Unit 2

Lipids

Lipids are organic compounds containing Carbon, hydrogen and oxygen. However, H and O_2 occur in a much higher ratio in lipids than water. Lipids form about 3.5% of the total chemical compostition of cell. Carbohydrates and lipids fulfil the majority of the energy requirment of the human body through oxidation. Carbohydrates yeild 4 Kcal of energy per gram and lipid yeild 9 kcal of energy per gram. However unlike Carbohydrates, lipid are reserved energy Sources. This is because system is incapable of storing a large amount of glycogen.

Defination:

Lipids is the name given to fatty acids and their derivatives and substances related biosynthetically or functionally to these compounds. Fatty acid are carboxylic acids with straight chains of Carbon atoms (aliphatic chains, commonly C14-C24). They may be saturated or unsaturated and can contain a varity of substituent groups. In general, fatty acids have the following molecular formula

$$CH-(CH_2)_n-COOH.$$

Fat, oil and wax are examples of fatty acid (or Lipids)

Constituents of a Lipid Molecule:

By defination, two major constituents of lipids are alcohol and fatty acid. The alcohol component may be saturated or

Unsaturated while the fatty component of lipids may be following four types:

① Saturated fatty acid (without double bond in its structure)
Example: palmitic acid and Stearic acid.

② Unsaturated fatty acid (with double bond in structure.)
Example: Oleic acid and linoleic acid.

③ Hydroxy fatty acid.
Examples: Ricinoleic acid, Cerebronic acid and Dihydroxy Stearic acid.

④ Cyclic fatty acid.
Example: Hydnocarpic acid and Chaulmoogric acid.

Functions of Lipid:
The following are some important functions of Lipid:

* They are $ Reserve source of energy.
* They provide high calorific value.
* They are structural component of cell membrane.
* They act as an insulating component.
* They help in absorption and transport of fatty acid.
* They are involved in biosynthesis of Cholesterol, Sex hormones and Vitamin D.
* They are carriers of fat-soluble Vitamins.

Physical properties of lipid:

Physical properties of lipids may be listed as follows:

(a) Lipids are colourless, odourless and testless.
(b) Lipids are amphipathic in nature, that is they have polar (-COOH) and non-polar (CH_3) groups.
(c) Lipids are capable of absorbing odur.
(d) Lipids are insoluble in water and soluble in organic solvents.
(e) Lipids have high melting point. This depends on the degree of unsaturation as melting point is inversely related to unsaturation.
(f) Lipids have specific gravity less than 1.
(g) They exibits geometrical isomerism due to the presence of double bond in unsaturated fatty acid.
(h) Lipids have high insulating power.
(i) Lipids exhibits emulsification property. (Emulsification is a prosses by which lipids combine with water or emulsifying agents, such as soaps, gums or proteins, and form aggregates or droplets called micelles.
(j) They function as precursors for the synthesis of keton bodies.

Chemical properties of lipids:

(a) Hydrolysis –

Lipids $\xrightarrow[\text{enzyme}]{\text{Lipase}}$ Fatty acid + Diacyl glycerol $\xrightarrow[\text{enzyme}]{\text{Lipase}}$ Fatty acid + Monoacyl glycerol

(b) Saponification or soap formation:

Fat + alkali (NaOH/KOH) → Glycerol + Sodium salt of fatty acid (Soap).

Sodium salt of higher fatty acid → Hard Soap

potassium salt of higher fatty acid → Soft soap.

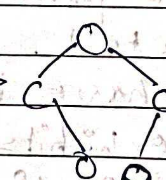
(c) Hydrogenation:

unsaturated fat (vegetable fat) (−CH=CH−) $\xrightarrow[H_2]{\text{Platinum/palladium}}$ Saturated fat (solid fat) $(-CH_2-CH_2-)$

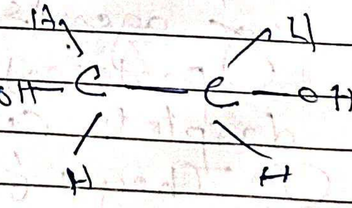
(d) Halogenation:

Unsaturated fat $\xrightarrow[\text{Acetic acid / Methanol}]{\text{Halogen}(x)}$ Chloride derivative (−CHCl−CHCl−)

(e) Oxidation:

−CH=CH− + Ozone →  $\xrightarrow{H_2O}$ Aldehyde

Ozonide

−CH=CH− $\xrightarrow{\text{Mild } KMnO_4}$ Glycol 

(f) Aldehyde formation:

Fat $\xrightarrow[KHSO_4]{\text{Heat, Dehydrating}}$ Unsaturated aldehyde → pungent odour.

Structure of lipids:

Lipids are esters (Ester is a compound formed by the combination of an acid with glycerol with the removal of water) of glycerol and fatty acid. They are formed by the combination of alcohol and fatty acids.

Usually a lipid is made up of a glycerol and three fatty acids. Such a lipid is called a triglyceride or a neutral fat.

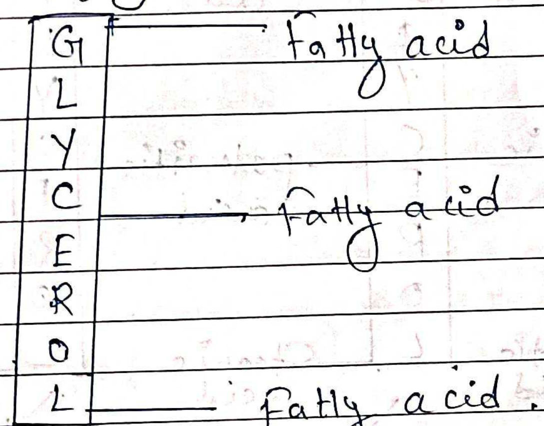
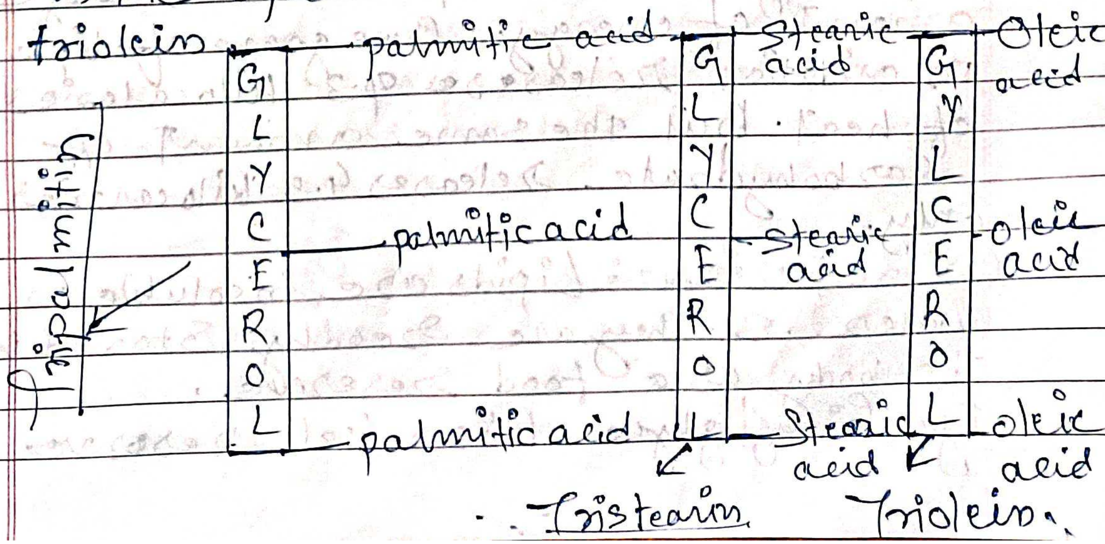


Fig.. A simple structure of a simple lipid.

When the fatty acids present in the lipid are palmitic acid, the lipid is called tripalmitin. Simillarly, when the fatty acids present in the lipid are Stearic acid, the lipid is called tristearin. When the fatty acids present in the lipid are oleic acid, the lipid is called triolein.



When the lipid contains two Stearic acids and one palmitic acids, the lipid is called distearopalmitin. The lipid dipalmito olein contains two palmitic acid and one oleic acid. The lipid dioleo Stearin contains two oleic acids and Stearic acid. The lipid palmito-oleo-Stearin contains one palmitic acid, one oleic acid and Stearic acid.

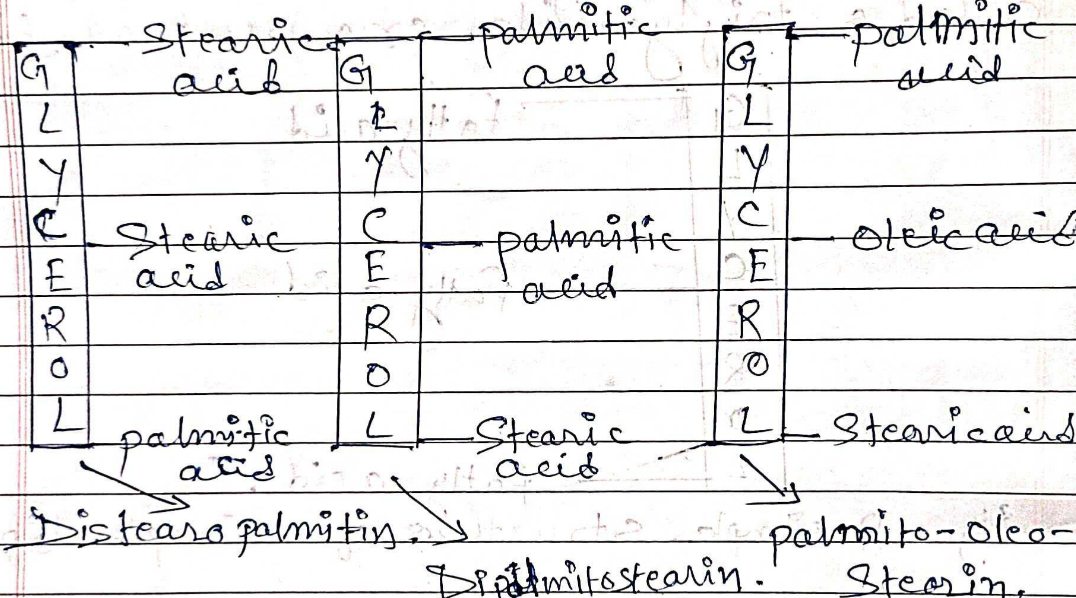


fig. Structure of lipids.

Significance of Lipids:

1. Energy source: Lipids contains large amount of energy. One gram of lipid on oxidation releases 9.3 kilocalories of heat. But the same amount of carbohydrate releases 4.5 kilocalories only.
2. Food Reserve: Lipids are insoluble in water. So they are readily stored in the body as a food reserve.
Eg: Triacylglycerol is a food reserve.

It is used as a substrate for oxidation.

(3) Structural component: Lipid constitute an important component of cell membrane

(4) Transportation: phospholipids transport cations across the lipid layer of biomembranes.

(5) Electric Insulation: Lipids serve as an electro insulating material in the myelin sheath of neurones.

(6) Heat Insulation: Subcutaneous fats of mamals act as a insulator against excessive heat loss to the enviroment.

(7) Emulsification: Amphipatic lipids are emulsifiers. The process of emulsification is great metabolic significance. In fact, the fats have to be emulsified before they can be absorbed by the intestinal wall. This process is accomplished by the bile juice secreted by the liver.

(8) Mechanical: Lipids of connective tissue of internal organs protects them from eventual damage on exposure to mechanical action.

(9) Dissolving capacity: Under physiological conditions, certain lipids function as solvents to dissolve other lipids. Eg. Bile acids are solvents for insoluble vitamins in the intestine

(10) Hormones: The major group of hormones is formed of steroids. They regulate a large variety of physiological functions.

(11) Prostaglandins: Prostaglandins are modulator of hormones, derived from fatty acids.

(12) Vitamins: Vitamin-D, calciferol is a steroid derivative. It possesses a steroid structure. It is synthesized from cholesterol.

(13) Vitamine carriers: Lipids acts as a carrier of natural fat soluble vitamins such as A, D and E.

(14) Enzyme Activation: Lipids are essential for the activation of enzymes. Eg. Glucose-6-phosphatase.

Physiologically important Saturated and Unsaturated fatty acids:

(a) Saturated fatty acid: The saturated fatty acids have single bond. Their general formula is $C_nH_{2n}+COOH$.

They have maximum possible number of hydrogen atoms. At one end there will be an acid group (COOH). At the other end there will be a methyl group (CH_3). In between these two groups there will be CH_2 group.

The saturated fatty acids end with the suffix -anoic.

Eg. Octanoic acid, Decanoic acid, Butanoic acid etc.

The saturated fatty acid (palmitic and stearic acid) found high percentages in fats.

Simple lipids containing a large numbers of saturated fatty acid are called fats and they have a solid consistency. Saturated fatty acids are also called animal lipids. Examples of saturated fatty acids are butter fat and beef.

Saturated Straight Chain fatty acid:

Sl. No	Trivial name	Systematic name	No. of Carbon	Structure	Common source
1	Butyric acid	Butanoic acid	4	$CH_3(CH_2)_2COOH$	Butter
2	Caproic acid	Hexanoic acid	6	$CH_3(CH_2)_4COOH$	coconut and palm oil
3	Caprylic acid	Octanoic acid	8	$CH_3(CH_2)_6COOH$	"
4	Capric acid	Decanoic acid	10	$CH_3(CH_2)_8COOH$	"
5	Lauric acid	Dodecanoic acid / Tetradecanoic acid	12 / 14	$CH_3(CH_2)_{10}COOH$	Kernel oil, Spermaceti
6	Myristic acid	Hexadecanoic acid	16	$CH_3(CH_2)_{12}COOH$	Butter and wool fats
7	palmitic acid	Octadecanoic acid	18	$CH_3(CH_2)_{14}COOH$	Animal and plant fats
8	Stearic acid	Eicosanoic acid	20	$CH_3(CH_2)_{16}COOH$	"
9	Arachidic acid	Docosanoic acid	22	$CH_3(CH_2)_{18}COOH$	ground nut oil
10	Behenic acid	Tetracosanoic acid	24	$CH_3(CH_2)_{20}COOH$	"
11	Lignoceric acid	Hexacosanoic acid	26	$CH_3(CH_2)_{22}COOH$	"
12	Cerotic acid			$CH_3(CH_2)_{24}COOH$	rapeseed oil wool fat.
13	Montanic acid	Octacosanoic acid	28	$CH_3(CH_2)_{26}COOH$	

Saturated branched chain fatty acid:

Sl. No	Systematic name	Trivial name	No of carbon		Common Source
1	Isohexadecanoic acid	Isopalmitic acid	16	$CH_3-CH(CH_3)(CH_2)_{12}COOH$	wool fat
2	14-methyl hexadecanoic acid	Anti-isopalmitic acid	17	$CH_3CH_2-CH(CH_3)(CH_2)_{12}COOH$	"
3	D(-)10-methyl octadecanoic acid	Tuberculostearic acid	19	$CH_3(CH_2)_7CH(CH_3)(CH_2)_8COOH$	bacteria

The saturated fatty acid 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.

But these are the minor components of natural fats and oils. Isopalmitic acid, ante-isopalmitic acid, tuberculostearic acids are some examples of branched chain fatty acids identified in fats.

(b) Unsaturated fatty acids:

The unsaturated fatty acids have one or more double bonds, i.e 1 to 6 double bonds. These double bonds may occur after 9, 12, 15, 18 etc. carbon atoms.

The unsaturated fatty acids are named with the suffix -enoic. Based on the number of double bonds unsaturated fatty acids may be called as monoenoic (one =) dienoic (two =) trienoic (three =) acid --- etc.

In the most unsaturated fatty acids there is a single double bond lying between carbon atom 9 and 10. This is designated as Δ (Δ = delta). The symbol Δ with the superscript number 9 indicates the position of double bond. When there are more than one double bond the additional bonds occur between the Δ^9 double bond and the methyl terminal end of the chain.

The symbol 18:0 denotes a C_{18} fatty acid with no double bonds. The number 18:2 signifies that there are two double bonds. Similarly the symbol 18:2, 9, 12 is used to denote an 18 carbon fatty acid with two double bonds in the 9 and 12 positions.

When two or more double bonds present in the fatty acid, the double bonds are never conjugated. But the double bonds are separated by a methylene group.

~~$-CH_2-CH=CH-CH=CH-CH_2-$~~

$-CH_2-CH=CH-CH_2-CH=CH-CH_2-$

Unsaturated fatty acid containing more than one double bond is called polyunsaturated fatty acid. The unsaturated fatty acids are common in living organism.

Nemotinic acid is one of the few naturally occurring compounds containing the allene group along with single, double and triple carbon-carbon linkages. It is excreted in the ~~group~~ growth median by citrivorium mold.

Santalbic acid, a major component of seed oil of sandal wood contains one acetylene group.

Due to the presence of C=C in unsaturated fatty acids geometrical isomerism is possible. Depending on the spatial arrangement of groups or atoms around the C=C two isomers are possible. They are cis and trans isomers. In cis isomers identical groups are ~~the~~ on the same side of the C=C. In trans isomers identical groups are occupying opposite sides of C=C. Example:- Oleic acid and elaidic acid.

In the unsaturated fatty acid, if the double bonds are in alternate carbon atoms then it is said to be a conjugated unsaturated fatty acid. Example :- α-elaeostearic acid.

If the double bonds are not in alternate positions unsaturated fatty acid is called non-conjugated fatty acid. Example: Linoleic acid.

The hydrocarbon chains of saturated fatty acid is in a zig-zag manner. The zig-zag configuration is a stable configuration. Example: Stearic acid.

When a cis double bond is inserted into a stearic acid, an oleic acid is formed. Oleic acid has got the bent structure.

Phospholipids:

→ Phospholipids are compound lipids. Phospholipids are the most abundant membrane lipids. They contain phosphorus in the forms of phosphoric acid group. They differ from triglycerides in possessing usually an hydrophilic polar "head" group and usually two hydrophobic non-polar "tails". Thus they are refferred as amphipathic. They contain fatty acid, glycerol, phosphoric acid and a nitrogenous compound. They are formed by glycerol, phosphoric acid and fatty acids. They are also called Phosphatids.

→ They are the structural component of membranes and so are abundant in brain, kidney etc.

→ Due to the presence of phosphoric acid group phospholipids behave as polar lipids.

→ They are hydrofilic in nature.

→ Phospholipids are amphipathic in nature.

→ phospholipids are further divided into
1. Lecithins 2. Cephalins 3. plasmologens
4. Phospho-inositides 5. Phosphingosides.

(a) Lecithins:

→ Lecithins are compound lipids. They are phospholipids.

→ Lecithins are the esters of glycerol with fatty acids.

→ Lecithins are yellowish grey solids, soluble in ether, alcohol etc.
→ They swell in water and form colloidal solutions.
→ They are dextrorotatory.
→ It has an important role in fat metabolism in liver.

CH_2OH — [Fatty acid]
|
$CHOH$ — [Fatty acid]
|
CH_2OH — [Phosphoric acid] — (Choline)

fig: Lecithin.

Functions of Lecithin:

1. It is a component of plasma membrane.
2. It transports fats and oils through the plasma membrane.
3. It brings about cell communications.
4. It is a source of B vitamins such as choline and inositol.
5. Lecithin improves memory.
6. Food additive.
7. It needs for healthy gall bladder and heart
8. It improves learning.

(b) Cephalins:

→ Cephalins are compound lipids. They are phospholipids.
→ It is the ester of glycerol and fatty acid.
→ The two hydroxyl groups of glycerol are linked to two fatty acid.
→ The third hydroxyl group of glycerol is linked to a phosphoric acid.
→ The phosphoric acid is linked to ethanolamine.

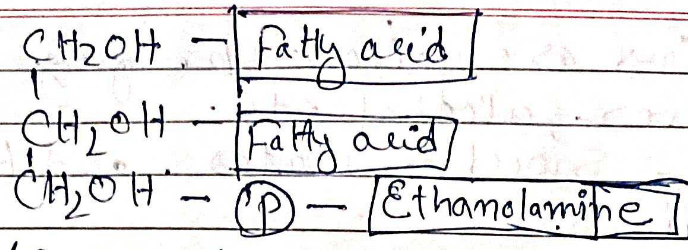


fig: Cephalin.

→ It occurs in all cells, soyabean oil, etc.
→ It is abundant in brain cells.

Functions of cephalins:

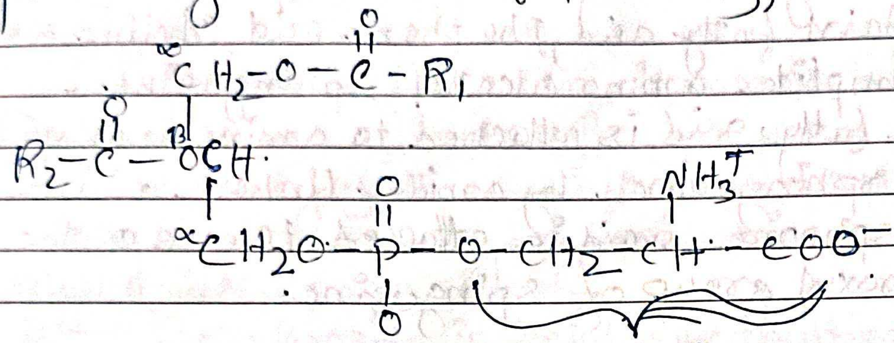
→ Cephalin is a component of plasma membrane.
→ It is found in the inner lipid layer of plasma membrane.

→ The brain cells contain 4.5% of cephalins.
→ It is involved in membrane fusion in cytokinesis.
→ It propagates infectious prions without the help of nucleic acids.
→ Improves blood clotting.
→ It causes vascular disease, diabetes and cancer.

ⓒ Plasmologens:

→ Plasmologens are phospholipids.
→ These are found in brain, muscles and seeds of higher plants.
→ Structurally, plasmologens resemble lecithins and cephalins except in having one unsaturated ether group in the place of fatty acids groups.

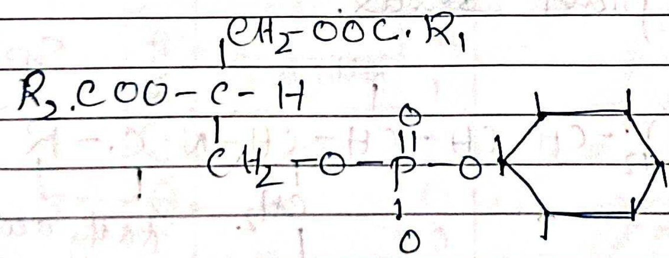
→ It is soluble in all lipids of solvents.
→ Since the base is a nitrogen base it may be Choline, ethanolamine or Serine. Due to this plasmalogens are of three types.



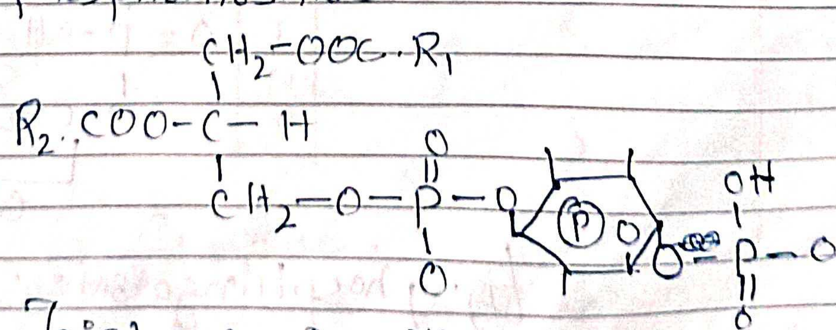
Serine

ⓓ phosphoinositides:

→ In these phospholipids a cyclic hexahydroxy alcohol inositol replaces the base. So these lipids may be otherwise known as lipoinositol.
→ It is found to occur in phospholipids of brain tissues, soyabeans and also in nervous tissue.
→ These are of highly important due to their role in transport processes in cells.



Monophosphoinositide.



Triphosphoinositide.

Fig. phosphoinositides.

(c) Phosphingosides:

→ These are phospholipids. Sphingomyelines differ radically from cephalin in composition. They contain fatty acid, phosphoric acid, choline and a complete amino alcohol sphingosine. The fatty acid is attached to amino group of sphingosine by amide linkase. The phosphoric acid is attached to one of the hydroxyl group of spingosine.

→ On hydrolysis, the phosphingosides yeild equimolecular mixure of fatty acid, phosphoric acid, choline and sphingosine or dihydrosphingosine. No glycerol is formed

→ It is commonly found in nerve tissue especially in the myelin sheath of the nerve. So the name is sphingomyelins. It is found in brain and spinal cord and in plant seeds.

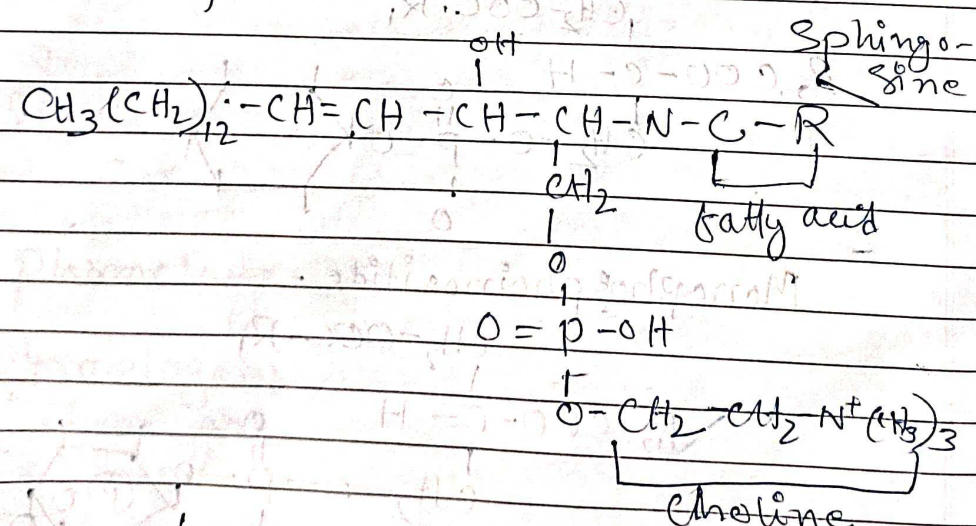


fig. phosphingo sides.

Glycolipids:

→ Glycolipids are compound lipids containing sugar and high molecular weight fatty acids.
→ It is found in the brain, adrenals, kidney, spleen, liver, leukocytes, thymus, lungs, retina, egg yolk and fish sperms.
→ Cerebroside and gangliosides are important glycolipids.
→ Cerebroside is relatively abundant in liver, spleen and medullated nerve fibres.
Cerebroside is made up of 3 components namely –
① Sphingosine ② fatty acid ③ Carbohydrate
The Sphingosine is an amino alcohol with a long unsaturated hydrocarbon chain.
The molecular formula is $C_{16}H_{37}NO_2$.

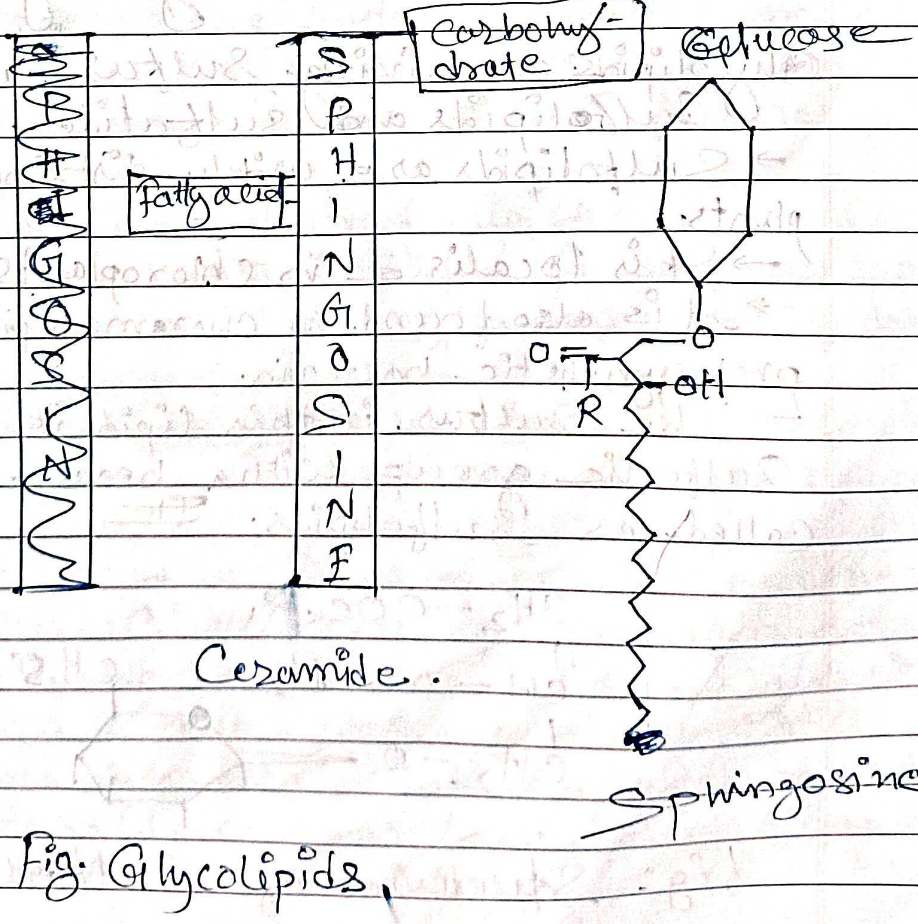


Fig. Glycolipids.

→ It is a nitrogen containing base.
→ The fatty acid linked to the amino ~~acid~~ group of sphingosine by an amide linkase.
→ The sphingosine and fatty acid together from a waxy substance called ceramide.
→ The carbohydrate is linked to the primary alcoholic group of sphingosine through a glycosidic linkase.
→ The carbohydrate may be glucose or galactose.
→ If the carbohydrate is a glucose unit then the cerebroside is called gluco-cerebroside.
→ If the carbohydrate is a galactose unit then the cerebroside is called galacto-cerebroside.

Sulfur Containing Glycolipids:

Glycolipids containing sulfur are called sulfolipids and sulfatides.
→ Sulfolipids are widely distributed in plants.
→ It is localised in chloroplasts.
→ It is also found in choramatophores of photosynthetic bacteria.
→ The sulfur in this lipid is in the sulfonic group with a hexose. So it is called as sulfolipids. ~~Th~~

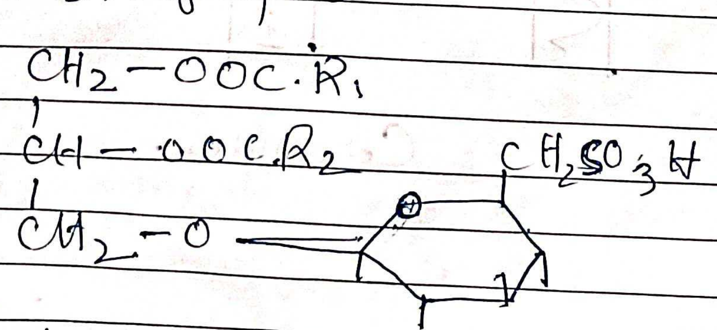


fig: Structure of sulfolipids.

Sulfatide:

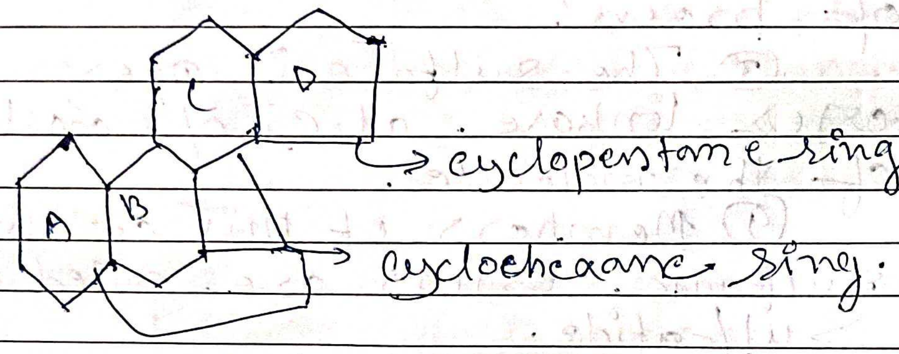
① It is surfur containing glyco-lipids. It is a sulfate ester analogue to phrenosin.
② It is present in the white matter of brain.
③ The sulfate is present in the ester linkage at C_3 of galactose portion of the molecule.
④ Members of this cerebroside sulfuric esters are called as ~~sulfi~~ Sulfatide.

Steroids

Steroids are non saponifible lipids. They can't yeild soap on hydrolysis because they don't contain fatty acid. compounds containing 1,2-cyclopentanoperhydro phenanthrene nuclei in their structures are called steroids. Steroids have following salient features:

① Steroids are derived lipids.
② They are non saponifiable lipids. They don't yeild Soap on hydrolysis because they don't contain fatty acid.
③ The steroids separated from fat when fat is saponified. Steroids occur in no saponifiable residue.
④ Steroids are readily soluble in ether, benzene, chloroform, petroleum and acetone but insoluble in water, acid and alkalise.
⑤ However, in the presence of bile salts, they are rendered soluble even in water.
⑥ The steroids contains four rings. They are named as A, B, C and D.

The rings A, B and C are hexagonal and called cyclohexame rings and the ring D is a pentagon called cyclopentane.
The 3 cyclohexane rings are fused in a non-linear or phenantherene manner.



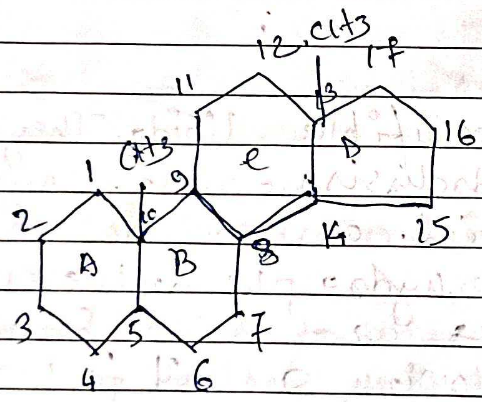


Fig: cyclopentanoperhydrophenanthrene, with numbering of carbon atoms.

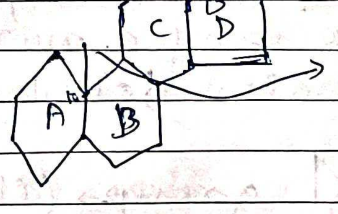
The cyclopentane ring is fused terminally. This ring system is called – Cyclopentanoperhydophenanthrene or Sterane.
The numbering of carbon atoms starts from the ring A to D.

(7) Most of the sterols possess a double bond at position 5 and some others at position 7.

(8) Cholesterol, a steroid, contains two angular methyl (CH_3) groups, namely C-18 and C-19. Methyl group C-18 is attached to the carbon atom number 13. Methyl group C-19 attached to the carbon atom number 10. A line above C-10 or C-13 denotes a methyl group.

(9) The steroids may have one or more alcoholic groups (OH). The steroids containing alcoholic groups are called sterols. These are crystalline compound containing secondary alcoholic group. They differ from common alcohols in being solids and due to this they are known as sterols. The OH group may be present on carbon atom 3.

(10) The steroids may contain a side chain at carbon 17. The number of carbon atoms in the side chain serves as a convenient basis for classification of steroids. For example, in sterols the side chain contains 8, 9 and 10 carbon atoms. In bile acids the side chain contains 5 carbon atoms. In adrenal cortical steroids and progesterone the side chain contains 2 carbon atoms and in oestrogens and androgens no carbon atoms.



This line indicate the presence of CH_3 group.

(11) The common steroids are cholesterol, coprostanol, ergosterol, bile acids, androgens, oestrogens, progesterone, adrenal corticoids.

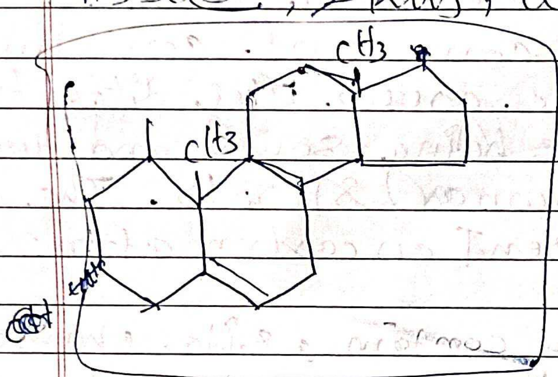
(1) Cholesterol:

(a) Cholesterol is a lipid. It is a derived lipid. It is an unsaturated solid alcohol.

(b) Cholesterol means solid bile alcohol. ~~It is~~

(c) It is found only in animals fats. They are absent from plants fats.

(d) They are abundant in the brain, nervous tissue, skin, liver, adrenal gland etc.



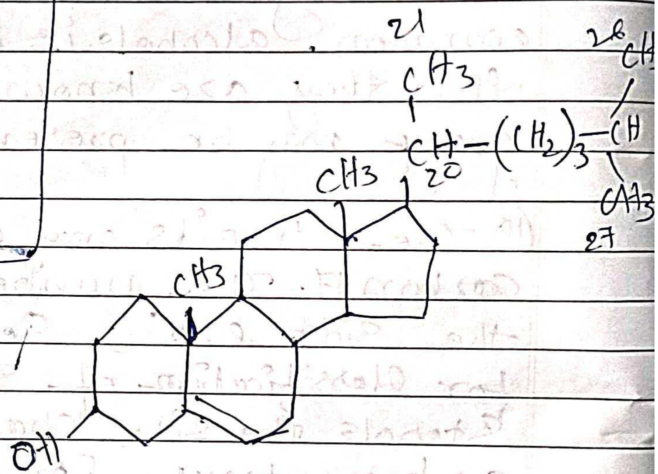


Fig: Cholesterol.

(e) The Cholesterol has a 1,2-cyclopentanoperhydrophenanthrene nucleus. It has four rings namely A, B, C and D. The rings A, B and C are hexagonal and D is pentagonal.

(f) It has an OH group at C number 3.

(g) It has an unsaturated double bond between C_5 and C_6.

(h) It has two methyl groups (CH_3) at C_{10} and C_{13}.

(i) It has 8 carbon side chain attached to C_{17}.

(j) The molecular formula of Cholesterol is $C_{27}H_{45}OH$.

Properties of Cholesterol:

(a) It is solid in nature and exists in Colourless crystals.
(b) It has high melting point: 150°C
(c) It is insoluble in water.
(d) It is not Saponifiable.

Biological functions of Cholesterol:

(a) It is found in the skin produces Vitamin D on exposure to sunlight.
(b) It is used for the synthesis of steroids hormone.
(c) It is a culprit causing heart attack.
(d) It is required to build and maintain plasma membrane.
(e) It can reduce membrane fluidity.
(f) It reduced the permeability of plasma membrane to neutral solutes, H^+ ions and Na^+ ions.
(g) It is essential for intracellular transport, Cell Signalling and Nerve conduction.

(2) Coprostanol:

It occurs in faeces. It is produced in intestine by the bacterial action on the double bond of cholesterol.

(3) Ergosterol:

Steroid hormones:

Among hormone Steroids hormone constitute the largest group. Cholesterol is the precursor fall all Steroids hormone. All the Steroids hormones are synthesis from Cholesterol. They contain less than 21 carbon atoms.

In animals, steroids hormone are synthesis in endocrine glands, such as adrenal cortex, testis, ovary and corpus luteum. The occurence of steroids hormones has also been discovered in insects and higher plants.

In insects moult stimulating hormones are steroids in nature.

In plants oestrogen and progesterone have been found out. These hormones regu blossoming in higher plants and are essentia for sexual reproduction in fungi. They are the regulators growth and reproduction for the plant cell.

"The formation of steroids hormones in plants emphasizes the unity of the plants and animal kingdom.

The sex hormones are synthesised from cholesterol. They contain 21 or 19 or 18 carbon atoms.

P.T.O.

Structure of Androgens:

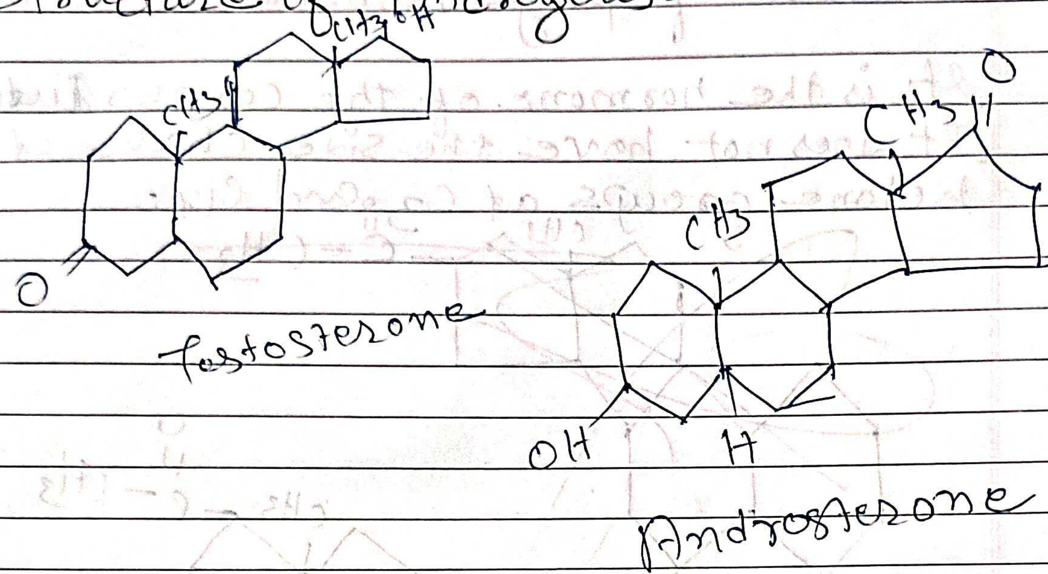


Fig: Structure of Androgens.

Structure of 3 estrogens:

estrogens includs - (i) Estrone (ii) Estradiol (iii) Estriol.

They don't have Side chain in position 17. All three hydroxyl group in position 3. Estrone has ketone group in position 17. Estradiol has a hydroxyl group in position 17. Estriol has hydroxyl group in position 16 and 17.

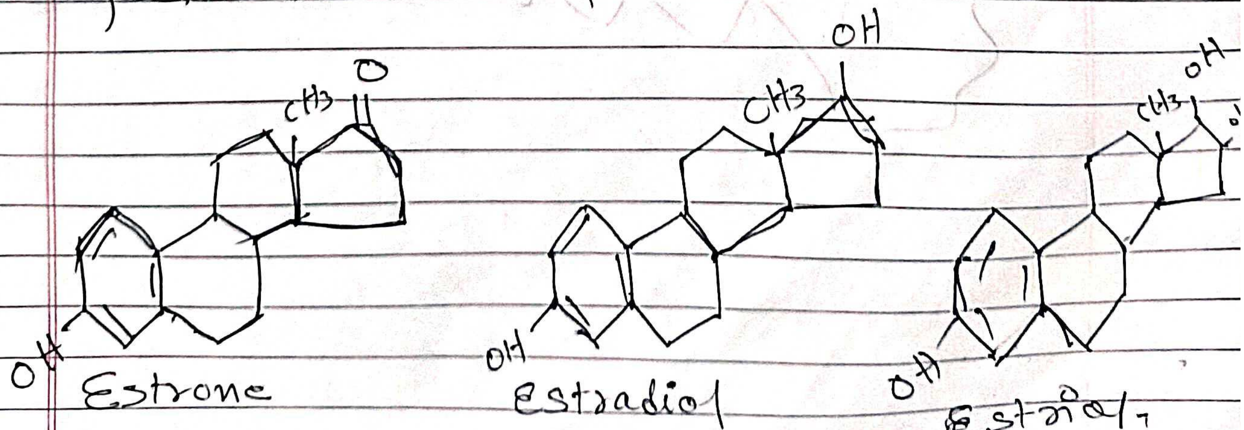


Fig: Structure estrogens.