipids in these products will only show a corresponding rise. Fats derived from plants, along with lanolin and its derivatives, are good ingredients in cosmetic applications, imparting emolliency with good skin compatibility. Lipids without doubt could provide unique active materials for formulating innovative products tailored to meet specific consumer requirements in the near future and beyond.

REFERENCES

1. Lanolin for Silky, Soft, Smooth Skin, *Chemical Weekly*, October 30, 2001