Chapter three
Lipids

Introduction:

Lipids are heterogeneous group of naturally occurring organic compounds relatively insoluble in water and soluble in organic solvents (non-polar), such as ethers, benzene, and chloroform.

Fats and oils are widely distributed in plant and animal tissues. They are the components of living systems consisting of basically carbon, hydrogen and oxygen; in addition some have nitrogen and phosphorus. Lipids include fats, oils, steroids, waxes, and related compounds.

Functions of lipids:

1- Lipids are a good source of energy for the body (9kcal/gm).

2- Most of the energy stored in the body is in the form of lipids (triacylglycerols), stored in fat cells called adipocytes, these fats are a particularly rich source energy for the body.

3- Lipids are major structural components of membranes, e.g., phospholipids, glycolipids and sterols. These lipids play a passive role in the cell by forming impermeable barriers that separate cellular components.

4- Cholesterol, a sterol, is a precursor of many steroid hormones and is also an important component of plasma membrane.

5- Lipid helps in absorption of fat soluble vitamins (A, D, E and K), it acts as a solvent for the transport of fat soluble vitamins.

6- Bile acids derived from cholesterol act as an emulsifying agent and facilitate the digestion and absorption of lipids.

7- As a protective water proof coating on the surface of leaves or fruits of plants, feathers of birds and as insect secretions.

Classification of lipids:

Lipids can be classified into:

1- Simple lipids.

2- Compound lipids.

3- Derived lipids.

Simple lipids:

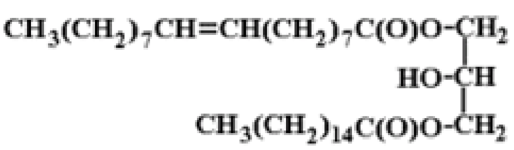
These are esters of fatty acids (F.A) with different alcohols. Simple lipids are sub-classified into two types, depending on the type of alcohols:

1- Neutral lipids.

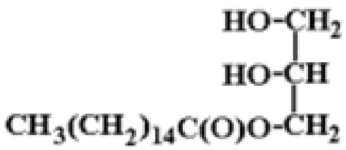
2- Waxes.

Neutral lipids:

Esters of fatty acid with glycerol are called acylglycerol (glyceride). There are three general acylglycerols occur, monoacylglycerol (monoglyceride), diacylglycerol (diglyceride) and triacylglycerol (triglyceride) consist respectively on one, two, three fatty acids esterified to glycerol. Monoacylglycerol and diacylglycerol are metabolic intermediates; they are normally present in small amounts. Triacylglycerol is the major storage and transport forms of fatty acids.



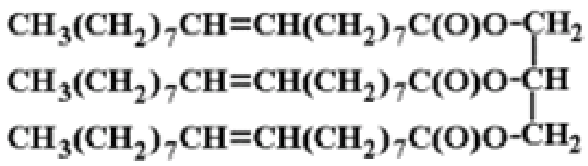
1,3-diglyceride



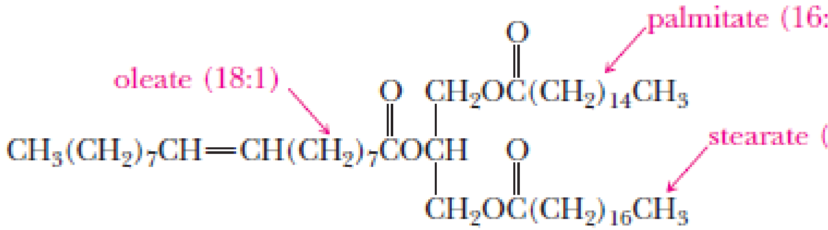
1-monoglyceride

Triglyceride (Triacylglycerols) containing the same type of fatty acids in all three positions is called simple triacylglycerol, like tripalmitin acid, triolein …

Triglyceride (Triacylglycerols) containing two or three different fatty acids are called mixedtriacylglycerol, like oleopalmitostearin, oleodipalmitin.



Simple triglyceride



Mixed triglyceride

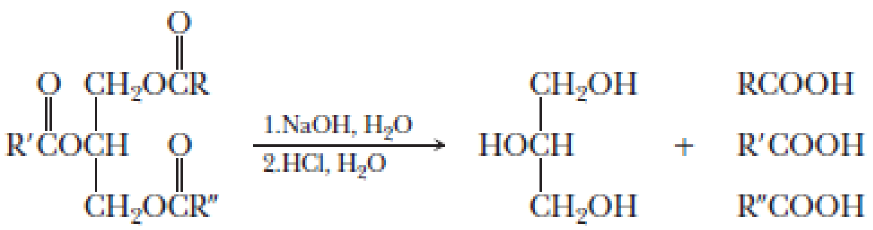
Most of the triglycerides which occur in nature are mixed triglycerides. All fats and oils from both animal and plant origin are triglycerides. Those obtained from animal are solid at room temperature which contain a higher percentage of saturated fatty acids and are called fats, while those of plant are liquid at room temperature which rich in unsaturated fatty acids and are called oils. Oils can be converted to solid fats by saturating the fatty acids. This process is utilized in the manufacturing of vegetable ghee from oils.

Plant fats are much higher in PUFA's than animal fats. Thus, fats are often referred to as "animal fats" and "vegetable oils." The fats we eat are mostly triacylglycerols.

Chemical Properties of triglyceride:

Hydrolysis of triacylglycerol:

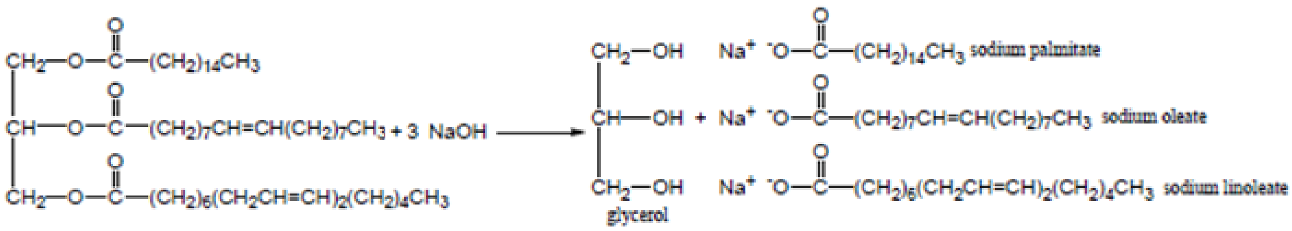
Ester bonds of triacylglycerols can be hydrolyzed by acid, base, or lipase enzyme to obtain fatty acids and glycerol.



A triglyceride — **1,2,3-Propanetriol (Glycerol, glycerin)** — Fatty acids

Saponification of Triglycerides

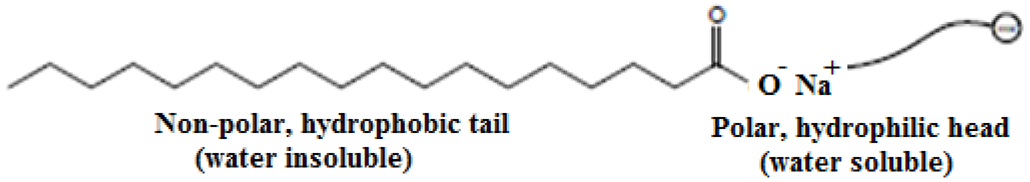
In saponification reactions, triglycerides react with strong bases (NaOH or KOH) to form the carboxylate salts of the fatty acids, called soaps



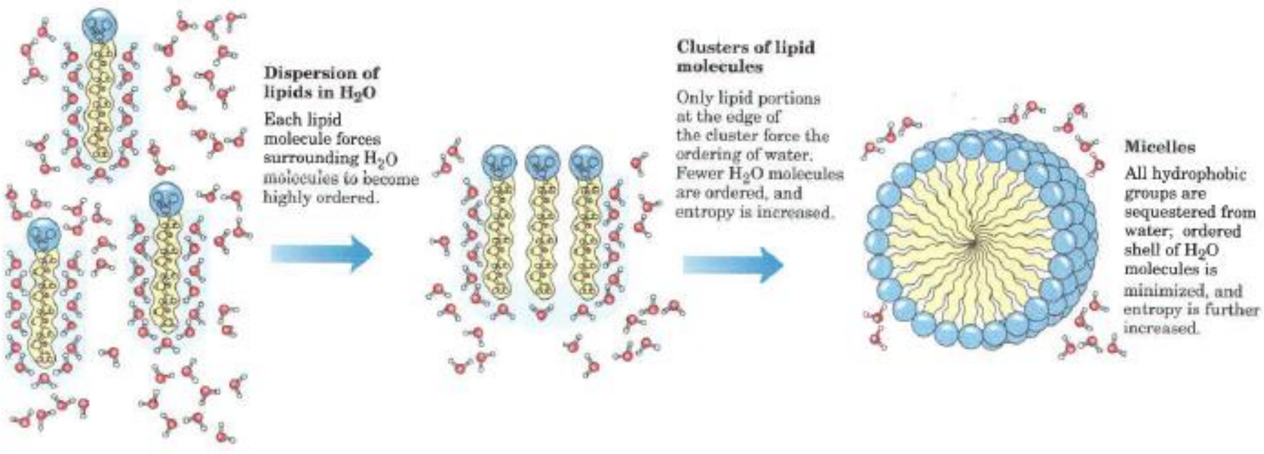
NaOH produces a "hard" soap, commonly found in bar soaps; KOH produces a "soft" soap, such as those in shaving creams and liquid soaps. These salts combine two solubility characteristics:

1- A long, non-polar, water-insoluble (hydrophobic) hydrocarbon "tail".

2- A charged, water-soluble (hydrophilic) "head".



In aqueous solutions, fatty acids associate with each other in spherical clusters called micelles, in which the hydrocarbon tails tangle each other up through dispersion forces, leaving the charged heads facing outwards, in contact with the water. Micelles are important in the transport of insoluble lipids in the blood, and in the actions of soaps.



Fatty acids:

Fatty acids are long hydrocarbon chain with a terminal carboxylic acid group and obtained from hydrolysis of lipids. Fatty acids which occur in neutral lipids usually contain an even number of carbon atoms (because they are synthesized from two carbon units) and occur as saturated, unsaturated, branched and cyclic acids. The straight chain of fatty acids may be saturated or unsaturated (containing one or more double bonds). The most common chain lengths are C_{16}, C_{18} and C_{20}. The lower members (C_4-C_{10}) occur mainly in milk fat, those of intermediate length (C_{10}-C_{14}) and higher members (C_{16}-C_{20}) are found in most animal and vegetable fats.

Fatty acids are amphipathic in nature, because it have hydrophilic (COOH) and hydrophobic (hydrocarbon chain) groups in the structure. Fatty acids serve as a major fuel for most cells and they are precursors of all other classes of lipid.

$$CH_3\text{-}(CH_2)_n - COOH$$

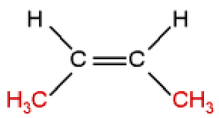
Hydrocarbon Carboxyl group

Saturated fatty acids have all of the carbon atoms in its chain saturated with hydrogen atoms. Monounsaturated fatty acids have one double bond in their structure, while polyunsaturated fatty acids have two or more double bonds. The double bonds in polyunsaturated fatty acids are separated at least by one methylene group.

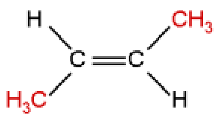
$$\text{-CH=CH-}CH_2\text{-CH=CH-}$$

Methylene group

The double bonds in a fatty acid are usually in the cis-configuration this causes a bend or kink in the fatty acid chain. This bend is very important for the structure of biological membranes. Saturated fatty acids can pack closely together to form ordered, rigid arrays under a certain conditions, but unsaturated fatty acids prevent such close packing and produce flexible, fluid aggregates. Example: Olive oil contains a high percentage of oleic acid.



cis-2-Buten



trans-2-Buten

The most abundant fatty acids in animal fats, vegetable oils, and biological membranes are:

Some saturated fatty acids naturally occurring:

Common (trivial name)	Systematic name	Structure	No. of carbons	Good source
Butyric	Tetranoic acid	$CH_3(CH_2)_2$ COOH	4:0	Butter, milk fat
Caproic	Hexanoic acid	$CH_3(CH_2)_4COOH$	6:0	Butter, coconut oil, palmoil
Caprylic	Otanoic acid	$CH_3(CH_2)_6COOH$	8:0	Coconut oil, palm oil
Capric	Decanoic acid	$CH_3(CH_2)_8COOH$	10:0	Coconut oil, palm oil
Lauric	Dodecanoic acid	$CH_3(CH_2)_{10}COOH$	12:0	Laurel, coconut oil, palm oil
Myristic	Tetradecanoic acid	$CH_3(CH_2)_{12}COOH$	14:0	Butter, woolfat, nutmeg
Palmitic	Hexadecanoic	$CH_3(CH_2)_{14}COOH$	16:0	Animal plant and bacterial fats
Stearic	Octadecanoic acid	$CH_3(CH_2)_{16}COOH$	18:0	Animal, plant and bacterial fats
Arachidic	Eicosanoic acid	$CH_3(CH_2)_{18}COOH$	20:0	Peanut oil, groundnut oil,

Some naturally occurring unsaturated fatty acids:

Palmitoleic	9-Hexa-decenoic acid	$CH_3(CH_2)_5CH=CH(CH_2)_7COOH$	16:1	Sardine Oil
Oleic	9-Octa-decenoic acid	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	18:1	Olive oil
Linoleic	9,12-Octa-decadienoic acid	$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$	18:2	Cottonseedoil, soybeanoil, linseed oil
Linolenic	9,12,15-Octadecatrienoic acid	$CH_3(CH_2CH=CH_3(CH_2)_7$ COOH	18:3	Linseed oil
Arachidonic	Eicosatetraenoic acid	$CH_3(CH_2)_3(CH_2CH=CH)_4(CH_2)_3COOH$	20:4	Animal fats, adrenal phosphatides

Nomenclature of fatty acids:

The most abundant fatty acids have common (trivial) name and systemic name that have been accepted for use in the official nomenclature. In IUPAC (International Union of Pure and Applied Chemistry) nomenclature, the carboxyl carbon is C-1 and other carbons are numbered sequentially. The carbon adjacent to the carboxyl carbon is designated as α and the other carbons are designated as β, γ, δ etc. The carbon farthest from the carboxyl carbon is ω carbon.

1- Saturated fatty acids end with the suffix (-anoic) for example:

——————COOH   octadecanoic acid.

2- Unsaturated fatty acids end with the suffix (-enoic) for example:

-------------=---------COOH   octadecenoic

-------=-----=---------COOH octadecadienoic

The structure of fatty acids is written as a symbol of two numbers separated by a colon: the first number denotes the carbon atoms in the chain and the second number denotes the number of any double bonds which are present. A fatty acid with 18 carbons and no double bonds is designated 18:0, while one with 18 carbons and two double bonds is 18:2.

Representation of double bonds of fatty acids:

Two systems are used to designate the position of double bond:

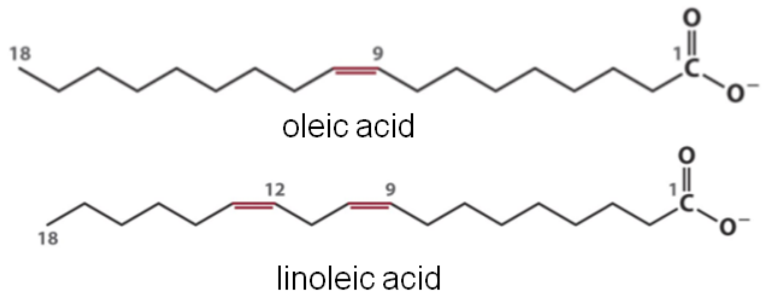
1- C- System

2- ω- System

C-System:

In C-System (C-1 being the carbonyl carbon) the position of double bond are indicated by the symbol Δ where the subscript indicates the position of the first carbon in the double bond, numbering from the carboxyl carbon as C-1. Thus Δ^9 shows a double bond between carbons 9 and 10 of the fatty acid chain.

Oleic acid (C18) with one double bond at C-9 is represented as C:18:1:Δ^9

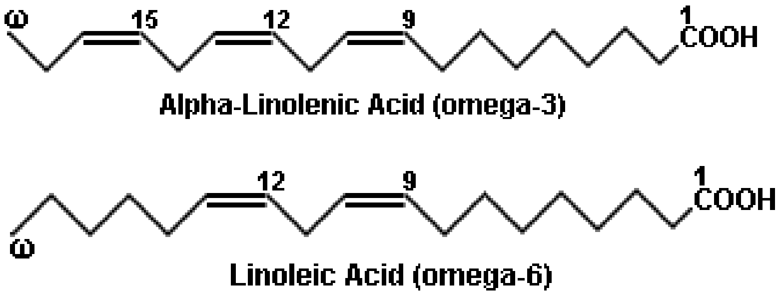


ω-System:

In this system ω refers to the carbon of their terminal methyl group in a fatty acid.

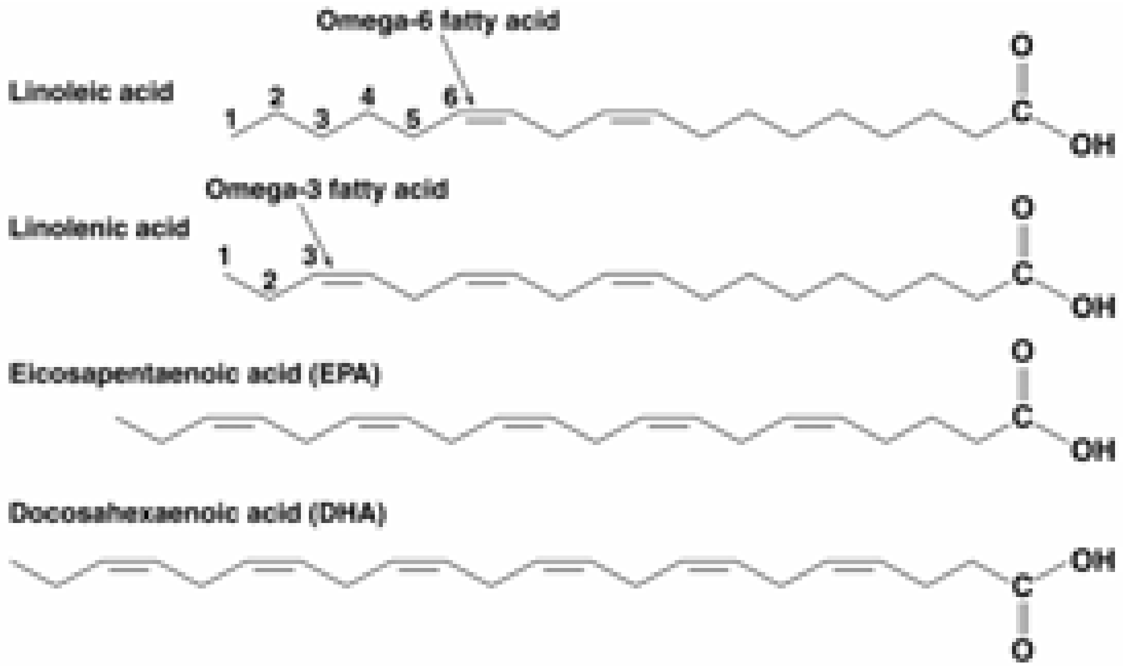
Linolenic acid (C18) with three double bonds (C:18:3:ω-3).

Linoleic acid (C18) with two double bond (C:18:2:ω-6).



Omega-6 and Omega-3 Fatty Acids

The first double bond: In vegetable oils is at carbon 6 (omega-6). In fish oils is at carbon 3 (omega-3) depending on the ω-system.



The properties of fatty acids:

The properties of fatty acids depend on their chain length and the number of double bonds. Shorter chain length fatty acids have lower melting temperatures than those with longer chains. Unsaturated fatty acids have lower melting temperatures than saturated fatty acids of the same chain length, whilst the corresponding polyunsaturated fatty acids have even lower melting temperatures

Essential fatty acids:

Essential fatty acids are fatty acids that cannot be synthesized in the body, and must be obtained from the diet and are required for optical health like linoleic, linolenic and arachidonic acid. Arachidonic acid is the precursor of a class of hormone like molecules known as eicosanoids. The eicosanoids include four groups of compounds:

1- Prostaglandin

2- Leukotrienes

3- Thromboxanes

4- lipoxins

Because prostaglandins, and the closely related leukotrienes and thromboxanes effects so many body processes and because they often cause opposing effects in different tissues. The following is some of the biological processes that are regulated by prostaglandins and related compounds:

1- Blood clotting

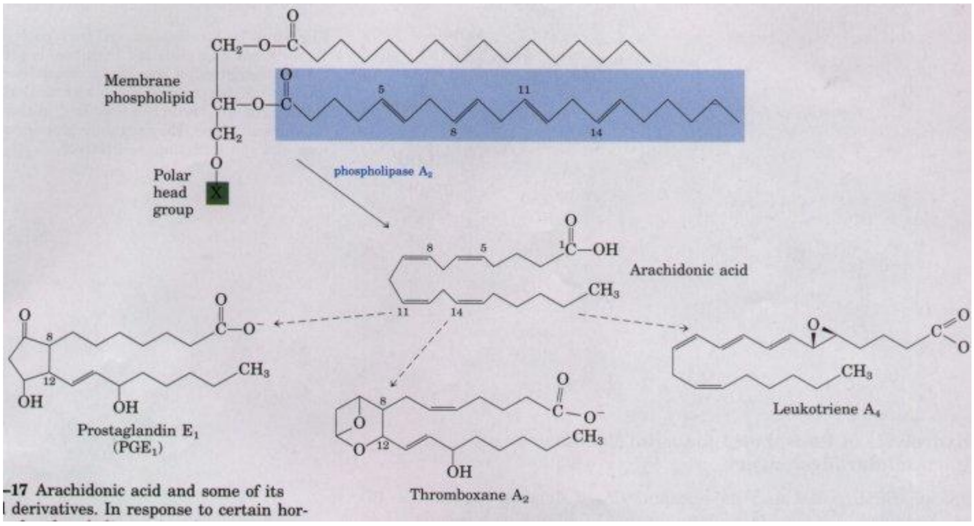
2- The inflammatory response

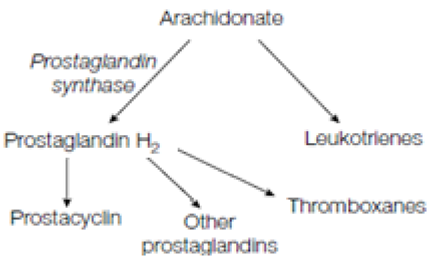
3- Reproductive system

4- Gastro intestinal tract

5- Kidneys

6- Respiratory tract

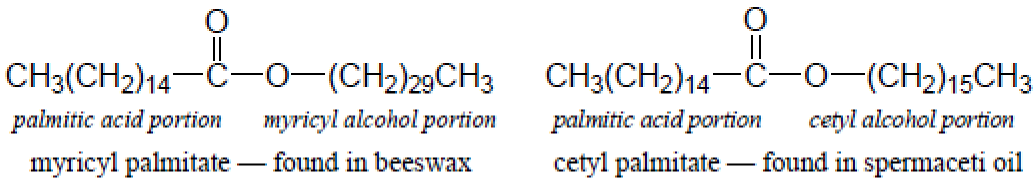




Biosynthetic relationship of the eicosanoids.

b- Waxes:

Waxes are esters of long-chain saturated and unsaturated fatty acids (having 14 to 36 carbon atoms) with long-chain alcohols (having 16 to 30 carbon atoms). Their melting points (60 to 100 °C) are generally higher than those of triacylglycerols. Waxes are solid at room temperature, owing to their molecular weight.



Waxes are found as protective coatings on skin, fur and feathers of animals and birds and on leaves and fruits of higher plants and on exoskeleton of many insects.

Sebum, secreted by the sebaceous glands of the skin, contains waxes that help to keep skin soft and prevent dehydration. Waxes are used commercially to make cosmetics, candles, ointments, and protective polishes.

2- Complex or Compound lipids:

These are esters of fatty acid with alcohol containing additional (prosthetic) groups. These are sub-classified according to the type of prosthetic group present in the lipid:

1- Phospholipids

2- Glycolipids

3- Lipoproteins

Phospholipids:

Phospholipids are lipids contain fatty acids, alcohol, and phosphoric acid residue as additional groups. They frequently have nitrogen containing base and other substituents. Phospholipids may be classified on the basis of the type of alcohol present in them as:

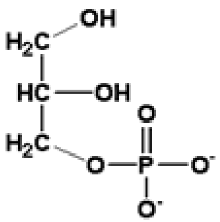
a- Glycerophospholipids.

b- Sphingophospholipids.

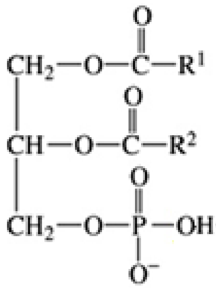
a-Glycerophospholipids:

Glycerophospholipids, also called phosphoglycerides (phosphoacylglycerols), are lipids contain fatty acids, glycerol, and phosphoric acid. Glycerophospholipids are the most

phospholipid molecules found in cell membranes in plant and animal tissues. The most abundant phospholipids are derived from a phosphatidic acid.
The simplest glycerophospholipid, phosphatidic acid, and it is the precursor for all other glycerophospholipid. Phosphatidic acid is composed of glycerol-3-phosphate that is esterified with two molecules of fatty acids at C-1 and C-2. Glycerophospholipid are classified according to which alcohol becomes esterified to the phosphate group.



Glycerol-3-phosphate (Gly3P)



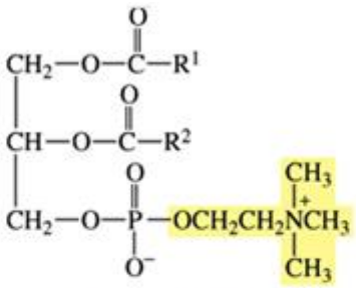
Phosphatidic acid

Glycerolphospholipids contain both a polar and non polar end and therefore are amphipathic.

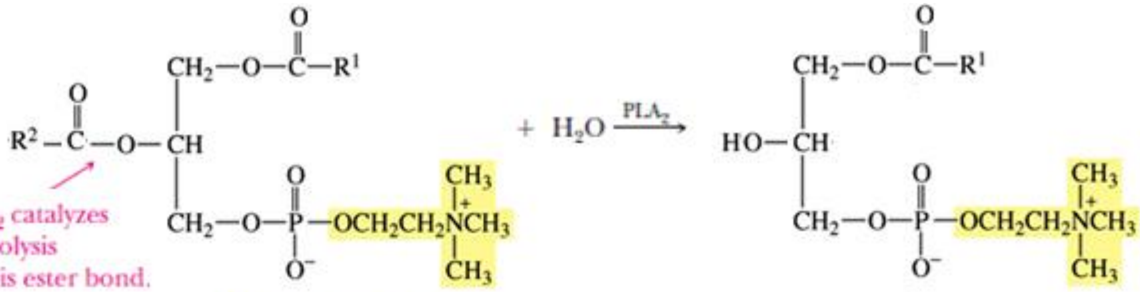
Examples on glycerophospholipids:

Phosphotidylcholin (Lecithin):

These are glycerophospholipids (phosphoacylglycerols) containing glycerol, fatty acids, and cholin. These are most abundant phospholipids of the cell membrane having both structural and metabolic functions. They occur in the liver, brain and in plasma as part of the lipoproteins. Lecithin contains both a polar head and non-polar tails therefore are amphipathic.
On complete hydrolysis, lecithin yields choline, phosphoric acid, glycerol and two molecules of fatty acids. But partial hydrolysis of lecithin by lecithinase (enzymes found in snake venous) causes removal of one fatty acid to yield lysolecithins, when subjected into bloodstream by sting the lysolecithins cause rapid rupture (hemolytic) of the red blood cells.



a phosphatidylcholine
a lecithin

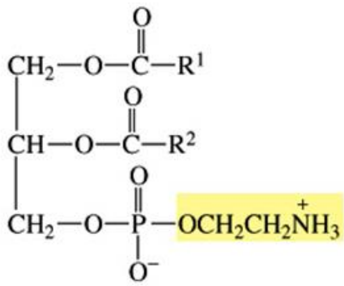


a phosphatidylcholine
a lecithin
A phospholipid

A lysolecithin

Phosphatidyl ethanol amine (Cephalin):

Cephalin differs from lecithin in that the nitrogen base ethanol amine is present instead of cholin. Cephalin is major components of most animal cell membranes and possesses amphipathic properties.

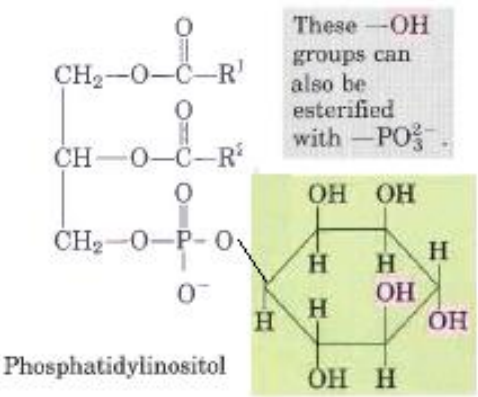


a phosphatidylethanolamine
a cephalin

Phosphatidyinositol:

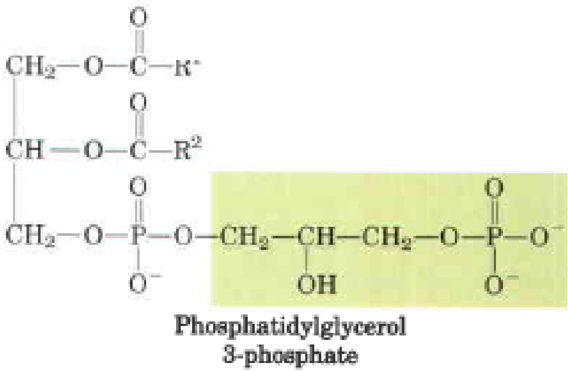
Phosphatidyl inositol differs from lecithin in that the nitrogen base inositol is present instead of cholin. Phosphatidylinositol and its phosphorylated derivatives

(Phosphatidylinositol bisphosphate PIP2) are present in cell membranes and play a vital role in the medication of hormone action on cell membranes.



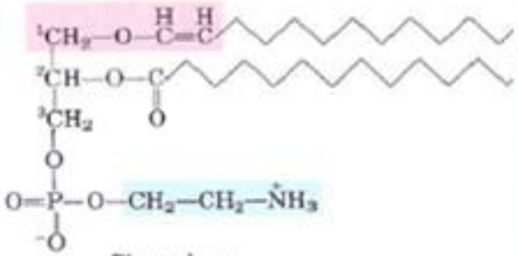
Phosphatidylglycerol (Cardiolipin):

Phosphatidic acid is erterified in C-3 to form diphosphatidyl glycerol or cardiolipin. It is found in mitochondrial membrane and in myocardium.

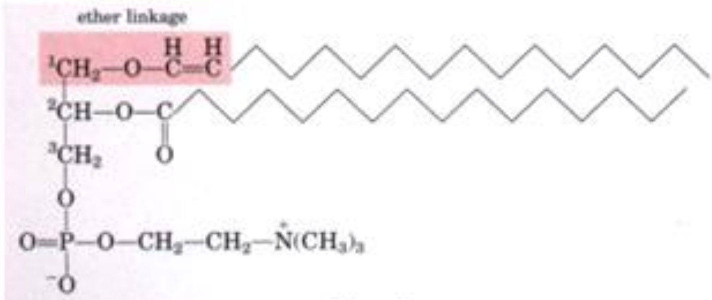


Phosphatidyl glyceracetals (Plasmalogens):

Phosphatidyl glyceracetals (Plasmalogens) are phospholipids which have an aliphatic long chain unsaturated either in C-1. The OH group in C-2 is esterified to a fatty acid. The phosphoric acid in C-3 is attached to cholin, ethanol amine or serine. Plasmalogens are found in cell membranes in brain and muscle of the animals and found in the seeds of higher plants.



Plasmalogen



Plasmalogen

Biological importance of phosphoglycerides:

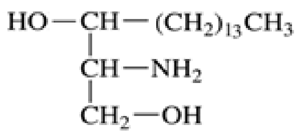
Phospholipids serve many biological functions some of which are as follows :

1. Major components of biological membranes and sub-cellular organelles
2. Regulation of the permeability of cell membrane
3. Maintenance of protoplasmic structure in view of their ability to form emulsions
4. Transport of other lipids in the blood stream and regulation of fat metabolism by activating certain enzymes and
5. As donors of arachidonic acid for the synthesis of prostaglandins and thromboxanes

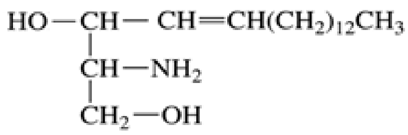
b- Sphingophospholipids:

Phospholipids derived from alcohol sphingosine instead of glycerol are called sphingophospholipids.

Sphingophospholipids are amphipathic, having a polar head group and two non polar fatty acid tails, and are structural components of cell membrane. They are derived from sphingosine, a long-chain, nitrogen-containing (amino) alcohol:



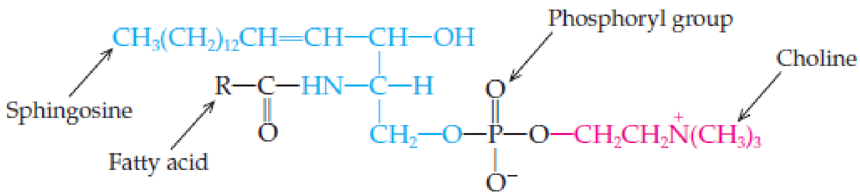
phytosphingosine



sphingosine

Sphingomyelins:

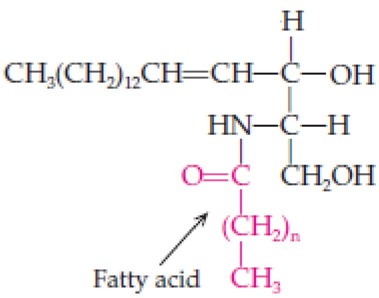
Sphingomyelins are phospholipids which contain sphingosine, one molecule of fatty acid, phosphoric acid and choline. Sphingomyelin is found in most animal cell membranes. They are found in abundance in the myelin sheath that surrounds and insulates cells of the central nervous system.



Sphingomyelin

2-Glycolipids:

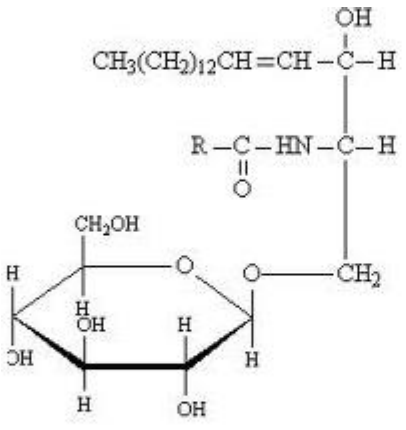
Glycolipids are molecules that contain carbohydrate and lipid. When glycolipids contain sphingosine is called **glycosphingolipids**. In sphingosine, when C-2 is attached to a long chain fatty acid via an amide linkage and they have one or more sugar residues, the resulting compound is a ceramide, so glycosphingolipids such as the cerebrosides and gangliosides, are derivatives of ceramide.



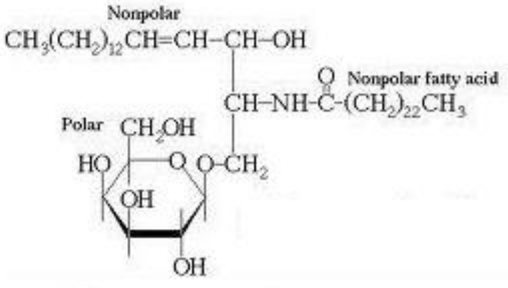
Ceramide

Glycosphingolipids are essential components of all membranes in the body, but they are found in greatest amounts in nerve tissue.

The simplest glycosphingolipids are the cerebrosides. Cerebrosides are cereamide monosaccharide that contain either a galactose (galactocerebroside- the most common cerebroside found in membranes of brain cells), or glucose (glucocerebroside found in the membranes of macrophages {cells that protect the body ingesting and destroying foreign microorganisms})

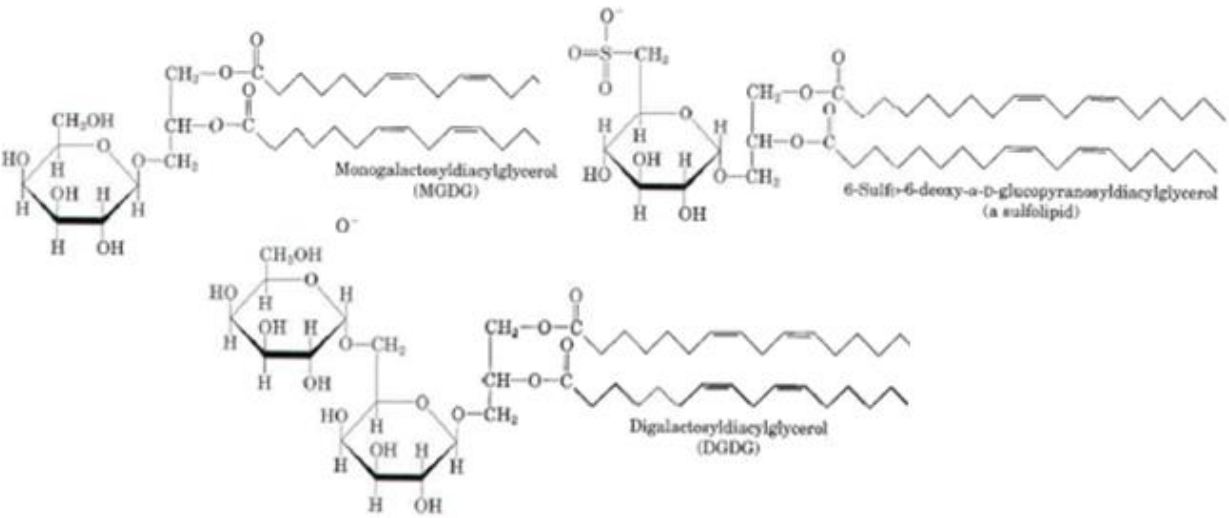


Glucocerebroside



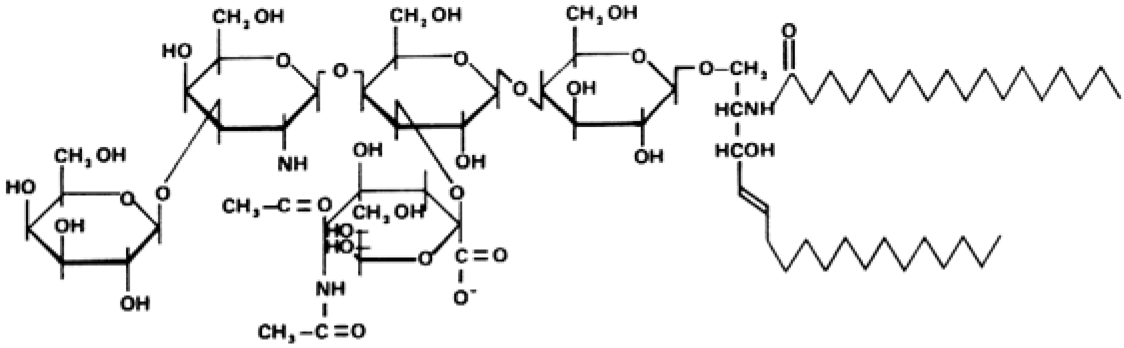
Galactocerebroside

Plant membranes also contain sulfolipids, in which a sulfonated glucose residue is joined to a diacylglycerol in glycosidic linkage. In sulfolipids, the sulfonate on the head group bears a negative charge like that of the phosphate group in phospholipids



Gangliosides:

Gangliosides are glycolipids that possess oligosaccharide groups, including one or more molecules of N -acetylneuraminic acid (sialic acid) and are a major constituent of most mammalian plasma membranes, particularly in brain cells. The lipid composition of the chloroplast thylakoid membranes in plant cells is highly distinctive: about 40% of the total lipids are galactolipids and 4% sulfolipids, with only 10% being phospholipids



3-Lipoproteins:

Lipoproteins are molecules contain lipid and protein and responsible for the transport lipid molecules (triacylglycerol, phospholipids and cholesterol) through the bloodstream from one organ to another. The protein components of lipoproteins are called apolipoproteins or apoproteins. Lipoprotein particles consist of a core of hydrophobic lipids surrounded by amphipathic proteins, phospholipid and cholesterol. Lipoproteins are classified according to their density to:

1-Chylomicrons:

Which are large lipoproteins of extremely low density, transport dietary triacyglycerol (triglyceride) from intestine to the tissues (especially muscle and adipose tissues).

2-Very low density lipoproteins (VLDL):

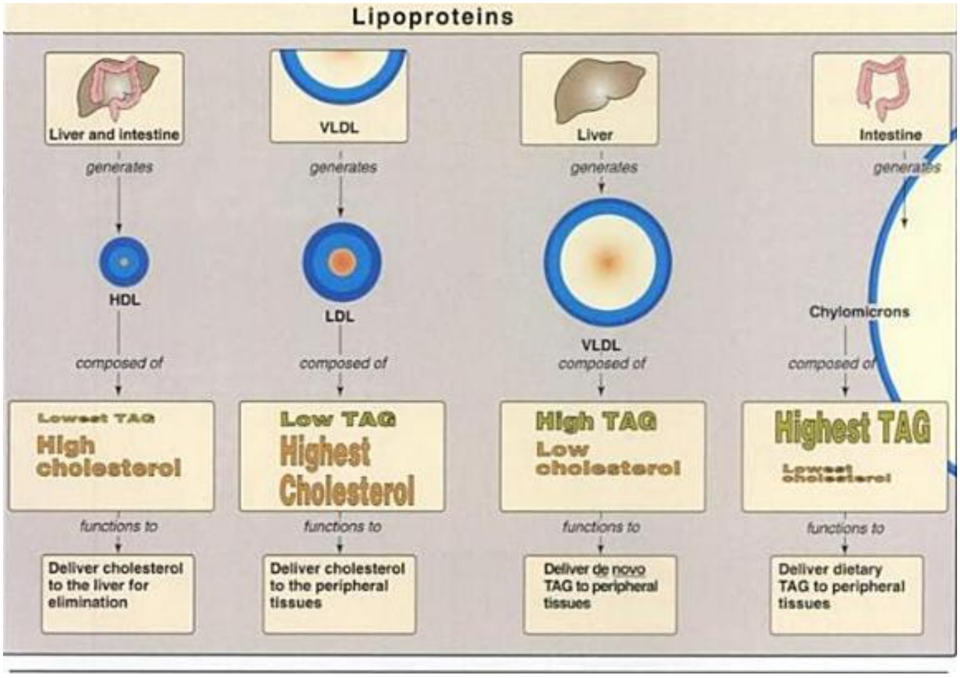
VLDL synthesized in the liver, are responsible for the transport of endogenous triglycerides to the tissues. As VLDL, are transported through the body, they became depleted of triglycerides, as well as some apoproteins and phospholipids. Eventually VLDL is converted to low density of lipoproteins (LDL).

3-Low density lipoproteins (LDL):

LDL carries cholesterol from the liver to tissues, so, it is called bad lipid

4-High density lipoproteins (HDL):

HDL transport cholesterol (ester) from the tissues to the liver, so, it is called good lipid

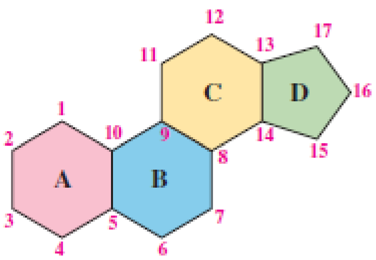


Derived lipids:

Derived lipids are a type of lipids which are derived of lipids like steroids, terpenoids, fatty acids and glycerol…..

Steroids:

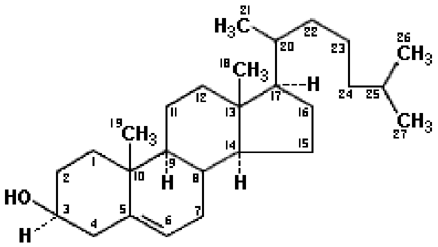
Sterols are a class of steroids which present in the membranes of most cells of plants, animals, fungi and yeasts.



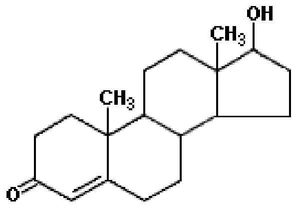
The tetracyclic ring system characteristic of steroids.

Cholesterol:

Cholesterol is the major sterol in animal tissues, it occurs only rarely in higher plants. Cholesterol is a major structural constituent of the cell membranes and plasma lipoproteins. Cholesterol is a precursor in the biosynthesis of all steroid hormones (like Testosterone), vitamin D and bile salts.

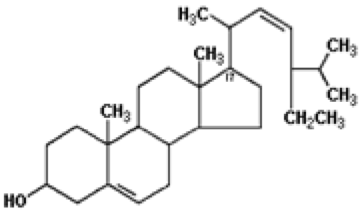


Cholesterol

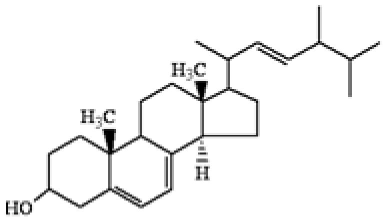


Testosterone

Plants contain little cholesterol but have instead a number of other sterols, mainly **stigmasterol** and β-**sitosterol**. Yeast and fungi have other membrane sterols, such as ergosterol.



stigmasterol



ergosterol

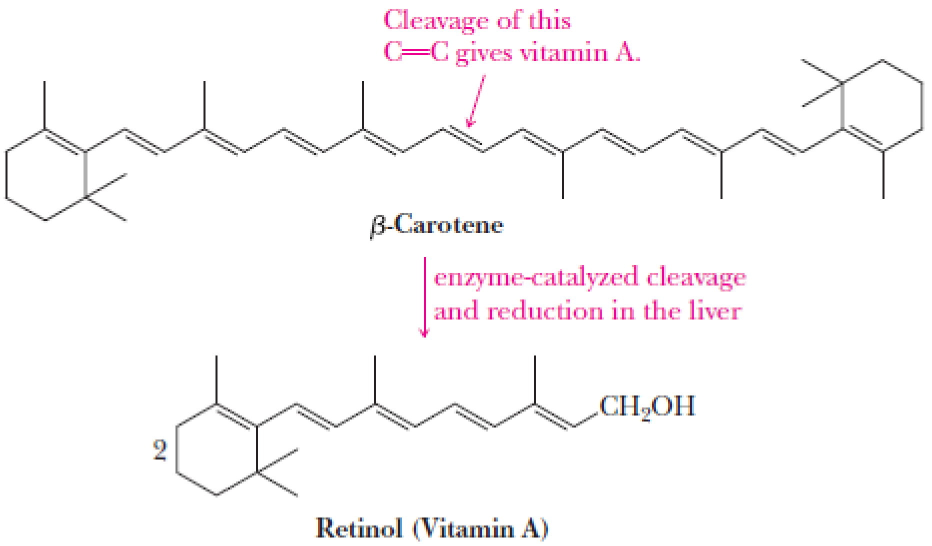
Terpenes:

Terpenes are a class of lipids formed from combination of two or more molecules of isoprene units.

Isoprene $CH_2{=}C(CH_3){-}CH{=}CH_2$

A monoterpenes consist of two isoprene units, asesquiterpens consist of three isoprene units, and a diterpenes consist of four isoprene units and so on. Monoterpenes occur in all high plants, where assesquiterpenes and diterpenes are less known. The triterpenes are containing 30 carbon atoms and include squalene and lanosterol, two of the precursors of cholesterol and other steroids. Tetraterpenes contain 40 carbon atoms, are less common but include carotenes, a class of colorful photosynthesis, pigments.

β-carotene is the precursor of vitamin A. β-Carotene is the precursor of vitamin A, whereas lycopene, similar to β-carotene, is a pigment found in tomatoes.



Rancidity:

is unpleased odor and taste in many fat and oils when stored for long time. There are two types of rancidity:

1- Hydrolytic rancidity

2- Oxidative rancidity

1- Hydrolytic rancidity

Hydrolytic rancidity is caused by the growth of microorganisms which secrete lipases and split triglycerides into mono- and diglycerides, glycerol and fatty acids. If fatty acids of low molecular weight are released, they impart unpleasant taste and odour. This kind of rancidity which commonly occurs in butter can be reduced by refrigeration (butter is stored at low temperature), by exclusion of water or destroying the microorganisms.

2- Oxidative rancidity:

Oxidative rancidity occurs due to the autooxidation of the unsaturated fatty acids at their double bonds yielding short chain acids and aldehydes having rancid taste and odors. This can be prevented by the addition of compounds like vitamin E (antioxidant).

In case of oxidative rancidity, oxygen adds to the double bonds of unsaturated fatty acids to produce either cleavage or polymerization. The slow oxidation of unsaturated fatty acids in edible fats is associated with a cleavage type of reaction.

Hydrogenation:

Hydrogen can be made to combine with unsaturated fats and oils to produce hydrogenated shortening. This reaction is used to enhance the keeping quality of vegetable oils used for food. The reaction of hydrogen with fats and oils is used commercially to produce hydrogenated shortening and oleomargarine.