Lipids

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The aims of the lecture

- To define the lipids
- To know the function of lipids.
- To classify the lipids.

Lipids:

- are defined as compounds which are relatively insoluble in water, but freely soluble in non-polar organic solvent like benzene, chloroform, ether, hot alcohol, acetone, etc.

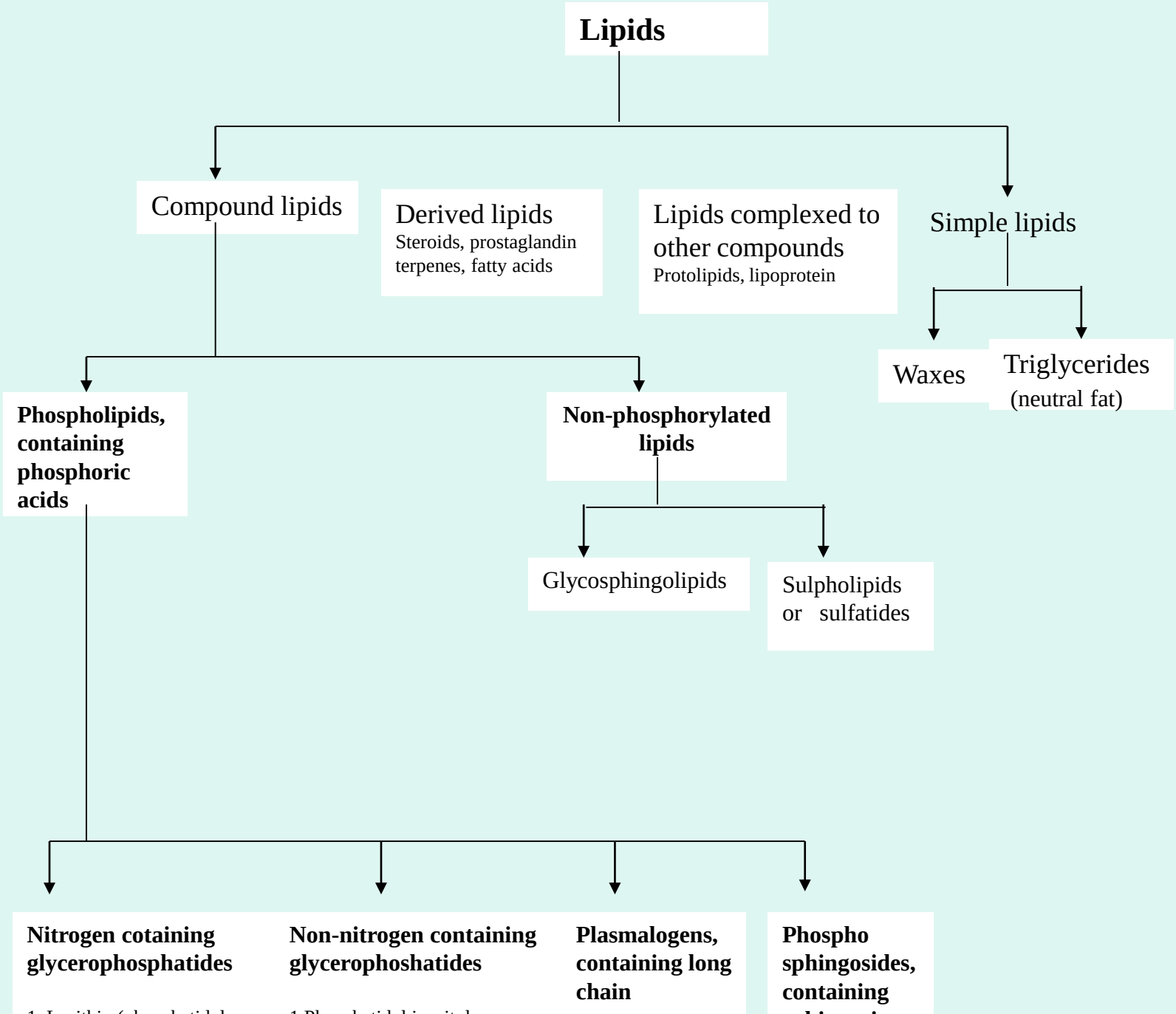
Functions of lipids:•

1. Storage form of energy (triglycerides) firstly because of their high energy content. The calorific value is 9Kcal\gm secondly they are storage in concentrated form in water in the tissues compared to carbohydrates which are highly hydrated and can not be stored in such concentrated form

2. Structural components of biomembranes (phospholipids and cholesterol).
3. As protective coating on the surface of many organs such as kidney, against injury.
4. Facilitation the absorption of the fat soluble vitamins A, D, E and K.

5. Providing insulation against changes in external temperature (subcutaneous fat).
6. Metabolic regulators (steroid hormone and prostaglandins).
7. As transport forms of various metabolic fuel.
8. Acting as electric insulator in neurons.

Classification of lipids: - we can classify lipid depending on the chemical nature.


Lipids
Compound lipids
Derived lipids
Steroids, prostaglandin terpenes, fatty acids
Lipids complexed to other compounds
Protolipids, lipoprotein
Simple lipids
Waxes
Triglycerides
(neutral fat)
Phospholipids, containing phosphoric acids
Non-phosphorylated lipids
Glycosphingolipids
Sulpholipids or sulfatides
Nitrogen cotaining glycerophosphatides
Non-nitrogen containing glycerophoshatides
Plasmalogens, containing long chain
Phospho sphingosides, containing

Fatty acids:- are the major unit of lipids. They are generally found in ester linkage in different glasses of lipids.

Fatty acids are represented as general formula R COOH.

Numbers of carbon atoms of fatty acids are even or odd number, but odd number fatty acids are very rare.

Fatty acids may be saturated or unsaturated.

Fatty acids that have double bonds are said to be *unsaturated*. If they have more than one double bond but no more than four they are commonly referred to as polyunsaturated fatty acids

Fatty acids that contain only single bond are called *saturated fatty acids*. For example palmitic and satiaric acids.

Name	Structure	Carbon atoms	Occurrence
Butyric	(C_3H_7COOH)	4	Butter fat
Caproic	($C_5H_{11}COOH$)	6	Butter fat
Caprylic	($C_7H_{15}COOH$)	8	Coconut oil
Capric	($C_9H_{19}COOH$)	10	Palm kernel oil
Lauric	($C_{11}H_{23}COOH$)	12	Coconut oil
Myristic	($C_{13}H_{27}COOH$)	14	Nutmeg oil
Palmitic	($C_{15}H_{31}COOH$)	16	Animal and vegetable fats
Stearic	($C_{17}H_{35}COOH$)	18	Animal and vegetable fats
Arachidic	($C_{19}H_{39}COOH$)	20	Peanut oil

Saturated fatty acids

Name	Structure	No. of carbon atom	Occurrence
Palmitoleic acid		16	Butter fat
Oleic acids		18	Olive oil
Linoleic acids		18	Linseed oil
Linolenic acid		18	Linseed oil
Arachidonic		20	Lecithin

Unsaturated and polyunsaturated fatty acids

The most common among the saturated fatty acids are palmitic acid (C16), stearic acid (C18) and among the unsaturated fatty acid, oleic acid (C18).

Fatty acids with one to eight carbons are liquids at room temperature while those with more carbon atoms are solids.

Most plant fats are liquid since they contain a large proportion of unsaturated fatty acids. Animal fats, on the other hand, contain a high proportion of palmitic and stearic acids, and are solid or semi-solid at room temperature.

Essential fatty acids: -
they are not synthesized in the body and hence, have to be provided in the diet. The deficiency of essential fatty acids in human give rise to dry, scaly skin, hair loss, poor wound healing, failure of growth an increase in metabolic rate.

Essential fatty acids	No. of carbon atoms	No. of double bonds	Position of double bonds from carboxyl end	Dietary source
Linoleic acid	18	2	9,12	Vegetable oil
Linolenic acid	18	3	9,12,15	Vegetable oil
Arachidonic acid	20	4	5,8,11,14	Vegetable oil
Timnodonic acid	20	5	5,8,11,14,17	Fish oil

Properties of fatty acids:-

*1- Hydrogenation *

Unsaturated fatty acids may be converted to the corresponding saturated fatty acids by the hydrogenation of the double bond.

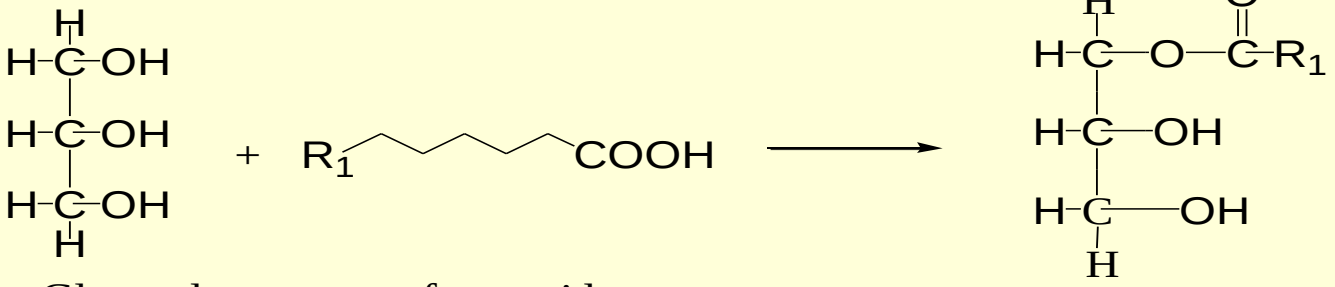
Hydrogenation oil can lead to solidification and saturation.

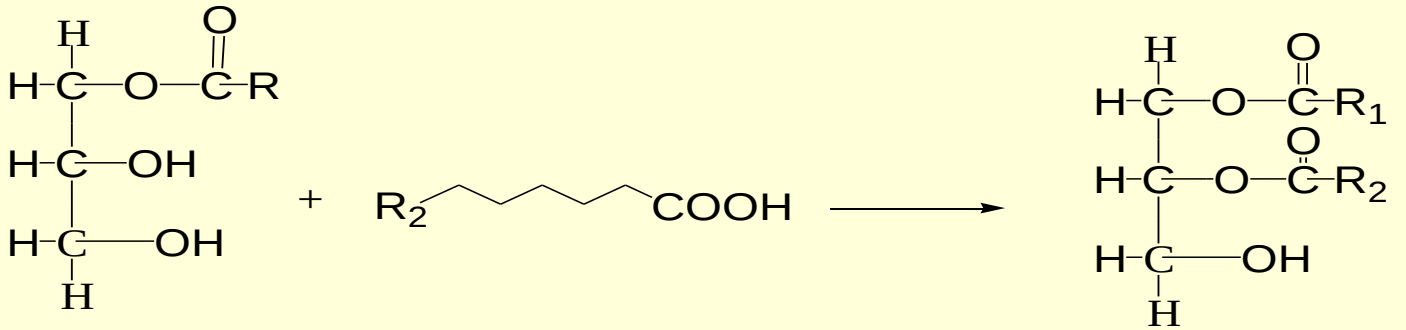
2- Melting point \ The short and medium chain fatty acids are liquids, whereas long chain fatty acids are solid at 25C°. The solubility in water decreases while melting and boiling points increase, with increase in chain length. The unsaturated fatty acids have lower melting point compared to saturated fatty acids with the same chain length.

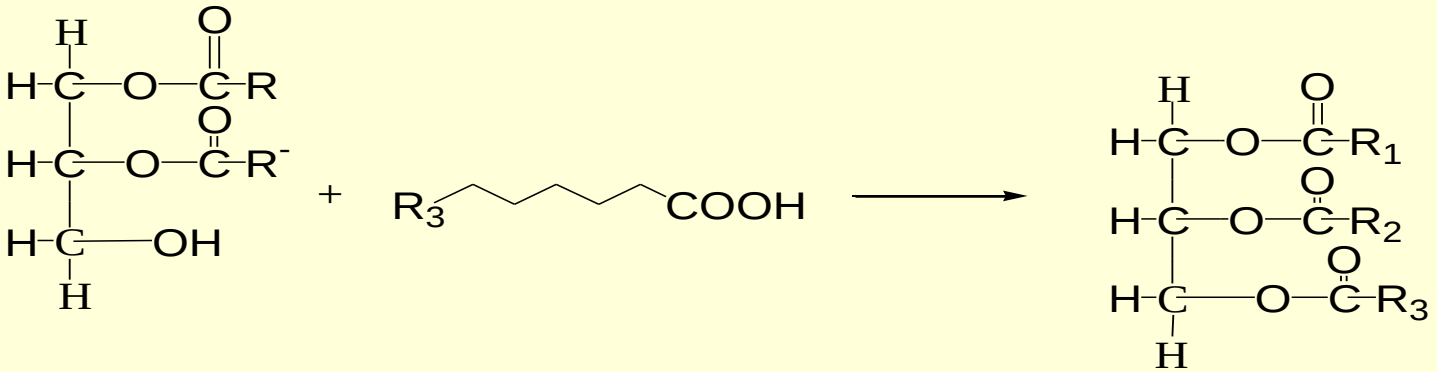
3- Salt formation \ Saturated and unsaturated fatty acids form salt with alkali. Sodium and potassium salt are called soaps. Calcium and magnesium soaps are insoluble.

$$CH_3 - COOH + NaOH \rightarrow CH_3 - COONa + H_2O$$

4- Ester formation: - Both saturated and unsaturated fatty acids form ester with alcohol, especially with glycerol. Fatty acids can form mono-, di- or tri- ester with alcohol groups of glycerol. Triglycerides or triacyl glycerol are also known as neutral fat.


Glycerol
fatty acid
monoacyl glycerol


diacyl glycerol


triacyl glycerol (Triglyceride)

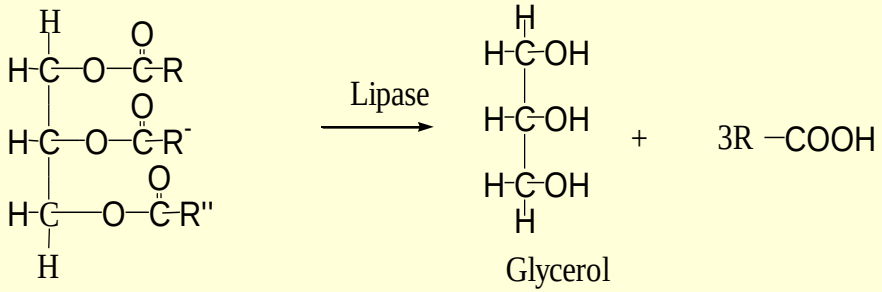
Oxidation of fatty acids: - All fatty acids undergo oxidation in the body to give energy. β- oxidation is the major process.

Triacyl glycerol (neutral fats)
They are also called triglycerides (TG). These are esters of the trihedral alcohol, glycerol with fatty acids.
The triglycerides are the storage form of lipids in the adipose tissue.

Oils are liquids at 20C ; they are triglycerides which contain a higher proportion of unsaturated fatty acids or short chain triglycerides. Oils are generally of plant origin. On other hand, fats are solids at room temperature and contain mainly saturated long chain fatty acids. Fats are mainly of animal origin

Triglycerides molecules are hydrophobic and are insoluble in water.

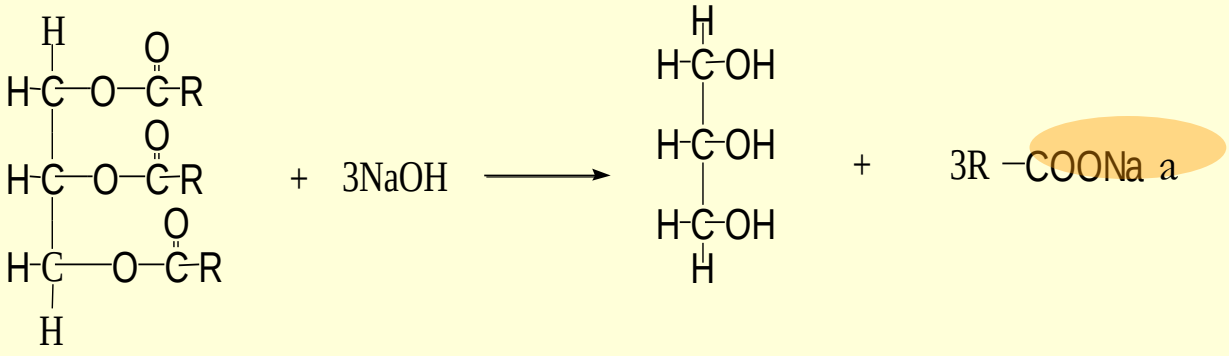
Triglycerides in the body are hydrolyzed by enzyme, lipases to diacyl glycerol and monoacyl glycerol and finally glycerol plus 3 fatty acids



triacyl glycerol (Triglyceride)

Saponification:-

When triglycerides are hydrolysed by alkali, the process is known as saponification. The products of hydrolysis are glycerol and alkali salts of fatty acids, which are called soaps



triacyl glycerol (Triglyceride)

Glycerol

Soaps

The ordinary hand soaps used in home are hard soaps. When KOH is used instead of NaOH for saponification soft soaps are produced which are used in shaving cream and liquid soaps.

How soaps clean: -
soap was defined as emulsifier, a substance that will hold oil and water together in one phase. Soap is capable of acting as an emulsifier because of its molecular structure

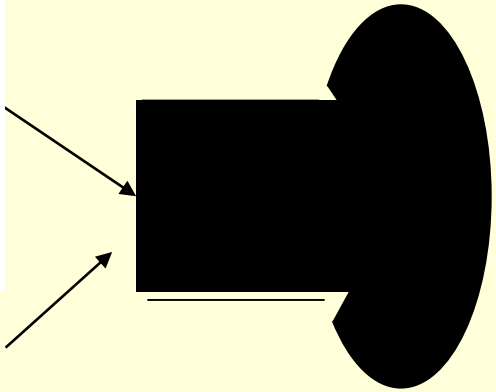
The soap molecule consists of a polar end containing the metal ion, and a long, nonpolar end consisting of the hydrocarbon chain

The polar end of the molecule will dissolve in water, which is also a polar substance; the nonpolar end will dissolve in grease and oil, which are non-polar substances.

Soap molecule

Carboxylate group,
water soluble

Carbon chain,
Grease soluble



Polar

Non polar

(Hydrophilic group)

(Hydrophobic group)

When soap is used to remove dirt, grime, and grease from clothes and other objects, the non polar, grease-soluble end of the molecule is attracted to the grime and grease

. The polar "head" is strongly attracted to polar water molecules and thus mechanically pull the dissolved away from the object being "cleaned" and holds it in the water as an emulsion.

As the grease particles are lifted away from the surface being cleaned, they are prevented from re-forming because the grease- soluble hydrocarbon chain pierces the particle- somewhat like pins in a pincushion

. This gives the grease particle, or oil droplet, a shell of negative charge from the water- soluble carboxylate groups, preventing them from being attracted to other such coated particles.

These tiny charged pockets of oil and grease are called *micelles*. They are kept in water suspension until they are flushed away in a rinse

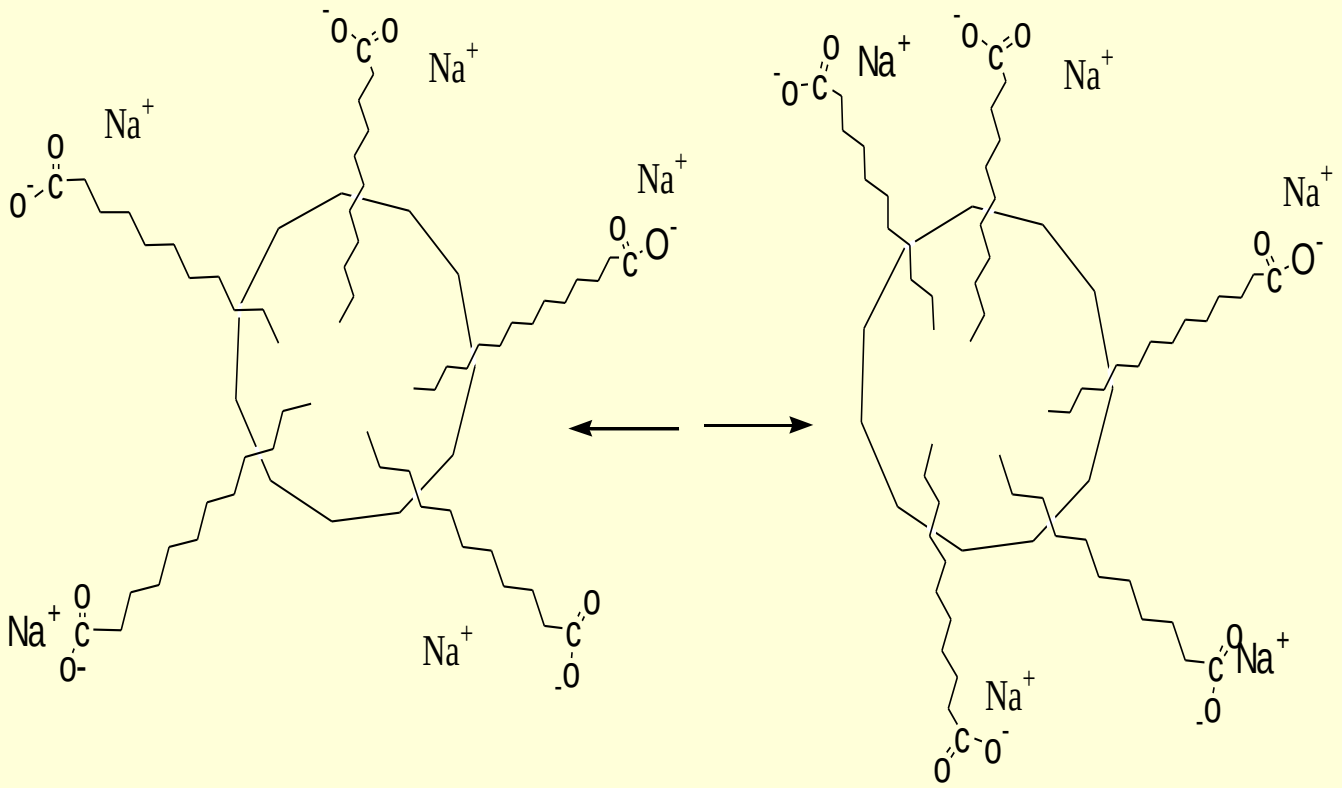


Fig. a typical micelle (two micelles will not coalesce because of the repulsions between their surrounding negatively charged carboxylate groups).

Saponification number:- is defined as the number of milligrams of potassium hydroxide required to saponify one gram of fat. Human fat has a saponification number of 194-198, and butter has 210-230.

Rancidity: - is a chemical change resulting in unpleasant odor and taste for fats and oils when they are exposed to light, heat, air and moisture. Rancidity may be due to hydrolytic or oxidative taking place at the double bonds of unsaturated fatty acids.

1- Hydrolytic rancidity \ is due to partial hydrolysis of the triacyl glycerol molecules due to traces of hydrolytic enzymes present in naturally occurring fats and oils.

2- Oxidative rancidity \ is the result of partial oxidation of unsaturated fatty acids resulting in short chain aldehydes or ketones which have unpleasant odor. The oxidation of unsaturated bonds in fatty acids when they are exposed to oxygen in the environment is referred to as either auto oxidation or

Antioxidants are generally added to many food fats to improve their storage quantities. The addition of certain substance, called antioxidant such as ascorbic acid and vitamin E prevents rancidity

They are oxidized, protecting the food containing them from being oxidized. Whereas addition of proxidants likes copper, lead and nickel quickens rancidity.

Waxes: -

they are esters of higher fatty acids with higher monohydroxy aliphatic alcohols and so have very long straight chains of 60-100 carbon atoms

They are insoluble in water and less greasy than fats, and are also more brittle and harder

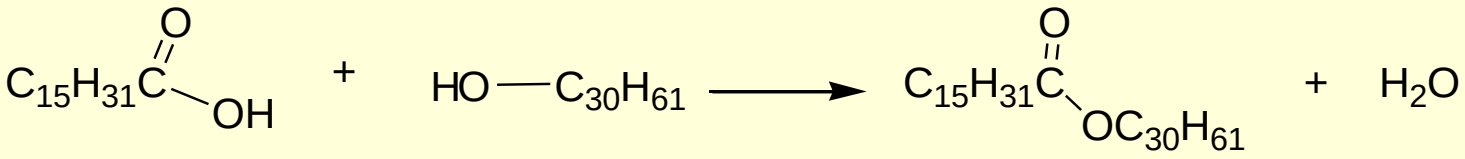
Because of their general unreactivity, waxes provide very good protective coating for plants and animals. Leaves and steams of most plants are coated with wax

which helps prevent dehydration and protects the plant from invasion by bacteria and other microorganisms

Many fruits (apples, for example) are also coated with wax for protection. Waxes also serve a protective function in animals. Feathers in birds are coated with wax

It is the way coating on ducks that allow them to float on water and swim. Earwax (cerumen) protects the delicate lining of the inner ear.

Waxes are important in medicine because they are used as ointment bases. They are also used to make cosmetics, polishes, candles, and phonograph records.



Palmitic alcohol

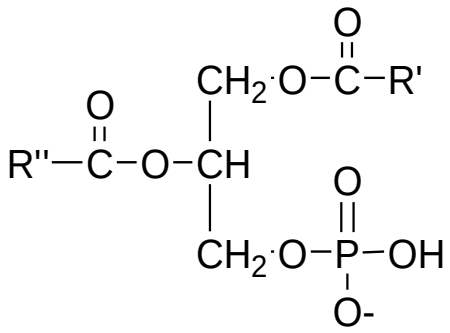
Myricyl alcohol

Myricyl palmitate(honeycomb)

Compound lipids

Phospholipids:- They are also known as phosphatides. They are present in all plant and animal cells and are the primary components of cell membranes. Phospholipids include the following groups:-

1.Phosphatidic acid \ on hydrolysis yield glycerol, fatty acid and phosphoric acid.



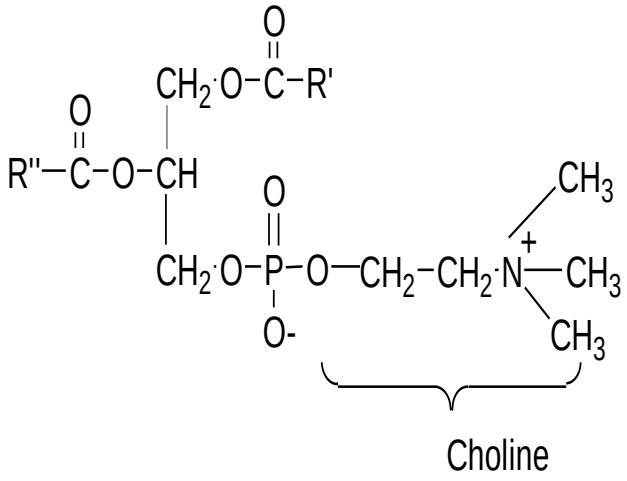
Phosphatidic acid

2.Lecithin \ contains saturated - position and αfatty acid at -βunsaturated fatty acid at the position of the glycerol. When lecithin are hydrolyze give glycerol, fatty acid, phosphoric acid and choline

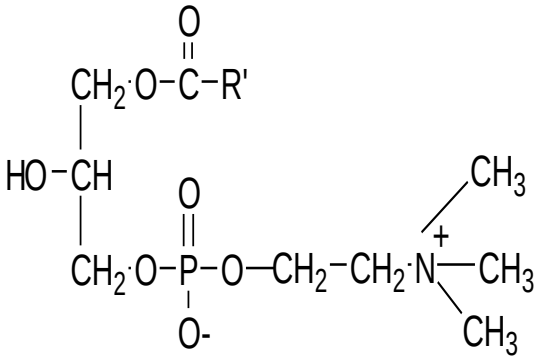
They are found in the brain, in nervous tissue, and in the protoplasm of practically all body cells also are found in egg yolk

Phospholipase A2 acts on an intact lecithin molecule hydrolyzing the fatty acid or second βesterified to the carbon atom producing Lysolecithin and fatty acid. Lysolecithin is a detergent and hemolytic agent.

The enzyme (Phospholipase A2) is present in the venom of viper snake. The hemolysis and consequent renal failure seen in viper poisoning could be thus explain.



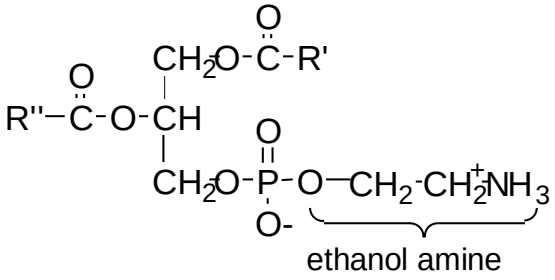
Lecithin



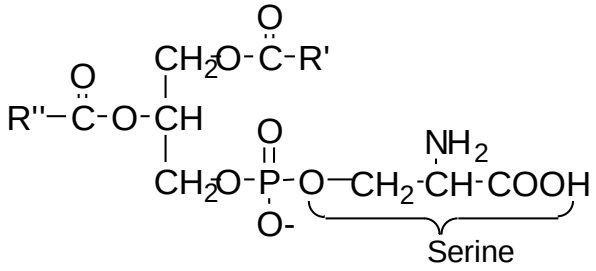
Lysolecithin

3.Cephalins \ differ from lecithins with respect to base attached to phosphoric acid. If the base is ethanol amine then it is called phosphatidyl ethanolamine or ethanolamine cephalin

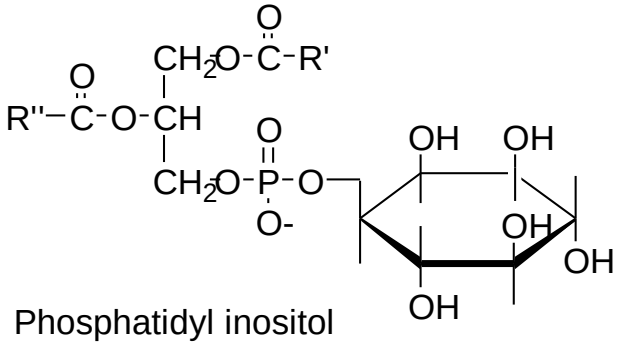
. If the base is amino acid serine then it is called phosphatidyl serine which is also called serine cephalin and if the base inositol then it is called phosphatidyl inositol .



Phosphatidyl ethanol amine

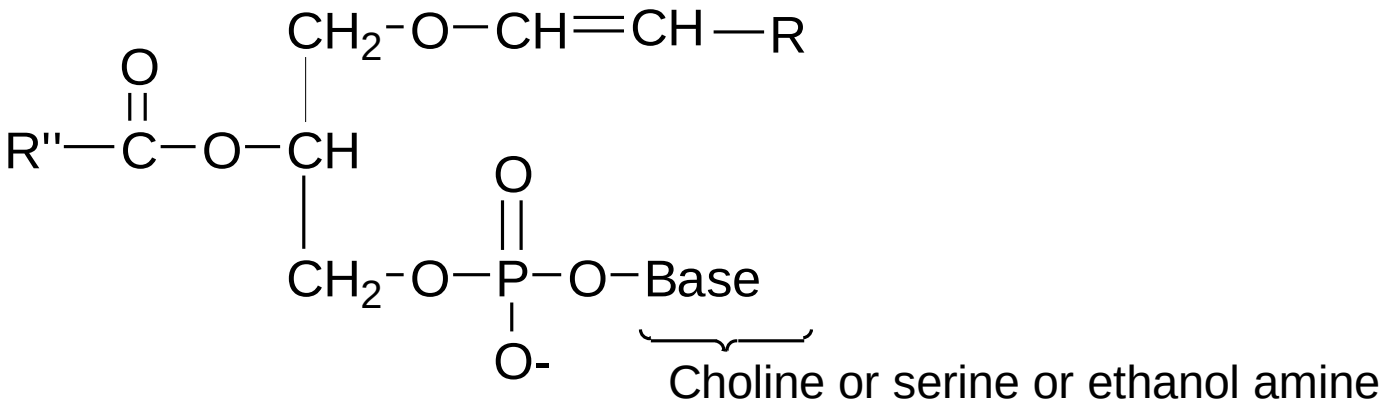


Phosphatidyl serine



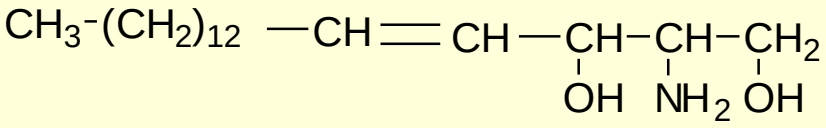
Phosphatidyl inositol

4. Plasmalogens \ these are phospholipids which have an aliphatic chain α-β unsaturated alcohol in ether linkage with the first hydroxyl group of glycerol. The second OH group is esterified to a fatty acid. The phosphoric acid is attached to choline, serine or ethanol amine. Plasmologens are found in biomembranes in brain, heart and muscle.

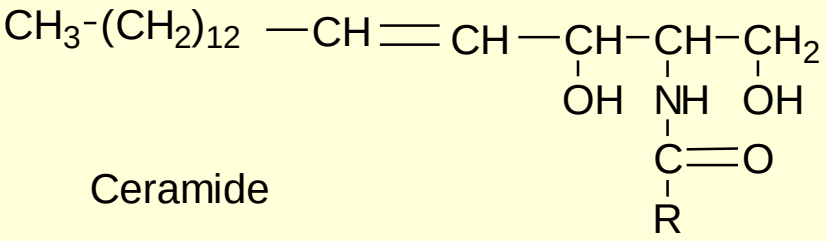


plasmologens

5. Sphingo lipids:- containing sphingosine which is attached to fatty acid in amide linkage to form a ceramide . Sphingosine contain a long chain unsaturated amino alcohol



Sphingosine

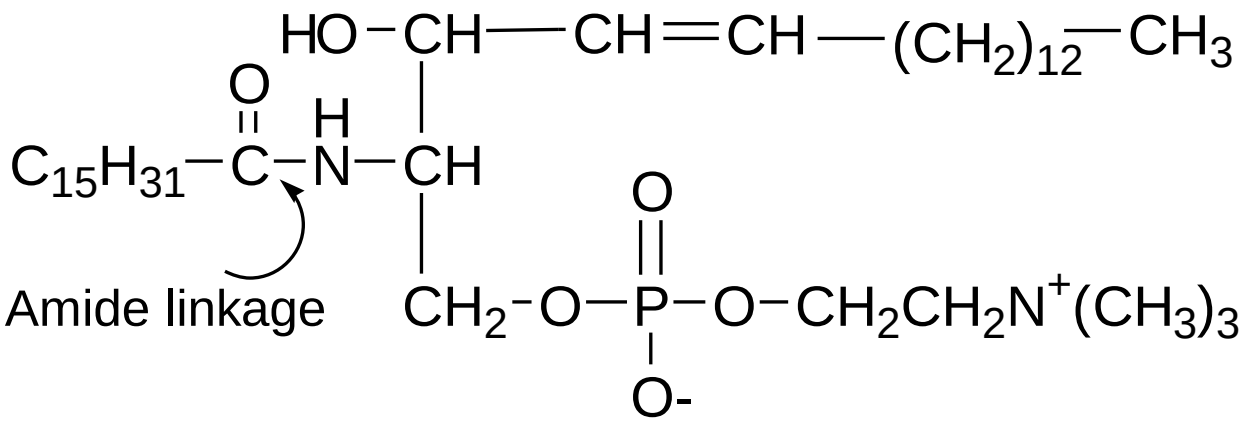


Ceramide

One of the more important sphingolipids is a compounds is called *Sphingomyelin*. sphingomyelins are present in all tissues especially in brain and other nervous tissues. Sphingomyelin on hydrolysis yield sphingosine, fatty acid, phosphoric acid and choline.

Because of its amphipathic nature sphingomyelin can act as an emulsifying agent and detergent

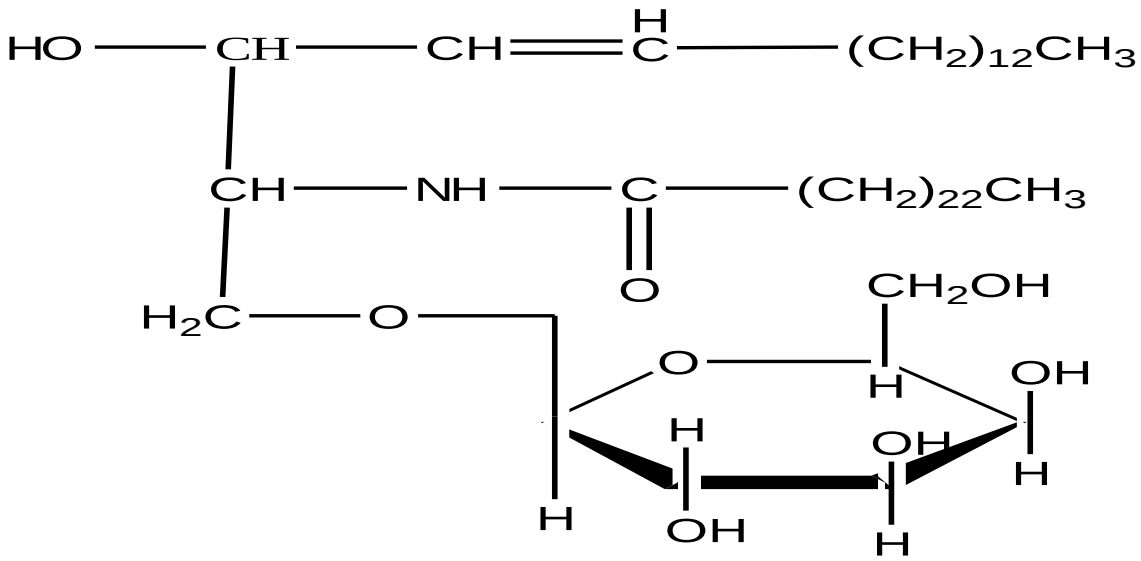
In Niemann-Pick disease, there is an above-normal concentration of sphingomyelin in the liver and spleen, but the concentration in the brain is normal. These disturbances are often fatal



sphingomyelin

(Non- phosphorylated lipids)
Glycolipids:- this group of lipids do not contain phosphoric acid; instead they contain carbohydrates usually glucose or galactose bonded by glycosidic linkage. For example:-

1- cerebrosides \ are in high concentration in the white matter of the brain. Cerebrosides are usually limited to glucose or galactose. In Gaucher's disease, excess cerebrosides containing glucose accumulate in the spleen and liver.



Galactocerobroside

2- gangliosides \ are found in greater concentration in the gray matter. The gangliosides contain several sugars. Gangliosides accumlatein large concentration in the neurons of children with Tay-Sachs disease, a severe disorder of the nervous system resulting in idiocy

Derived lipids

Derived lipids are substances which are derived from other lipids by hydrolysis. These include fatty acids of various series, steroids, bile acids and substances associated with lipids in nature such as carotenes, vitamin A, D, E and K.

1- Terpenes:- they are linear or cyclic compounds formed by condensation of two or more isoprene units. Terpenoid compounds include, tocopherol (vitamin E), Coenzyme Q(ubiquinone), Vitamin K (a napthaquinon), carotenes, squalene etc.

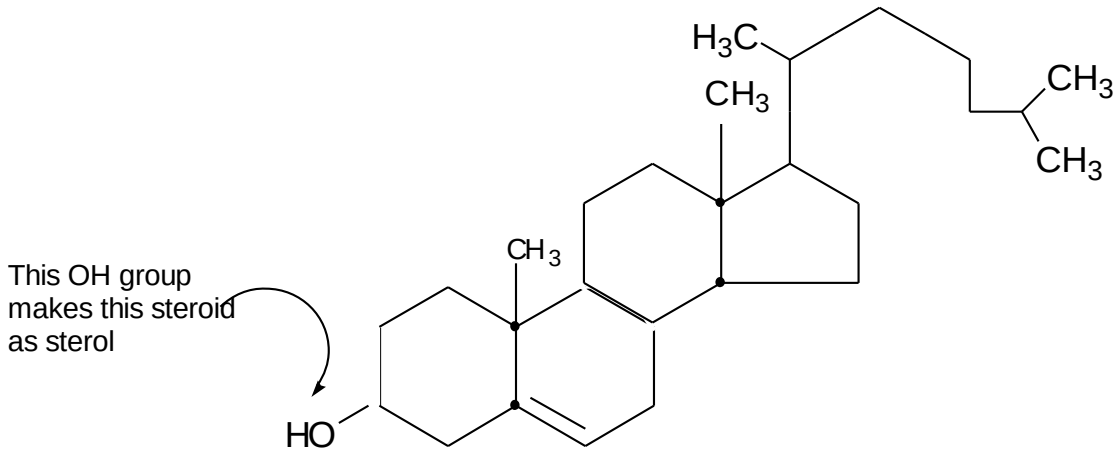
2- Steroids:- They are considered lipids because they are soluble only in organic solvents. They are derivatives of cyclopentano-perhydro-phenanthrene ring (consists of four fused rings). Steroids are steroidal alcohol

A- Cholesterol \ It is the most common steroid, found in large concentration in the brain and spinal cord. Cholesterol is found only in animal cells, although plants have their own steroids called "phytosterols"

. Cholesterol, as amphipathic lipid is an important component of membranes and starting material, or precursor, of all steroids of animal origin such as bile acids, vitamins, hormones and miscellaneous group of steroids.

When present in excess it is deposited in the arteries as a component of a lipid- type plaque and in the gallbladder as gallstone. Some people suffer from hypercholesterolemia, an abnormally level of cholesterol in the body

Those people are more likely to develop cardiovascular disease, especially heart attacks. There are two sources of cholesterol. One is cholesterol from the diet. Secondly, it is synthesized from sugar in the body



Cholesterol

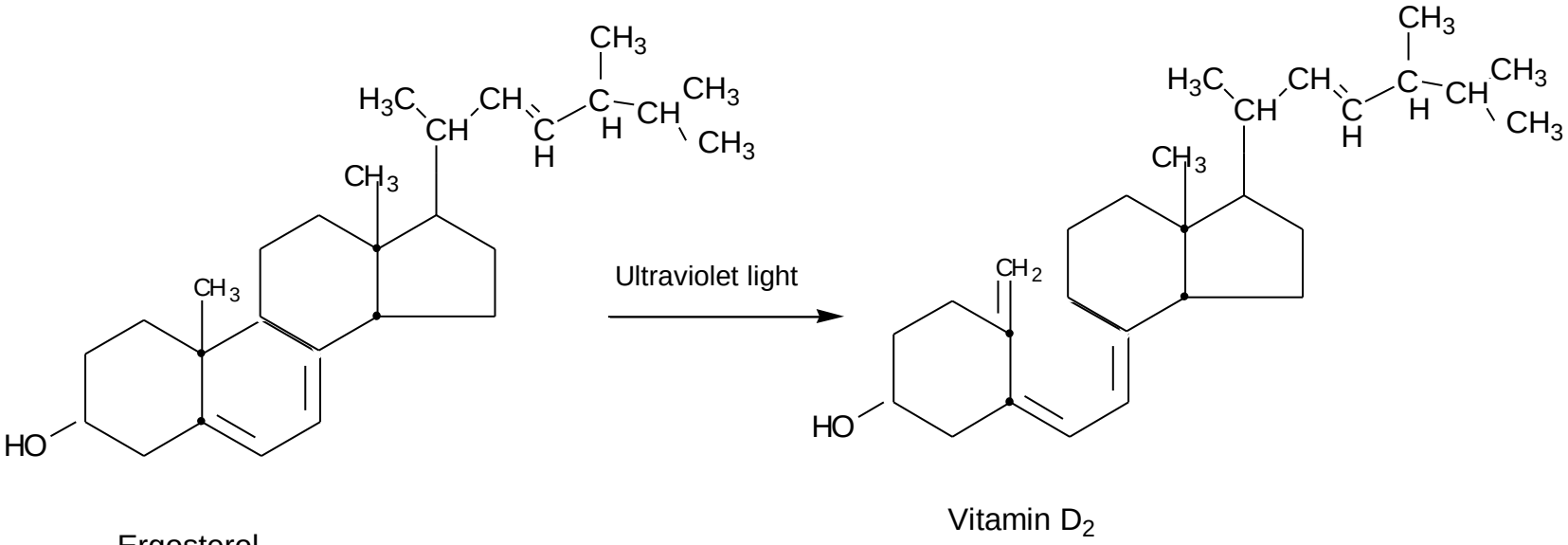
B- Bile acids \ are simply steroids with an acid group. Fat are insoluble in water. In order for fat to be transported through the walls of the intestine and absorbed, they must be emulsified. Bile acids secreted as components of bile serve this function. Although cholic acid is the most common bile acid, other bile acids contain amino acids

C- Steroid hormones \ the most important group of steroids hormones are the sex hormones. Male sex hormones are called androgens; the two most important are *androsterone* and *testosterone.* Female hormones include *progesterone* and *estrogen*. Also (adrenal gland) cortisone, cortisol, aldosterone and corticosterone are steroids hormones

D- The fat soluble vitamins \

The structure of many of the fat soluble vitamins does not include a sterol nucleus. For example, vitamin D2, produced by the action of sunlight on the skin, has an open benzene ring in its structure and thus is not a true

steroid. However, the compound ergosterol, which reacts with ultraviolet light to produce vitamin D2, is a true steroid. Vitamin A, E and K are the other fat soluble vitamins.



Ergosterol

Vitamin D_2

THANK YOU