

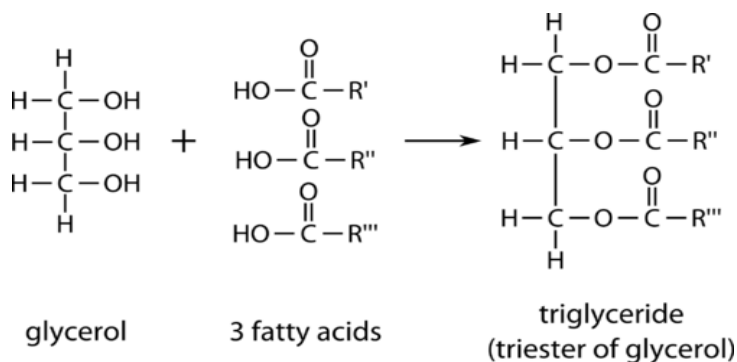
## MODULE-2

### INTRODUCTION TO FAT AND OILS

Fats and oils are water-insoluble, hydrophobic substances of vegetable, land animal, or marine animal origin which consist predominantly of glyceryl esters of fatty acids, so-called triglycerides. Reversible changes in state owing to variation in temperature may obliterate the common conception that fats are solids and oils are liquids, so that today this distinction between the terms fat and oil is largely academic. The terms are still used commercially, but they have only limited significance.

#### 1. GLYCERIDES

**1.1. TRIGLYCERIDES:** Structurally, a triglyceride is the reaction product of one molecule of glycerol with three molecules of fatty acids to yield three molecules of water and one molecule of a triglyceride



When the three fatty acids are identical, the product is a simple triglyceride; when they are dissimilar, it is a mixed triglyceride. Simple triglycerides are synthesized in the laboratory by the direct esterification of glycerol with a fatty acid, and mixed triglycerides of known structure are obtained by special methods usually involving blocking of certain of the hydroxyls, esterification of the unblocked hydroxyls.

#### Triglyceride composition of natural fats:

Natural fats and oils vary widely in their physical properties, even though they are made up of the same or similar fatty acids. This is because (a) individual fats and oils vary over relatively large ranges in the proportions of the component fatty acids, and (b) the structures of the individual component triglycerides vary.

Many hitherto unappreciated factors are now known to influence the fatty acid composition as well as the triglyceride structure of natural fats and oils. Among the factors which affect the composition of fats and oils in the vegetable kingdom are

- Climatic conditions [e.g., hot or cold. Wet or dry]
- Soil type in which the parent plant was grown
- geography of the growing location (soybeans in Minnesota are different from those grown in Illinois)

- Maturity of the plant
- Health of the plant
- Numerous environmental conditions (proximity of certain molds, bacteria, and enzymes, etc.)
- Specific location of oilseeds within the flower itself
- Genetic variations in the plant [rapeseed containing 0-40% erucic acid in the oil can be grown with proper attention to plant genetics.

In the land animal kingdom, fat and oil composition varies according to the animal species. In addition, however, it varies in a very complex fashion (a) with the diet of the animal [increased linoleic content in milk fat with supplemented diet, and (b) with the location of the fat within the animal [bovine milk fat is much different from bovine depot fat. Also, liver fat in many animals differs from adipose tissue fat in the proportion of palmitic acid in the 2-position and there are large differences in composition in pork, beef, and lamb fats. In addition, composition varies in relation to the health and well-being of the animal and the environment in which it matured.

Marine animal fats and oils are not only characteristically different in many ways from those of land animal or vegetable origin, but they show differences depending on whether the fish was an oceanic or freshwater species and, within a particular species, whether it was cold or warm water derived, or whether it was caught in, for example, May or September [such as Baltic herring.

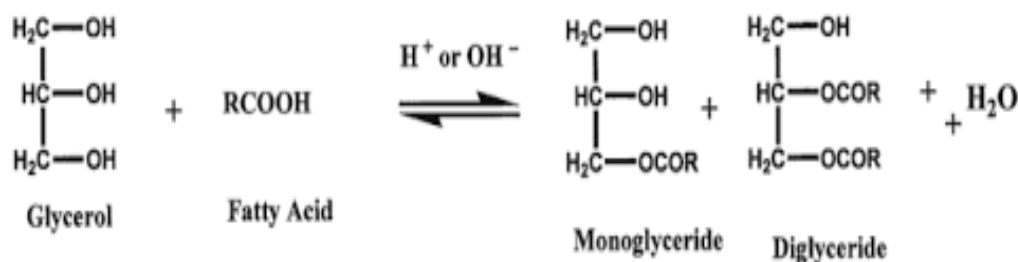
The great number and variety of fats and oils in nature and the effect of slight and imperceptible changes in the environment on their composition make it unlikely that the structures of fat and oil triglycerides are governed by a series of simple rules. Yet fat and oil chemists have attacked the subject of triglyceride structure with a sweeping array of generalizations, only to find that the list of exceptions to the rules were too numerous to ignore, thus, in effect, invalidating the developed rules. Nevertheless, each theory indirectly contributed somewhat to the understanding of the complexity of the subject. Today it is increasingly apparent that we will need to generate a huge amount of additional reliable data, and eliminate much of the earlier unreliable data, before a thoroughly comprehensive understanding of the structure of triglycerides is possible. Within the limitations of each theory, a brief review of them is both helpful and illustrative.

## **1.2.MONO- AND DIGLYCERIDES**

Monoglycerides and diglycerides contain, respectively, one and two combined fatty acids, and have two and one free hydroxyl groups. They do not occur naturally in appreciable quantities except in fats and oils that have undergone partial hydrolysis. One can assume that fats and oils that are damaged or spoiled in the field or in storage, and have abnormally high free fatty acid contents, will have a correspondingly high di- or monoglyceride content. When soybeans are stored for long periods with a mean moisture content of 16-18% instead of a normal moisture content of 11% or lower, they undergo several deteriorative changes including hydrolysis, and free fatty acid contents as high as 47% can result. Industrial mono- and diglycerides prepared by direct esterification of glycerol are mixtures of mono-, di-, and triglycerides and, depending on the molar ratios used to prepare them, also contain quantities of free glycerol. These products represent an important class of food emulsifiers and as such are used in ice cream and peanut butter, and for many other uses. By far the most important method of preparation, especially for monoglycerides,

is the glycerolysis of fats and oils, a transesterification reaction. Depending on the ratios of fat to glycerol employed, the product mixtures are called commercially “40% monos” or “60”, monos.” Molecular distillation is quite effective in separating monoglycerides from di- and triglycerides. A “90% mono” type is prepared by molecular distillation of the optimum reaction product resulting from glycerolysis of a fat or oil. Commercial 90% monoglycerides are primarily, but not entirely, of the  $\alpha$ -monoglyceride structure. 90%-Monoglycerides derived from lard, hydrogenated tallow, hydrogenated soybean, cottonseed, coconut, and palm oils are available commercially.

When pure monoglycerides are desired, special methods are required for their preparation. 2-Monoglycerides are more stable than their B-isomers; the latter are readily converted (isomerized) into the former. Polymorphism is important in this class of compounds.



## 2. FATTY ACIDS

The molecular weight of the glyceryl portion ( $\text{C}_3\text{H}_7\text{O}_2$ ) of a triglyceride molecule is 41. The combined molecular weight of the fatty acid radicals ( $\text{RCOO}-$ ) comprising the remainder of the molecule will vary with different fats from about 650 to 970. Thus the fatty acids contribute 94-96% of the total weight of the molecule. Because of their preponderant weight in the glyceride molecules, and also because they contribute to both the chemical and physical properties of the glycerides, the fatty acids greatly influence both the physical (hydrophobic character) and chemical character of the glycerides.

Any contributions that a fatty acid makes to hydrophobic character of triglycerides are limited to the amount of hydrophobic character in the fatty acid itself. The naturally occurring fatty acids are, in general, normal, monobasic carboxylic acids consisting of a single carboxylic group attached to the end of a straight hydrocarbon chain. In organic chemistry, the term "fatty acids" is applied to the entire series commencing with formic acid (methanoic,  $\text{C}_1$ ), acetic acid (ethanoic,  $\text{C}_2$ ), and propionic acid (propanoic,  $\text{C}_3$ ), and continuing up the homologous series to stearic acid (octadecanoic,  $\text{C}_{18}$ ) and higher. It is broadly understood that the term "fatty acid" is a general one, and it is well appreciated that the lower four members of the series are not at all "fatlike" in character; in fact, they are hydrophilic substances with complete miscibility with water. The triglycerides of formic, acetic, and propionic acids, as expected, are also not fatlike, but are only slightly more hydrophobic than the acids themselves. If fatty acids were strictly defined as those occurring naturally in fats and oils, perhaps the series would logically commence with butyric acid (tetraoic or butanoic,  $\text{C}_4$ ), a component of butterfat, which shows little hydrophobicity (miscible with water in all proportions), or certainly with caproic acid (hexanoic,  $\text{C}_6$ ), a component of coconut, palm, and babassu oils, which is water-insoluble (only 1.10 parts soluble in 100 parts

Those fatty acids in which all carbon atoms in the chain contain two hydrogen atoms and thus contain no double bonds are termed saturated. The fatty acids that contain double bonds are termed unsaturated. The degree of unsaturation of an oil depends on the average number of double bonds in its fatty acids.

[illegible]

A skeletal structure of a branched alkane is shown. The main chain is highlighted in blue. A red arrow points to a double bond between two carbon atoms in the main chain, with the text "double bond" written below it.

The most common saturated fatty acids occurring in fats and oils are listed in the table

No. of Carbon Atoms	Fatty Acid
4	Butyric
6	Caproic
8	Caprylic
10	Capric
12	Lauric
14	Myristic
16	Palmitic
18	Stearic
20	Arachidic
22	Behenic
24	Lignoceric

At a given temperature, the vapor pressure of fatty acids decreases with increase in the chain length. The difference in boiling point between adjacent members of the series is sufficient to permit efficient separation by fractional distillation. Unfortunately, many fatty acid mixtures are not completely hydrogenated during the course of processing, so that fractional distillation is limited in separative efficiency because of the presence of small amounts of unsaturated fatty acids. For example, the separation of mixtures of oleic, palmitic, and stearic acids by fractional distillation is not practical. The lower members of the fatty acid series are liquids at ordinary temperatures, whereas those with 10 or more carbons are solids having progressively higher melting points with an increase in the length of the chain. The even progression of melting points and the length of the carbon chain gives a smooth curve only if the even-membered homologues are considered; when all the fatty acids are included, the curve becomes a steplike one, with each odd-carbon acid having a melting point somewhat lower than that of the even-chain acid immediately before it. The phenomenon is a common one for various series of homologous fatty acid derivatives and other straight chain aliphatic compounds.

Formic, acetic, and propionic acids evidently do not occur as components of fats and oils. Butyric acid is found to the extent of 2-4% by weight of the total fatty acids in milk fats of various mammals.

Caproic (hexanoic) acid also occurs in milk fats (1-3%) and in smaller amounts in coconut and palm kernel oils. Caprylic (octanoic) acid constitutes about 3-10% of the total fatty acids of the latter oils, and about 1-4% of the acids of the more common milk fats. Several herbaceous plants, such as *Cuphea hookeriana* and *C. painteri* contain approximately 70% of caprylic acid in their seed fats. Capric (decanoic) acid likewise is a characteristic component of milk fats (2-4%) and *Palmae* seed oils (3-8%). The rare herbaceous plant *Cuphea allavieva* contains more than 80% of capric acid in its seed fatty acids, and *C. carthagenensis* has about 18%. The total acids of the seed oil of the elm tree are reported to contain as much as 50% capric acid. Pelargonic acid contains nine carbon atoms and, although available commercially by ozonization cleavage of oleic acid, is not known to occur naturally in vegetable seed oils in more than the barest traces.

Lauric acid is one of the three most widely distributed naturally occurring saturated fatty acids, the others being palmitic and stearic. Lauric acid derives its name from the seed fats of the laurel family (*Lauraceae*), some members of which are reported to have more than 90% lauric acid in the mixed fatty acids of the seed oil. The richest common sources of lauric acid are coconut oil, palm kernel oil, and babassu butter, which contain 40-50%.

Myristic acid is a minor constituent (5% or less) of the mixed fatty acids of most animal and vegetable fats. It constitutes 8-12% of the fatty acids of milk fats and 15-30% of coconut oil. It is a major component of the seed fats of the *Myristicaceae*, such as nutmeg and ucuhiba fats, where it may constitute as much as 80-80% of the total fatty acids. Pentadecanoic acid also occurs in many vegetable oil seed-fats, although the amounts are quite small. It has been identified as a component of cotton seed oil by a programmed temperature GLC procedure on methyl esters. Palmitic acid is the most widely distributed saturated fatty acid. It occurs in practically all animal, vegetable, and marine animal fats to the extent of at least 5%, and is a major component of lard

and tallow (25-30%), palm oil (30-50%), cocoa butter (25%), and other vegetable butters. In Chinese vegetable tallow (*Stillingia*), it constitutes 60-70% of the total fatty acids.

Arachidic, behenic, and lignoceric acids are widely distributed but do not occur in quantity in any common fats. Olive, soybean, cottonseed, corn peanut, rapeseed, and safflower oils all contain small amounts of saturated fatty acids above. Can some as high as hexacosanoic acid. Linolenic acid, once thought to be present in small amounts in lard and tallow glycerides has been proved to be arachidic acid instead. Behenic acid was detected in soybean oil, lignoceric acid was found in four oils out of 19 of Indian origin, and odd-numbered fatty acids containing from 11 to 23 carbon atoms were detected in peanut germ oil and rice bran oil.

## 2.2. UNSATURATED FATTY ACIDS

A large number of unsaturated fatty acids occur naturally; they are more difficult to isolate, purify, and characterize than the saturated fatty acids. Their study is complicated by the fact that they are less stable and are readily converted into positional and geometric isomers. Many of the naturally occurring acids contain an even number of carbon atoms (most frequently 18). In most cases the double bonds have the *cis* configuration, and a preferred position for the double bond is between the ninth and tenth carbon atoms in the fatty acid chain. Butterfat is possibly the best example of a common fat which is now known to contain unsaturated fatty acids with odd numbers of carbon atoms. Mullet (fish) oil probably contains the most its fatty acids contain about 25". Odd-numbered unsaturated fatty acids, an unexpectedly high proportion.

Fatty acids with as many as seven double bonds have been reported as components of fats and oils; these are more likely to be of aquatic origin as the number of double bonds exceeds three. Those containing one, two, and three double bonds and 18 carbon atoms are the important unsaturated fatty acids of vegetable and land animal origin: those with four or more double bonds and 20-24 carbon atoms are found principally in the marine oils, a group that is still little investigated despite the large number of fish and other marine animals, the interesting differences among them, and the possible utility of their oils as fat foodstuffs. Today the knowledge of marine oil fatty acid composition is still sparse, although information continues to be acquired.

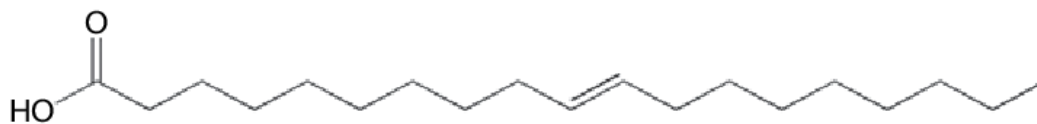
Acids with One Double Bond (Monounsaturated). Monounsaturated fatty acids contain two less hydrogen atoms than the corresponding saturated fatty acids and have the empirical formula  $C_nH_{2n-2}O_2$ . With the exception of crotonic acid,  $CH_3CH=CHCOOH$ , which occurs in croton oil, naturally occurring monounsaturated fatty acids contain 10 or more carbon atoms. The most common monounsaturated fatty acid is oleic acid having 18 carbon atom and a double bond at 9<sup>th</sup> carbon.

Acids with Two and Three Double Bonds (Di- and Triunsaturated): Diunsaturated fatty acids contain four less hydrogen atoms than the corresponding saturated fatty acids and have the empirical formula  $C_nH_{2n-4}O_2$ . Triunsaturated fatty acids have the empirical formula  $C_nH_{2n-6}O_2$ . The most important and widely distributed polyunsaturated fatty acid is linoleic (*cis,cis*-9,12-octadecadienoic) and linolenic (*cis,cis,cis*-9,12,15-octadecatrienoic) acids. Polyunsaturated fatty

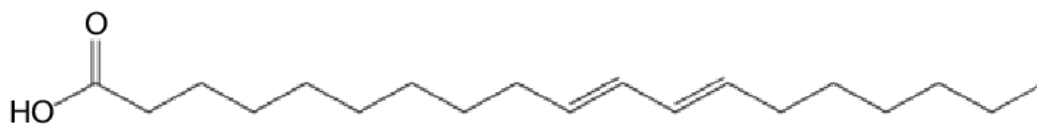
acids with fewer than 18 carbon atoms either do not occur in or are extremely minor components of animal and vegetable fats, but the occurrence of C<sub>14</sub> and C<sub>16</sub> polyunsaturated fatty acids are detected in marine animal oils.

Linoleic acid [Safflower oil (75%), sunflower oil (60%), cottonseed oil (45%), and many seed fats]

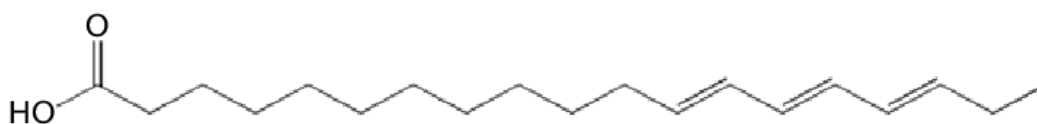
Linolenic acid [Linseed oil (45-50%), perilla oil (65%), and other drying oils and seed fats]



**Oleic acid**



**Linoleic acid**



**Linolenic acid**

- Chemically, a fatty acid is an organic acid that has an acid group at one end of its molecule, and a methyl group at the other end.<sup>1</sup> Fatty acids are typically categorized in the omega groups 3, 6 and 9 according to the location of their first double bond (there's also an omega 7 group, but these are less important to human health).<sup>2</sup> Now don't panic if you're not up on your chemistry; this isn't going to be a chemistry lesson. I just wanted you to understand why a fatty acid might be called an omega 3 or omega 6 fatty acid.

The term *essential fatty acid* refers to a fatty acid which the body cannot manufacture, and must obtain from dietary sources. These essential fatty acids were originally designated as Vitamin F, until it was realized that they must be classified with the fats.<sup>3</sup> There are two fatty acids designated as essential fatty acids: linoleic acid and alpha-linolenic acid. This does not mean that the other 15 or so fatty acids found in the omega 3, 6 and 9 groups aren't important, just that a healthy body can manufacture them as long as it gets enough linoleic acid and alpha-linolenic acid. Nevertheless, research demonstrates that there are health benefits to be had by obtaining some of the other *non-essential* fatty acids directly; more on this later. Now let's discuss the roles of essential fatty acids (EFAs) in the body, as well as sources of EFAs.

#### Evening Primrose & Borage Oils: Sources of GLA

The oils from the Evening Primrose plant and Borage seed are rich in the omega 6 fatty acid, gamma linolenic acid (GLA); as well as EFAs. Although fatty acids are found in significant quantities in a variety of plants, GLA is only found in a few. GLA is a precursor to various natural chemicals found in the body. Among these are prostaglandins, a type of short-term hormone-like substances, which play a variety of roles in the body. Published research on these sources of GLA

have demonstrated them to be useful in PMS, pregnancy and lactation inflammatory conditions, rheumatoid arthritis, skin conditions, stress and performance, as well as migraine headaches. Furthermore, the unique balance of GLA to EFAs in any one of these sources may have a distinct benefit over another source depending on the condition in question. For more detailed information on EPO and BO, read the *Intelligent Supplementation* article “GLA: Gamma Linolenic Acid from Evening Primrose & Borage Oils.”

#### Fish Oils: Sources of EPA/DHA Omega 3 fatty acids

Eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) are omega 3 fatty acids (O3FA). O3FA supplements are mostly derived from the oils of coldwater species of fish like salmon, sardines, herring, and mackerel. There are many therapeutic applications for O3FA, primarily due to its cardiovascular-enhancing and anti-inflammatory benefits. Research has shown that O3FA cardiovascular benefits include reducing the risk of atherosclerosis, modifying cholesterol levels (i.e., increasing “good” HDL cholesterol, while decreasing “bad” LDL cholesterol) and decreasing triglycerides, and decreasing high blood pressure. O3FA have also been shown to block the production of certain inflammatory chemicals in our body. Consequently, studies have demonstrated the ability of O3FA to reduce inflammation in such disorders as rheumatoid arthritis, asthma, colitis, Crohn’s disease, and Lupus. In addition, O3FA have shown to reduce the symptoms of other disorders including angina, migraine headaches, psoriasis and tinnitus. For more detailed information on O3FA, read the *Intelligent Supplementation* article “Omega 3 Fatty Acids.”

#### Flax Seed Oils: Sources of Omega 3, 6 & 9 fatty acids

Flax seed naturally contain a complex of different categories of fatty acids, including alpha-linolenic acid (omega-3), linoleic acid (omega-6), and oleic acid (omega-9). Much of Flax seed’s benefits are a function of its alpha linolenic acid (ALA) content, and the fact that ALA can be converted by the body into EPA—the same omega-3 found in fish oil. As a matter of fact research has found that supplementation with Flax seed oil can effectively increase EPA concentrations in tissues. Lignans, also found in Flax seed, account for various benefits offered by this plant. Studies involving Flax seed have been conducted on its anti-inflammatory properties, its anti-lupus properties and its cardiovascular enhancing properties.

Just a quick note to mention that the omega9 fatty acid oleic acid has been shown in research to lower heart attack risk and arteriosclerosis, and aids in the prevention of breast cancer.

#### **Note:**

In addition to the two essential fatty acids, there are other fatty acids whose consumption may have benefits for human health. Both the essential and non-essential fatty acids can be obtained from dietary supplement sources including Evening Primrose oil, Borage oil, Flax seed oil and



Fish oils (marine lipid concentrate). Each of these sources has their own potential advantages. Perhaps a combination of all of them may yield the broadest spectrum of both essential and non-essential fatty acids.

#### **4. NONGLYCERIDE COMPONENTS OF FATS AND OILS**

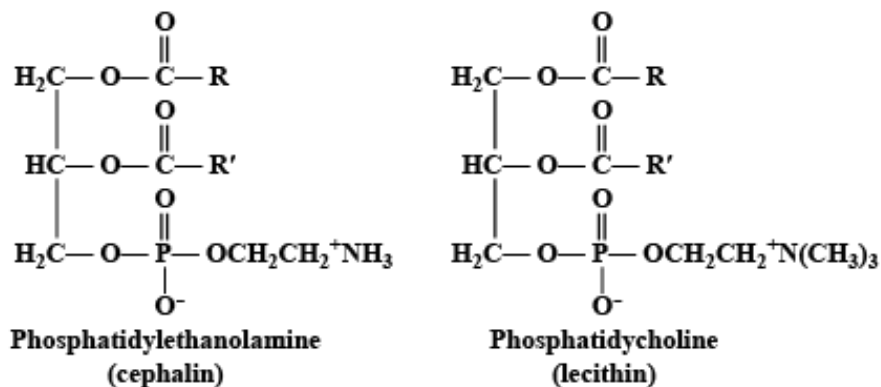
All fats contain small amounts of nonglyceride components, crude vegetable oils contain less than 5%, and the refined oils less than 2%, in many instances less than 0.2%. Some of these are completely or substantially removed from the crude fats during refining or bleaching and hence do not appear in the manufactured products. Of those that persist, some are without flavor, odor, or color, or else are relatively inert from a chemical standpoint. These may be considered of minor importance, since their presence is neither objectionable nor undesirable insofar as most of the uses of fats are concerned. Certain other components, however, particularly those that have pro- or antioxidant properties, or are strongly flavored or highly colored or even synergistic in action, may considerably affect the character of the fat, even though they are present in mere traces. In the following section the various nonglyceride components are considered from the standpoint of their practical significance, rather than grouped and discussed on the basis of their chemical constitution.

In most fats, the greater part of the nonglyceride portion is removed by hydration or by reaction with alkali during the course of ordinary refining. A smaller portion is sometimes removed by clay bleaching adsorption operations. The amount of removable nonglyceride substances other than free fatty acids varies considerably. Cottonseed, corn, and soybean oils are relatively high in nonglycerides; peanut and coconut oils are relatively low, as are common fruit pulp oils, such as olive oil and palm oils. Animal fats such as lard and edible tallow, which are derived from more or less pure fatty tissues, are very low in impurities of this class, although this may not be the case with fish oils, low grade tallows or greases, or other animal fats rendered from entire carcasses or other stock containing nonfatty tissues. The substances commonly removed in refining are generally phosphatides, carbohydrates and carbohydrate derivatives, protein fragments, and various resinous and mucilaginous materials of uncertain identity. In addition, alkali refining removes any free fatty acids resulting from the partial hydrolysis of the oil, and effects a partial removal of sterols, carotenoid pigments, etc.

##### **4.1. Phosphatides**

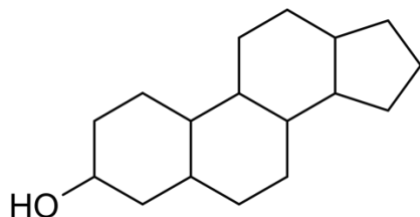
Phosphatides, which are associated with fats and oils in many plant and animal tissues, consist of a polyhydric alcohol (usually but not always glycerol) which is esterified with fatty acids and also with phosphoric acid. The phosphoric acid is, in turn, combined with a basic nitrogen-containing compound such as choline, betaine, or ethanolamine.

Two common phosphatides, lecithin and cephalin, are substituted triglycerides in which one fatty acid radical has been replaced with phosphoric acid. The fatty acid radicals may vary and are both saturated and unsaturated. In lecithins the phosphoric acid is further esterified through the hydroxyl of a choline molecule.



## 4.2.STEROLS

Sterol is an organic compound with formula  $\text{C}_{27}\text{H}_{48}\text{O}$ , whose molecule is derived from that of gonane ( $\text{C}_{10}\text{H}_{18}$ ) by replacement of a hydrogen atom in position 3 by a hydroxyl group. It is therefore an alcohol of gonane. More generally, any compounds that contain the gonane structure, additional functional groups, and/or modified ring systems derived from gonane are called steroids. Therefore, sterols are a subgroup of the steroids. They occur naturally in most eukaryotes, including plants, animals, and fungi, and can also be produced by some bacteria (however likely with different functions). The most familiar type of animal sterol is cholesterol, which is vital to cell membrane structure, and functions as a precursor to fat-soluble vitamins and steroid hormones.



Sterols of plants are called phytosterols and sterols of animals are called zoosterols. The most important zoosterol is cholesterol; notable phytosterols include campesterol, sitosterol, and stigmasterol. Ergosterol is a sterol present in the cell membrane of fungi, where it serves a role similar to cholesterol in animal cells. Phytosterols, more commonly known as plant sterols, have been shown in clinical trials to block cholesterol absorption sites in the human intestine, thus helping to reduce cholesterol absorption in humans.

## 4.3.FATTY ALCOHOLS

Fatty alcohols (or long-chain alcohol) are usually high-molecular-weight, straight-chain primary alcohol, but can also range from as few as 4–6 carbons to as many as 22–26, derived from natural fats and oils. The precise chain length varies with the source. Some commercially important fatty alcohols are lauryl, stearyl and oleyl alcohols. They are colourless oily liquids (for smaller carbon numbers) or waxy solids, although impure samples may appear yellow. Fatty alcohols usually have an even number of carbon atoms and a single alcohol group ( $-\text{OH}$ ) attached to the terminal carbon.

Some are unsaturated and some are branched. They are widely used in industry. As with fatty acids, they are often referred to generically by the number of carbon atoms in the molecule, such as "a C<sub>12</sub> alcohol", that is an alcohol having 12 carbons, for example dodecanol.

Most fatty alcohols in nature are found as waxes which are esters with fatty acids and fatty alcohols. They are produced by bacteria, plants and animals for purposes of buoyancy, as source of metabolic water and energy, biosonar lenses (marine mammals) and for thermal insulation in the form of waxes (in plants and insects). Fatty alcohols were unavailable until the early 1900s. They were originally obtained by reduction of wax esters with sodium by the Bouveault-Blanc reduction process. In the 1930s catalytic hydrogenation was commercialized, which allowed the conversion of fatty acid esters, typically tallow, to the alcohols. In the 1940s and 1950s, petrochemicals became an important source of chemicals, and Karl Ziegler had discovered the polymerization of ethylene. These two developments opened the way to synthetic fatty alcohols.

The traditional sources of fatty alcohols have largely been various vegetable oils, which remain a large-scale feedstock. Animal fats (tallow) were of historic importance, particularly whale oil however they are no longer used on a large scale. Tallows produce a fairly narrow range of alcohols, predominantly C<sub>16</sub>–C<sub>18</sub>, while plant sources produce a wider range of alcohols from (C<sub>6</sub>–C<sub>24</sub>), making them the preferred source. The alcohols are obtained from the triglycerides (fatty acid triesters), which form the bulk of the oil. The process involves the transesterification of the triglycerides to give methyl esters which are then hydrogenated to produce the fatty alcohols. Higher alcohols (C<sub>20</sub>–C<sub>22</sub>) can be obtained from rapeseed or mustard seed oil. Midcut alcohols are obtained from coconut oil (C<sub>12</sub>–C<sub>14</sub>) or palm kernel oil (C<sub>16</sub>–C<sub>18</sub>).

Fatty alcohols are mainly used in the production of detergents and surfactants. They are components also of cosmetics, foods, and as industrial solvents. Due to their amphipathic nature, fatty alcohols behave as nonionic surfactants. They find use as co-emulsifiers, emollients and thickeners in cosmetics and food industry. About 50% of fatty alcohols used commercially are of natural origin, the remainder being synthetic. Very long-chain fatty alcohols (VLCFA), obtained from plant waxes and beeswax have been reported to lower plasma cholesterol in humans. They can be found in unrefined cereal grains, beeswax, and many plant-derived foods. Reports suggest that 5–20 mg per day of mixed C<sub>24</sub>–C<sub>34</sub> alcohols, including octacosanol and triacontanol, lower low-density lipoprotein (LDL) cholesterol by 21%–29% and raise high-density lipoprotein cholesterol by 8%–15%.

#### **4.4.COLOURS AND PIGMENTS (Carotenoids, Gossypol, Chlorophyll):**

One of the best-known classes of pigments in oil is the carotenoids, which are largely responsible for the yellow to red color of most fats. The carotenoids are highly unsaturated, polyisoprene hydrocarbons, and their oxygenated derivatives. They are soluble in fats and fat solvents but insoluble in water. Their color ranges from yellow to deep red depending on their structure. One of the most important carotenoids is  $\beta$ -carotene. About 75 carotenoids are known: the best known are the isomeric hydrocarbons  $\alpha$ -,  $\beta$ -, and  $\gamma$ -carotene, lycopene, C<sub>40</sub> H<sub>56</sub>, and lutein (xanthophyll), C<sub>40</sub> H<sub>56</sub> O<sub>2</sub>, the latter containing two hydroxyl groups. The carotenoids are widely distributed in crude animal and vegetable fats although their concentration is low of the common fats, crude unbleached palm oil has the highest content of carotenoids (0.05-0.2%). Rapeseed oil has been shown to contain about 6-7 ppm of  $\beta$ -carotene total carotenoids are 25-50 ppm with the major components said to be neolutein A and neolutein B. The major carotenoids of peanut oil are also

$\beta$ -carotene and lutein (xanthophyll), and these pigments, particularly the former, decrease with maturity of the peanut during growth. The  $\beta$ -carotene content of peanut oil from immature peanuts is about 60 $\mu$ g per liter of oil. while that from mature peanuts is certainly less than 1  $\mu$ g per liter of oil.

Most of the pigments in cottonseed oil are of the gossypol type, and the characteristic yellow color in the refined oil is primarily due to gossypols.

Certain fats and oils, notably olive oil. soybean oil derived from green beans (sometimes climatic conditions in the growing areas necessitate green bean accumulation), and some inedible tallows, have a greenish color from the presence of chlorophyll or related compounds. Except in olive oil, a green tinge is generally undesirable. Green color presents a problem chiefly in the processing of soybean oil to produce edible products. Hydrogenated soybean oil frequently has an even greener color than the crude oil because the red and yellow pigments of the oil, which ordinarily mask green, are very readily reduced by hydrogenation, whereas chlorophyll is only partly bleached.

#### **4.5.ANTIOXIDANTS**

It is well appreciated that because antioxidants contain minute amounts of substances capable of inhibiting oxidation, natural fats and oils are much more resistant to oxidative deterioration than are pure triglycerides. In spite of voluminous contributions to the knowledge of fat and oil antioxidants, both the nature and the mechanism of action of these substances are not entirely understood. The greater stability of vegetable oils toward oxidative rancidity, compared to that of animal fats, is attributed to the higher content of naturally occurring antioxidants in vegetable oils.

**Tocopherols:** The tocopherols, the best-known and most universally distributed antioxidants, constitute fat-soluble vitamin E. First isolated and characterized by investigators in the field of nutrition, they were discovered and named by Evans and co-workers during 1936 and 1937. There are four principal tocopherols; three were identified by earlier workers. They were later demonstrated to be effective antioxidants and to be the active substances in the "inhibitols" previously isolated from a number of vegetable oils. The four principal tocopherols are designated  $\alpha$ -, B-,  $\gamma$ -, and  $\delta$ -tocopherols.

**Sesamol:** Sesame oil contains about 0.3-0.5% sesamol, a glucoside of the phenolic compound sesamol, about 0.5-1% of sesamine, and, depending on the processing to which it has been subjected, small amounts of sesamol itself. Sesamol is produced by hydrolysis of sesamol; it is a powerful antioxidant that is used in some Asiatic countries as a mandatory hydrogenated vegetable oil additive (India: vanaspati). Sesame oil exhibits an unusual synergistic effect on pyrethrum insecticides, promoting the rapid knockdown and paralysis without undesirable toxic effects on mammals.

**Gossypol :** Gossypol, complex phenolic substances occurring in crude but not refined cottonseed oil, has been shown to have strong antioxidant properties. The natural antioxidants appear to be generally high in molecular weight and essentially nonvolatile, since they are not largely removed during high temperature steam deodorization. It is interesting that the gossypol which was isolated as the dianilino derivative from representative samples of cottonseed from the United States

cottonbelt gave only 43-54% of the optical activity that was shown by the pure (+)-dianilino derivative of (+)-gossypol.

**Ferulic acid:** Rice bran oil contains an unusual antioxidant component, ferulic acid, which is esterified with triterpene alcohols in the form of cycloartenyl Ferulate, 24-methylenecycloartanyl ferulate esterified with sterols in the form of B-sitosterolferulate, and esterified with methanol in the form of methyl ferulate (0.006-0.027% of the oil). Several other oils and fats contain ferulates: dihydro- $\beta$ -sitosterolferulate in corn oil, dihydro-7-sitosterol ferulate in wheat oil, and n-eicosanylferulate in oils of linseed and rapeseed. Glyceryl ferulate was reported in the antioxidants extracted from oats.

#### **4.6.ODORIFEROUS MATERIALS**

Relatively few of the compounds responsible for the flavor and odors of fats and oils have been identified, except in butter oil and milk fat, where the flavor and odor properties are of paramount importance. The chief difficulty involves ascertaining whether the flavor and odor components are natural to the oil, or whether the compounds responsible are the result of hydrolytic and/or oxidative degradation, or some other type of chemical reaction during storage or processing of the fat or oil. Fortunately, most of the natural components, but not all, give rise to desirable fatlike odors characterized as pleasant, fresh, or bland, whereas most of the components arising as a result of chemical changes, particularly oxidation, give rise to objectionable odors and flavors ranging from mildly "off-flavor" to putrid. Furthermore, the microquantitative influence of the compounds responsible for most of both the desirable and undesirable odors and flavors and the difficulties of isolation contribute to the difficulty of thoroughly understanding this complex field.

Certain ketones of high molecular weight have been isolated from lauric type oils (361). From the fractional distillation and analysis of deodorizer distillates it has been estimated that the following amounts of terpenoid hydrocarbons occur in several oleic-linoleic oils: palm 0.025%. peanut 0.019% cottonseed 0.025%. sunflower 0.0135%. The terpenoid fractions have a strong odor and a nauseating flavor. The observation of previous workers that methyl nonyl ketone and other ketones contribute largely to the odor and flavor of coconut and palm kernel oils was confirmed.

Soybean oil exhibits a "buttery" flavor in the very early stages of autoxidation. Standard diacetyl added to fresh soybean oil faithfully reproduced the "buttery" flavor. The flavor cannot be said to be objectionable, but it was certainly derived from chemical change and was not characteristic of the fresh oil. Compounds contributing to flavor and odor are among the most difficult to study. As mentioned, they occur in the merest traces but, further, they are sensitive materials and are frequently altered by the processes used to isolate them. In this regard it is important to recognize that the flavors and odors of oils are rarely regenerated exactly by adding back to them the materials which have been removed from them, particularly if steam distillation has been employed as a unit operation. Nor are all the flavor and odor constituents volatile materials, although it is likely that most are. Complete deodorization requires prolonged vacuum treatment at elevated temperatures, for example, 230-260°C, and such treatment is not entirely desirable.

#### **4.7.FAT SOLUBLE VITAMINS AND MINERALS:**

Fat and oils are important source of the fat soluble Vitamins A, D and E and many minerals such as Cu, Fe, Na, Ca, Mg, Zn, Co etc. Vitamin 'A' may be considered to be derived from  $\beta$ -carotene by cleavage of a molecule of the latter in the middle of the hydrocarbon chain and the addition of one molecule of water to each fragment. A "neovitamin A" have been reported in fish liver oils. The D vitamins are related to the derived from sterols its condensed ring system differs from that in the sterols in having no second ring. Sterols can be obtained by irradiation of ergosterol. Butter contains 0.003 to 0.0015 % of vitamin A and 0.121 unit of Vitamin D.