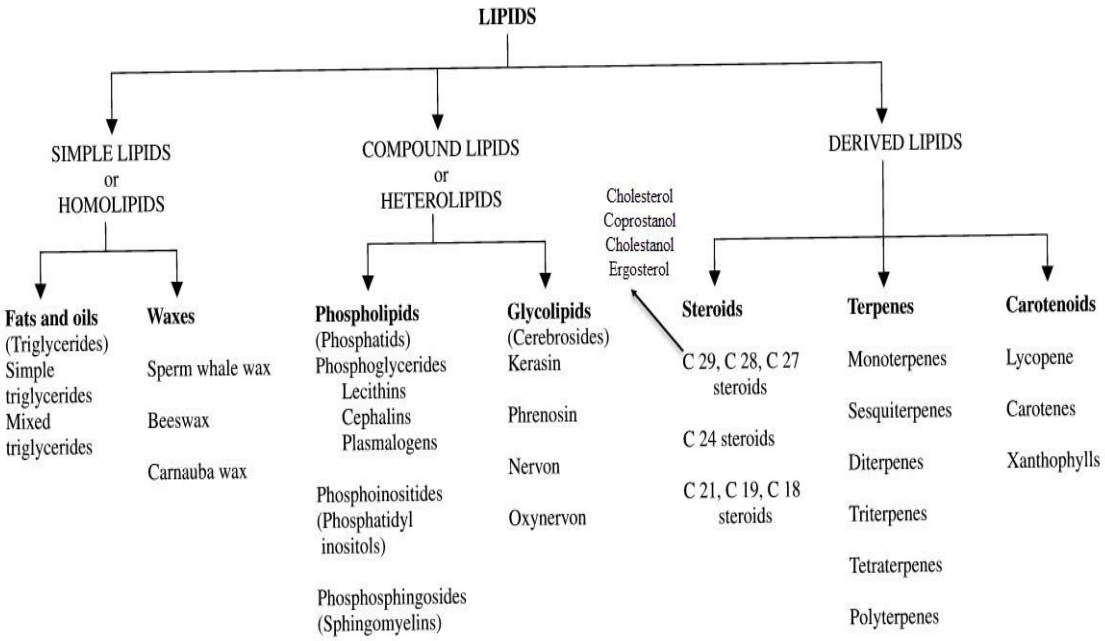
LIPIDS

Lipids are a very important heterogonous group of organic substances which are widely distributed throughout the plant and animal kingdom. The plant they are present in seeds, nuts and fruits, while in animals they are stored in adipose tissues, bone marrow and nervous tissues. Chemically they are various types of esters of fatty acids and alcohol. The addition to fatty acids and alcohols, some of the lipids may contain phosphoric acid, nitrogenous group and carbohydrate. Lipids are relatively insoluble in water and readily insoluble in water and readily soluble in organic solvents such either, chloroform, carbon disulphide benzene, hot alcohol etc. Bloor [1947] defined lipids as "naturally occurring compound which are insoluble in water, and soluble in one or more organic solvent such as benzene, chloroform, either acetone the so called fat solvent on hydrolysis field fatty acids which are utilized by the living organisms''

CLASSIFICATION OF LIPIDS

Lipids are generally classified into three main classes

1. Simple Lipids
2. Compound Lipids
3. Derived Lipids



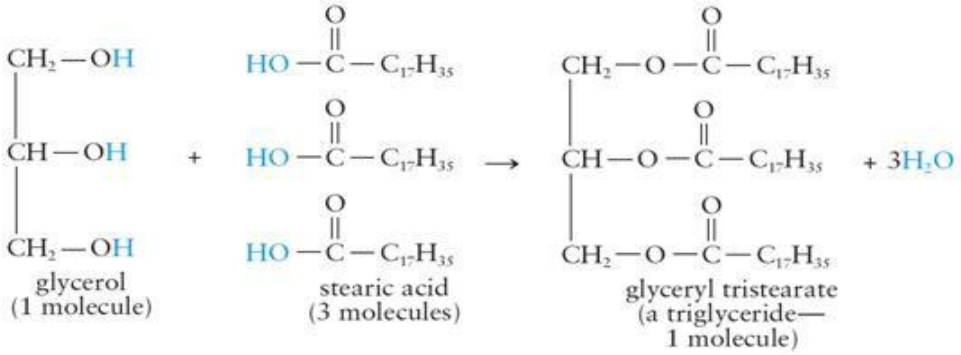
Classification of Lipids

SIMPLE LIPIDS

Simple lipids are the esters of fatty acids with various alcohols. These can be further categorized into fats and waxes. Fats are triesters of glycerol and fatty acids. A fat in the liquid state is called oil. Waxes are the esters of fatty acids with long chain (higher mol.wt.) monohydric alcohols.

Fats

Fats are solids at room temperature. Chemically, fats are triglycerides since, three molecules of fatty acids condense with one molecule of glycerol, e.g. three molecules of stearic acid are linked to glycerol to yield glyceryl tristearate, a fat.



If all the three molecules of fatty acids are similar, the product is a simple glyceride. If fatty acids molecules are different, it is called a mixed glyceride. Natural fats are largely composed of mixed glycerides. Since these glycerides have no acid or basic groups, they are often called natural fats. The melting point of fats depends upon the chain length and degree of saturation of fatty acids. The melting points of fats are always higher than the solidification point, e.g. tristearin melts at 72^0C but solidifies on cooling at 52^0C.

Fats develop unpleasant odor on aging, this is due to auto oxidation of fat. This is called rancidification.

The chemical changes that occur during rancidification are called rancidity. Fats which are liquid at room temperature are called oils. Oils are also esters of fatty acids and glycerol, but the fatty acids found in oils are unsaturated fatty acids. The unsaturated fatty acids have one or more double bonds. They have low melting point and are insoluble in water. Hydrolysis of fats with alkali or enzymes lipase yields fatty acids and glycerol. When the fats are hydrolyzed with alkali, the few fatty acids react with alkali to form salts. These salts are soaps and this process is called saponification.

Waxes

Waxes are another class of simple lipids. These are the esters of fatty acids with high molecular weight alcohol. Waxes contain one molecule of fatty acids and one molecule of alcohol. The bees wax, the fatty acid constituent is a smaller chain acid, palmitic acid and [16^0C] and alcohol is myristic palmitate. Ambretolide found in the seeds of abelmoschus esculentus is a hay hydro nil acid and is responsible for the characteristic smell of the seed. Being highly insoluble in water and having no double bonds in their hydrocarbon chains, waxes are chemically insert. And very resistant to atmospheric condition also not digested by the fat splitting enzymes. They can be split slowly with hot alcoholic KOH, however. They also have higher melting point. They serve as protective coating on fruits and leaves. They play on important role in provide water barrier for insects, birds and animals. They are used in furniture polishing.

Fatty Acids

Fatty acids are obtained from the hydrolysis of fats. Since all the fats contain glycerol, their properties differ according to the nature of fatty acids present in them. A fatty acid can be defined as an organic acid that occurs in a natural triglyceride and is a monocarboxylic acid ranging in chain length from C_4 to about 24 carbon atoms. A few have branched chain or contain hydromel group or have a cyclic

chain at the end. Fatty acids that occur in natural fats usually contain an even number of carbon atoms, one carboxylic group and are straight chain derivatives. On the basis of presence or absence of double bonds, fatty acids may be classified into two main classes-

i. Saturated fatty acids (saturated with hydrogen)
ii. Unsaturated fatty acids

1. Saturated fatty acids

The fatty acids which do not contain any double bond are called saturated fatty acids. The general formula is $C_n\ H_{2n+1}$ COOH e.g. Butyric acid $C_3\ (CH_2)_2$ COOH. The most abundant saturated fatty acids in nature are palmitic acid (C_{18}) and stearic acid (C_{16}). The saturated fatty acids are straight chain acids. In addition to these straight chain acids, there are some branched chain acids, with odd or even number of carbon atoms.eg. Isopalmitic acid, anti-isopalmitic acid and tuberculostearic acid.

2. Unsaturated fatty acids

The fatty acids which contain one or more double bonds are called unsaturated fatty acids. On the basis of number of double bonds, the unsaturated fatty acids may be divided into two groups-
Monosaturated fatty acids: - having one double bond e.g. crotonic acid, oleic acid, palmitoleic acid, nervonic acid etc.
Polyunsaturated fatty acids:-having more than one double bonds e.g. linoliec acid, eleostearic acid etc.
In most of the monosaturated fatty acids there is a single bond lying between carbon atoms 9 and 10. This is designated as Δ^9. The symbol Δ with the superscript number nine (9) indicates the positions of the double bond. When there are more than one double bond (polyunsaturated fatty acids), the additional bonds occur between the Δ^9 double bond and the methyl terminal end of the chain. The symbol 18:3 signifies that there are three double bonds and symbol $\Delta^{9,12,15}$ signifies that the position of double bonds are between carbon atom 9 and 10, 12 and 13 and 15 and 16. Presences of double bonds in the fatty acids lower their melting point considerably. Most plant fats contain unsaturated fatty acids as oleic acid and linoleic acid and hence they are liquid at room temperature. Contrary to this animal fats have more of saturated fatty acids and hence solid at room temperature.

FATTY ACIDS

Common Saturated Fatty Acids

Number of Carbon Atoms	Formula	Common Name	Source
4	$CH_3(CH_2)_2COOH$	Butyric acid	Butter
6	$CH_3(CH_2)_4COOH$	Caproic acid	Butter
8	$CH_3(CH_2)_6COOH$	Caprylic acid	Coconut oil
10	$CH_3(CH_2)_8COOH$	Capric acid	Coconut oil
12	$CH_3(CH_2)_{10}COOH$	Lauric acid	Palm kernel oil
14	$CH_3(CH_2)_{12}COOH$	Myristic acid	Oil of nutmeg
16	$CH_3(CH_2)_{14}COOH$	Palmitic acid	Palm oil
18	$CH_3(CH_2)_{16}COOH$	Stearic acid	Beef tallow
18	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	Oleic acid	Olive oil
18	$CH_3(CH_2)_4CH{=}CHCH_2CH(CH_2)_7COOH$	Linoleic acid	Soybean oil
18	$CH_3CH_2(CH{=}CHCH_2)_3(CH_2)_6COOH$	Linolenic acid	Fish oils
20	$CH_3(CH_2)_4(CH{=}CHCH_2)_4(CH_2)_2COOH$	Arachidonic acid	Liver
22	$CH_3(CH_2)_{20}COOH$	Behenic acid	Sesame oil

Common Unsaturated Fatty Acids

Number of Carbon Atoms	Formula	Common Name	Source
16	$CH_3(CH_2)_5CH{=}CH(CH_2)_7COOH$	Palmitoleic acid	Whale oil
18	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	Oleic acid	Olive oil
18	$CH_3(CH_2)_4CH{=}CHCH_2CH(CH_2)_7COOH$	Linoleic acid	Soybean oil, safflower oil
18	$CH_3CH_2(CH{=}CHCH_2)_3(CH_2)_6COOH$	Linolenic acid	Fish oils, linseed oil
20	$CH_3(CH_2)_4(CH{=}CHCH_2)_4(CH_2)_2COOH$	Arachidonic acid	Liver

Essential and Non Essential Fatty Acids

Essential fatty acids: The fatty acids which cannot be synthesized by human body but are essential for the normal maintenance of the body are called essential fatty acids .These fatty acids must be included in our diet. Three polyunsaturated fatty acids, linoleic acid, linolenic acid and arachidonic acid are the essential fatty acids.

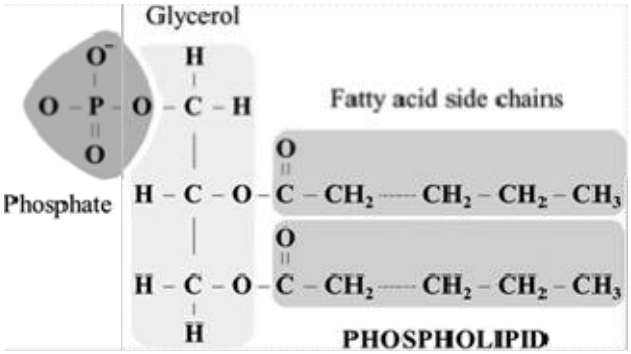
Non essential fatty acid: These are the fatty acids which can be synthesized by our body. Thus they need not be included in our diet. They are unsaturated fatty acids and are synthesized from their corresponding saturated fatty acids by introducing a single bond .e.g. palmitoleic acid and oleic acid.

COMPOUND LIPIDS

Compound lipids contain some additional groups or elements besides fatty cids are alcohol. The addition group may contain phosphorus, nitrogen, sulpher or it may be a protein. Compound lipids can be categorized into the following: Phospholipids, Glycolipids, Other compound lipids.

Phospholipids

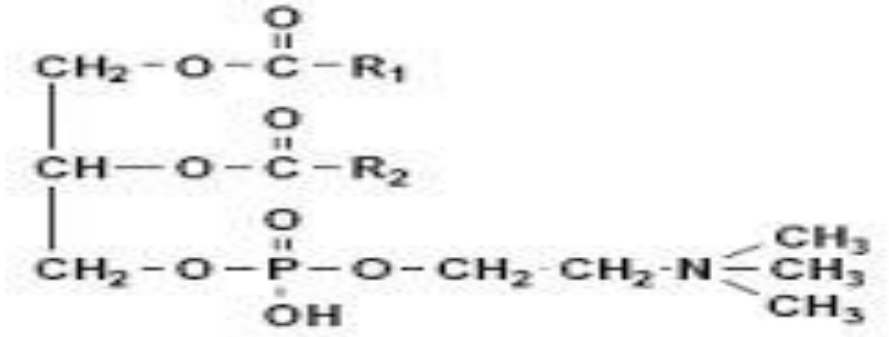
Phospholipids are those compound lipids which contain a phosphorus atom. Phospholipids are wide spread in bacteria, animal and plant tissues and their general structures are quiet similar. These have been termed as amphipathic and compound since they process both polar and non polar function.



In addition to phosphorus, phospholipids may also contain nitrogen as a key component. There are various types of phospholipids including- lecithin, cephalins, plasmalogens, phosphoinositides and phosphosphingosides.

Lecithin

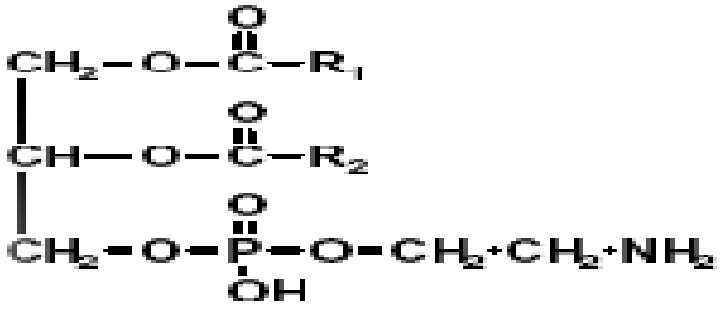
Lecithin is widely distributed in nature. In animals it is found in liver, brain, nerve tissues, sperm and egg yolk. In plant it is abundant in seeds and sprouts. On hydrolysis, lecithin yields glycerol, fatty acids, phosphoric acid and nitrogenous base - choline. It is also called phosphatidyl choline. The fatty acids commonly found in lecithin are palmitic, stearic, oleic, linolenic and arachidonic acids. Lecithin is yellowish grey solid which is soluble in with soluble in ether and alcohol but insoluble in acetone. On exposure to air they rapidly darken colour and absorb water, forming dark grassy mass. Lecithins are broken down by the enzyme lecithinase to lysolesithin which is present in venoms of bee and cobra. When injected into the blood, lysolecithins cause rapid haemolysis of the red blood cells.



Lecithin (phosphatidyl choline)

Cephalins

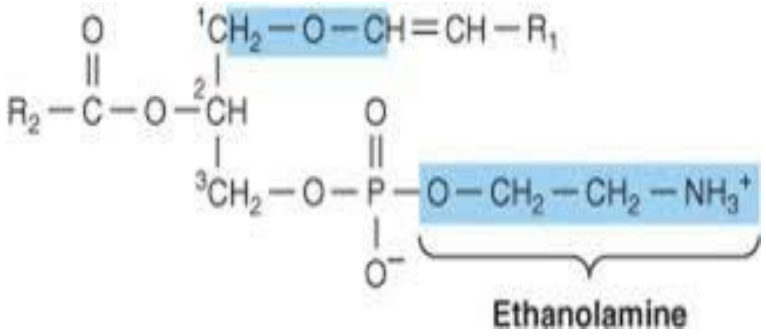
Cephalins are found in animal tissues in close association with lecithin. They are also found in soya bean oil. The basic difference between cephalins and lecithin is the nature of nitrogenous base. Cephalins contain ethanolamine in place of choline. The fatty acid components of cephalins are stearic, oleic, linoleic and arachidonic acid. They are less soluble in alcohol then lecithin.



Cephalin
(Phosphatidyl ethanolamine)

PLASMALOGENS

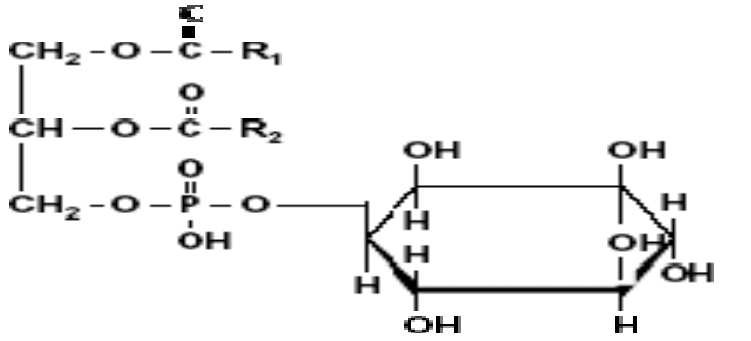
Plasmalogens are abundant in brain and muscles they are also found in the seeds of higher plants. Structurally, they resemble lecithin and cephalins except in having an aldehyde group attached to ex – carbon atoms of glycerol. They are soluble in all lipid solvents.



Plasmalogen

Phosphoinositides

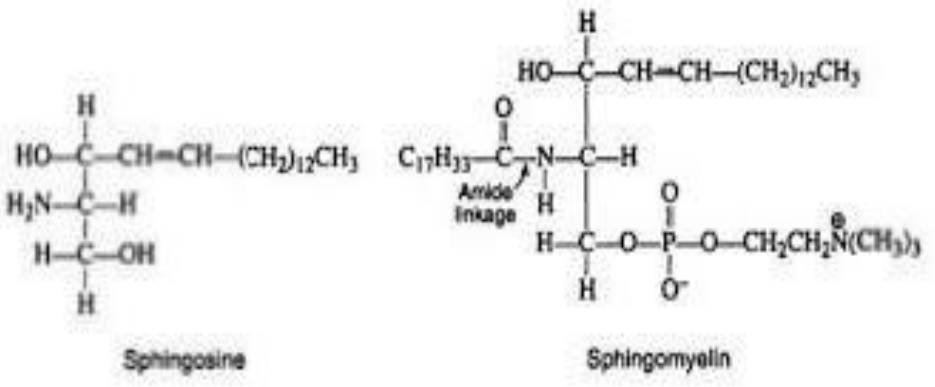
They are present in brain tissues and nervous tissues. They can be either mono or diphosphoinositides. Monophosphoinositides contain hexahydric alcohol inositol. The name lipoinosital was also proposed for them.



Phosphatidyl inositol

PHOSPHOSPHINGOSIDES

These lipids are abundant in lacking in plant and microorganisms. In these lipids glycerol is replaced by an 18 carbon unsaturated amino alcohol called ‘sphingosine’. On hydrolysis they yield fatty acids, phosphoric acid, choline and sphingosine.



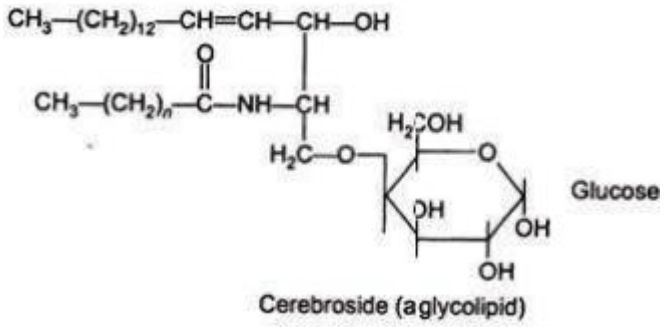
Sphingosine Sphingomyelin

Glycolipids

Glycolipids are compounds containing carbohydrates and high molecular weight fatty acids like sphingosine but no phosphoric acid. These are of two types: Cerebrosides and Gangliosides.

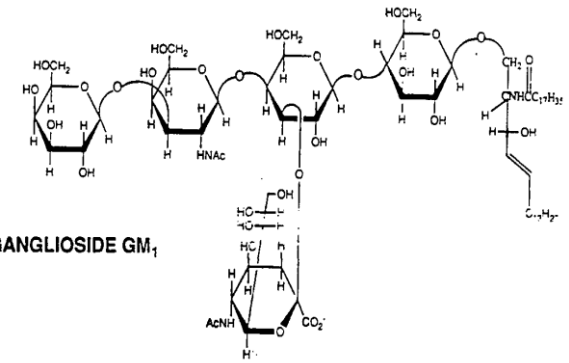
Cerebrosides: They occur in large amount in brain and myelin sheath of nerves. The structure of cerebrosides is somewhat similar to sphingomyelin. Here the fatty acid ceramide is linked either to galactose or glucose.

Gangliosides: These are found in ganglion cells of nervous tissues and also in parenchymatous tissues like spleen and RBCS, They are the most complex glycosphingolipids. They are ceramides with attached oligosaccharides that include at least one sialic acid residue.



Cerebroside (aglycolipid)

Glucose



GANGLIOSIDE GM_1

Other compound lipids

Sulfolipids: Lipids containing sulfer, widely distributed in plant (localized in chloroplast) and bacteria.

Lipoprotein: They are the component of membranes found in the membranes of mitochondria, ERL

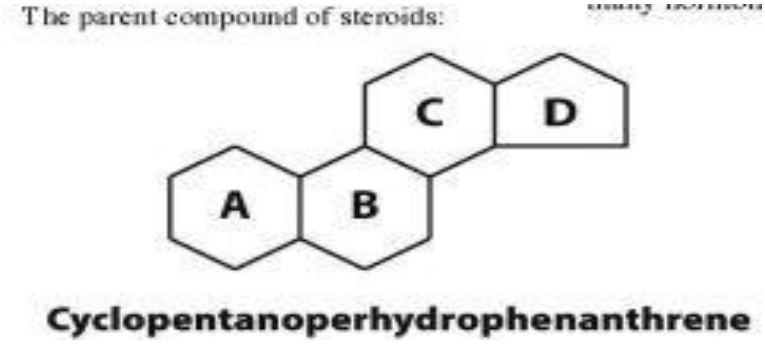
The lipid component consists of triacylglycerol, phospholipids and cholesterol. The protein components of lipoprotein have a relatively high portion of non polar acid residues.

DERIVED LIPIDS

Derived lipids are the product of hydrolysis of simple lipids and compound lipids and in addition other lipid like compounds such as steroids, terpenes, fatty acids, alcohols, carotenoids, essential oils etc.

Steroids

Steroids are the derivatives of cyclopentanoperhydrophenanthrene, a compound consisting of four fused non planer rings. They are named as A, B, C and D. The rings A, B and C are hexagons and are called cyclohexane rings while D is a pentagon and is called cyclopentane.



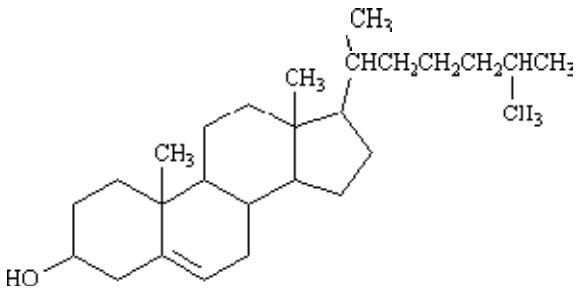
Sterols

The steroids may have one or more alcoholic groups. The steroids having alcoholic groups are called sterols. They are crystalline compounds and differ from alcohols in being solids that is the reason they are called so. Steroids are widely distributed in plant, animals and microorganism. They are found in cell membranes and other cellular component containing lipids. Unlike other lipids, sterols cannot be saponified and by this process they can be separated from other lipids. Ergosterol is present in food in small amount. It has been isolated from parasitic fungus Claviceps pupurea (Ergon) growing on rye plants. Other plant sterols are spinasterol obtained from spinach and cabbage, stigmasterol from coconut and soyabeans and sitosterol from cereal seeds.

Cholesterol

The best known animal sterol is cholesterol, which is a major component of animal plasma membrane. It is classified as sterol because of its C30H group It is present in relatively high concentration in

nervous tissues and in bile. Cholesterol is a crystalline solid with rhombic crystals and its solution is levorotatory. It has a high melting point.



Cholesterol

In mammals, cholesterol is the metabolic precursor of steroid hormones – adrenocorticoids and sex- steroids.

Adrenocorticoids

They are secreted by the adrenal cortex hormone contains – glucocorticoids, aldosterone, cortisterone, desoxycortisterone adrenosterone and other mineral corticoids influence a wide variety of vital functions.

SOURCES OF LIPIDS

Lipids are widely distributed in plants and animals. Common sources of fatty acids are butter, coconut oil, animal fats and some bacteria. Lecithin, a type of phospholipids is found in liver, brain, nerve tissue, sperm and yolk sac in animals while in plants it is abundant in seeds and sprouts. Similarly other phospholipids and glycolipids are also found in animal tissues like brain, muscles and nervous tissues. Terpenes and carotinoids are types of derived lipids which are exclusively of plant origin.

BIOLOGICAL SIGNIFICANCE OF LIPIDS

1. Rich source of energy: fats provide food of high calorific value (1g fat produces about 9.3 kilo calories of heat).
2. As food reserve: Fats are stored in body as reserve food material, because these could be readily stored in the body on account of insoluble character sticks. Triglycerides stored in adipocytes (fat cells) of adipose tissue are the principal fat reserve.
3. As heat insulators: Fats deposited in the subcutaneous tissues act as insulators conserving body heat.
4. Solvent: Lipids act as a solvent for fat soluble vitamins like vitamin A, D and E.

5. Structural constituents: Phospholipids, glycolipids and sterols are structural components of all the membrane system of cell (i.e. cell membrane, nuclear membrane, membranes of the endoplasmic reticulum etc.)
6. Fat transport: Phospholipids play an important role in the absorption and transportation of fatty acids.
7. Hormone synthesis: Adrenocorticoids, sex hormones, vitamin D and cholic acids are synthesized from cholesterol.
8. As shock absorber: The fat deposited around the visceral organs and underneath the skin acts as cushion and absorbs mechanical shocks.
9. As electric insulators: Myelin sheath around medullated nerve fibres forms an electric insulation.
10. Prostaglandins: They control local activities in the body.
11. Protective layers: Lipids form a protective waxy covering on the aerial parts of plants to check loss of water by evaporation.
12. Thrombokinase: helps blood clotting.
13. Leukotrienes: a group of eicosanoid helps in respiration.
14. Some isoprenoids form insect hormones.
15. Some insoprenoids form volatile oil and pigments. Natural rubber is also an isoprenoid.
16. Glycolipids help in cell recognition.
17. Complex lipids form phospholipid bilayer of plasma membrane.
18. Steroid act as hormones and neurotransmitters in mammals.

DEFICIENCY DISEASES OF LIPIDS

The deficiency of lipids in human body causes dry, scaly skin, hair loss, loss of mensuration, cold intolerance, power resistance to infection and bruising, poor growth, poor wound healing and low body weight.