4- Biochemistry of Lipids

Introduction

Lipids (Greek: **lipos-fat**) may be regarded as **organic substances** relatively insoluble in water, soluble in organic solvents (alcohol, ether etc.), actually or potentially related to fatty acids and utilized by the living cells.

Unlike the polysaccharides, proteins and nucleic acids, **lipids are not polymers**. Lipids are mostly small molecules.

Classification

Lipids are broadly classified into simple, complex, derived and miscellaneous lipids, which are further subdivided into different groups-

1 . **Simple lipids** : Esters of fatty acids with alcohols. These are mainly of two types

(a) Fats and oils (triacylglycerols):- These are esters of fatty acids with glycerol. The difference between fat and oil is only physical. Thus, oil is a liquid while fat is a solid at room temperature.

(b) Waxes:- Esters of fatty acids (usually long chain) with alcohols other than glycerol. These alcohols may be aliphatic or alicyclic. Cetyl alcohol is most commonly found in waxes.

2.Complex (Compound) lipids: These are esters of fatty acids with alcohols containing additional groups such as phosphate, nitrogenous base, carbohydrate, protein etc. They are further divided as follows

(a) Phospholipids: They contain phosphoric acid and frequently a nitrogenous base This is in addition to alcohol and fatty acids.

(i) Glycerophospholipids:- These phospholipids contain glycerol as the alcohol e.g., **Lecithin**, Cephalin.

(ii)Sphingophospholipids:- Sphingosine is the alcohol in this group of phospholipids.

e.g., Sphingomyelin

(b) Glycolipids: These lipids contain a fatty acid, carbohydrate and nitrogenous base.

The alcohol is sphingosine, hence they are also called as glycosphingolipids. Glycerol and phosphate are absent e.g., Cerebrosides, Gangliosides.

(c) Lipoproteins: Macromolecular complexes of lipids with proteins.

(d) Other complex lipids: Sulfolipids, aminolipids and lipopolysaccharides are among the other complex lipids.

3. Derived lipids: These are the derivatives obtained on the hydrolysis of group 1 and group2 lipids which possess the characteristics of lipids. These include glycerol and other alcohols, fatty acids, mono- and diacylglycerols, lipid (fat) soluble vitamins, steroid hormones, hydrocarbons and ketone bodies.

4. Miscellaneous lipids: These include a large number of compounds possessing the characteristics of lipids e.g., carotenoids, squalene, hydrocarbons such as pentacosane (in bees wax), terpenes etc.

NEUTRAL LIPIDS: The lipids which are uncharged are referred to as neutral lipids. These are mono-, di-, and triacylglycerols, **cholesterol** and cholesteryl esters.

Functions

Lipids perform several important functions-

1. They are the concentrated fuel reserve of the body (triacylglycerols).
2. Lipids are the constituents of membrane structure and regulate the membrane permeability (phospholipids and cholesterol) .
3. They serve as a source of fat soluble vitamins (A, D, E and K).
4. Lipids are important as cellular metabolic regulators (steroid hormones and prostaglandins).
5. Lipids protect the internal organs, serve as insulating materials and give shape and smooth appearance to the body.

Fatty acids

Fatty acids are carboxylic acids with hydrocarbon side chain. They are the simplest form of lipids.

Occurrence-

Fatty acids mainly occur in the esterified form as major constituents of various lipids. They are also present as free (unesterified) fatty acids.

Fatty acids of animal orgin are much simpler in structure in contrast to those of plant origin those contain groups such as epoxy, keto, hydroxy and cyclopentane rings.

Nomenclature of fatty acids

Even and odd carbon fatty acids-

Most of the fatty acids that occur in natural lipids are of even carbons (usually 14 C-20 C). This is due to the fact that biosynthesis of fatty acids mainly occurs with the sequential addition of 2 carbon units. Palmitic acid (16 C) and Stearic acid (18 C) are the most common. Odd chain fatty acids, propionic acid (3C) and valeric acid (5C) are well known.

Saturated and unsaturated fatty acids-

Saturated fatty acids do not contain double bonds, while unsaturated fatty acids contain one or more double bonds. Both saturated and unsaturated fatty acids almost equally occur in the natural lipids. Fatty acids with one double bond are monounsaturated, and those with 2 or more double bonds are collectively known as polyunsaturated fatty acids (PUFA).

The naming of a fatty acid (systematic name) is based on the hydrocarbon from which it is derived.

The saturated fatty acids end with a **suffix-anoic** (e.g., Octanoic acid) while the unsaturated fatty acids end with a **suffix-enoic** (e.g., Octadecanoic acid). In addition to systematic names/ fatty acids have common names which are more widely used. **Numbering of carbon atoms** : It starts from the carboxyl carbon which is taken as number 1. The carbons adjacent to this (carboxyl C) are 2, 3, 4 and so on or alternately α, β, γ and so on.

The terminal carbon containing methyl group is known omega (ω) carbon. Starting from the methyl end, the carbon atoms in a fatty acid are numbered as omega 1, 2, 3 etc. The numbering of carbon atoms in two different ways is given below-

7	6	5	4	3	2	1
CH_3-	CH_2-	CH_2-	CH_2-	CH_2-	CH_2-	$COOH$
ω_1	ω_2	ω_3	ω_4	ω_5	ω_6	

Length of carbon chains, fatty acids are categorized into 3 groups-**short chain** with less than 6 carbons; **medium chain** with 8 to 14 carbons and **long chain** with 16 to 24 carbons.

Shorthand naming system of fatty acids:-

The general rule is that the total number of carbon atoms are written first, followed by the nunrber of double bonds and finally the (first carbon) position of double bonds, starting from the carboxyl end.

Example- saturated fatty acid, palmitic acid is written as 16 : 0, oleic acid as 18 : 1; 9, arachidonic acid as 20 : 4; 5, 8, 11, 14.

There are other conventions of representing the double bonds. Δ^9 indicates that the double bond is between 9 and 10 of the fatty acid. ω 9 represents the double bond position (9 and 10) from the ω end. Naturally occurring unsaturated fatty acids belong to ω 9, ω 6 and ω 3 series.

ω 3 series	Linolenic acid (18 : 3; 9, 12, 15)
ω 6 series	Linoleic acid (18 : 2; 9, 12) and arachidonic acid (20 : 4; 5, 8, 11, 14)
ω 9 series	Oleic acid (18 : 1; 9)

II. Unsaturated fatty acids

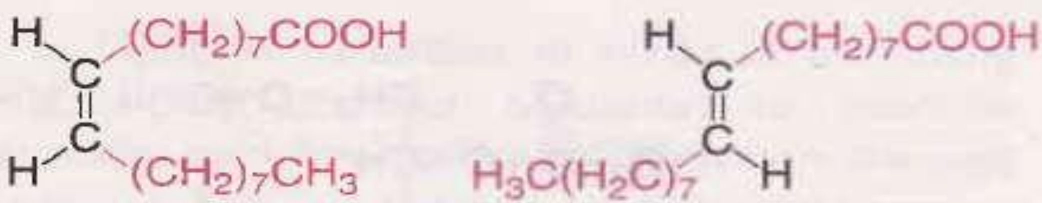
Palmitoleic acid	*cis*-9-Hexadecenoic acid	16 : 1; 9	$CH_3(CH_2)_5CH = CH(CH_2)_7COOH$
Oleic acid	*cis*-9-Octadecenoic acid	18 : 1; 9	$CH_3(CH_2)_7CH = CH(CH_2)_7COOH$
Linoleic acid **	*cis*, *cis*-9,12–Octadeca-dienoic acid	18 : 2; 9, 12	$CH_3(CH_2)_4CH = CHCH_2CH = CH(CH_2)_7COOH$
Linolenic acid **	All *cis*–9,12,15–Octa-decatrienoic acid	18 : 3; 9, 12, 15	$CH_3CH_2CH = CHCH_2CH = CHCH_2CH = CH(CH_2)_7COOH$
Arachidonic acid	All *cis*–5,8,11,14–Eicosatetraenoic acid	20 : 4; 5, 8, 11, 14	$CH_3(CH_2)_4CH = CHCH_2CH = CHCH_2CH = CHCH_2CH = CH(CH_2)_3COOH$

* *Total number of carbon atoms, followed by the number of double bonds and the first carbon position of the double bond(s).*

** *Essential fatty acids.*

I. Saturated fatty acids

Acetic acid	Ethanoic acid	2 : 0	CH_3COOH
Propionic acid	n-Propanoic acid	3 : 0	CH_3CH_2COOH
Butyric acid	n-Butanoic acid	4 : 0	$CH_3(CH_2)_2COOH$
Valeric acid	n-Pentanoic acid	5 : 0	$CH_3(CH_2)_3COOH$
Caproic acid	n-Hexanoic acid	6 : 0	$CH_3(CH_2)_4COOH$
Caprylic acid	n-Octanoic acid	8 : 0	$CH_3(CH_2)_6COOH$
Capric acid	n-Decanoic acid	10 : 0	$CH_3(CH_2)_8COOH$
Lauric acid	n-Dodecanoic acid	12 : 0	$CH_3(CH_2)_{10}COOH$
Myristic acid	n-Tetradecanoic acid	14 : 0	$CH_3(CH_2)_{12}COOH$
Palmitic acid	n-Hexadecanoic acid	16 : 0	$CH_3(CH_2)_{14}COOH$
Stearic acid	n-Octadecanoic acid	18 : 0	$CH_3(CH_2)_{16}COOH$
Arachidic acid	n-Eicosanoic acid	20 : 0	$CH_3(CH_2)_{18}COOH$
Behenic acid	n-Docosanoic acid	22 : 0	$CH_3(CH_2)_{20}COOH$
Lignoceric acid	n-Tetracosanoic acid	24 : 0	$CH_3(CH_2)_{22}COOH$



Oleic acid (*cis* form) **Elaidic acid** (*trans* form)

Fig. 3.1 : Cis-trans isomerism in unsaturated fatty acids.

Essential Fatty Acids (EFA)

The fatty acidst hat cannot be synthesized by the body and, therefore, should be supplied in the diet are known as essential fatty acids (EFA).

Chemically, they are polyunsaturated fatty acids, namely **linoleic acid (18 : 2; 9, 12) and linolenic acid (18 : 3; 9, 12, 15).** Arachidonic acid (20 :4;5,8, 11,14) becomes essential, if its precursor linoleic acid is not provided in the diet in sufficient amounts.

Biochemical basis for essentiality: Linoleic acid and linolenic acid are essential since humans lack the enzymes that can introduce double bonds beyond carbons 9 to 10.

Functions of EFA:- Essential fatty acids are required for the membrane structure and function, transport of cholesterol, formation of lipoproteins, prevention of fatty liver etc. They are also needed for the synthesis of another

important group of compounds, namely eicosanoids.

Eicosanoids: These compounds are related to eicosapolyenoic fa tty acids and include prostaglandins, prostacyclins, leukotrienes and thromboxanes.

Deficiency of EFA:- The deficiency of EFA results in phrynoderma or toad skin, characterized by the presence of horny eruptions on the posterior and lateral parts of limbs, on the back and buttocks, loss of hair and poor wound healing.

Isomerism in unsaturated fatty acids

Unsaturated fatty acids exhibit **geometric isomerism** depending on the orientation of the groups around the double bond axis.

If the atoms or acyl groups are present on the same side of the double bond, it is a cis configuration. On the other hand, if the groups occur on the opposite side, it is a trans configuration. Thus oleic acid is a cis isomer while elaidic acid is a trans isomer. Cis isomers are less stable than trans isomers.

Most of the naturally occurring unsaturated fatty acids exist as cis isomers.

In the cis isomeric form, there is a molecular binding at the double bond e.g. oleic acid exists in an L-shape while elaidic acid is a straight chain. Increase in the number of double bonds will cause more bends (kinks) and arachidonic acid with 4 double bonds will have a U-shape.

The cis isomers of fatty acids with their characteristic bonds will compactly pack the membrane structure.

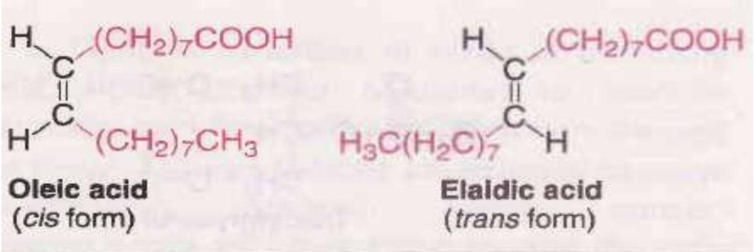


Fig. 3.1 : Cis-trans isomerism in unsaturated fatty acids.

Hydroxy fatty acids:- Some of the fatty acids are hydroxylated. β-Hydroxybutyric acid, one of the ketone bodies produced in metabolism, is a simple example of hydroxy fatty acids. Cerebronic acid and recinoleic acid are long chain hydroxy fatty acids.

Cyclic fatty acids:- Fatty acids with cyclic structures are rather rare e.g., Chaulmoogric acid found in chaulmoogra oil (used in leprosy treatment) contains cyclopentenyl ring.

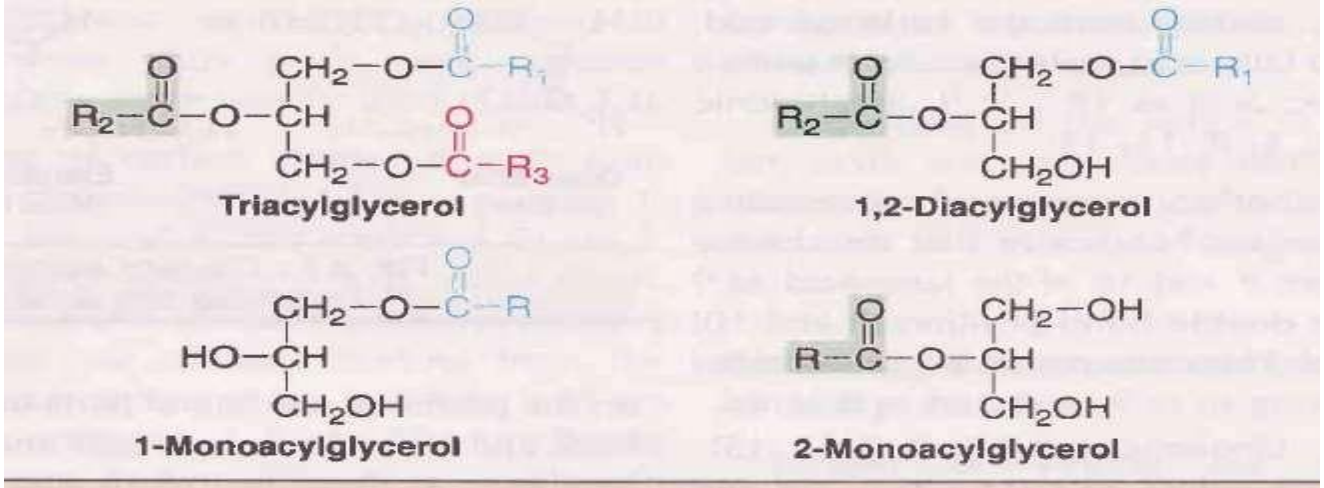


Fig. 3.2 : General structures of acylglycerols
(For palmitoyl R = $C_{15}H_{31}$; for stearoyl R = $C_{17}H_{35}$; For linoleoyl R = $C_{17}H_{31}$)

Triacylglycerols

Triacylglycerols (formerly triglycerides) are the esters of glycerol with fatty acids. The fats and oils that are widely distributedi n both plants and animals are chemically triacylglycerols.

They are insoluble in water and non-polar in character and commonly known as neutral fats.

Fats as stored fuel :- Triacylglycerolsa re the most abundant group of lipids that primarily function as fuel reserves of animals. The fat reserve of normal humans (men 20 %, women 25 % by weigh) is sufficient to meet the body's caloric requirements fo r 2-3 months.

Fats primarily occur in adipose tissue : Adipocytes of adipose tissue-predominantly found in the subcutaneous layer and in the abdominal cavity-are specialized for storage of triacylglycerols. The fat is stored in the form of globules dispersed in the entire cytoplasm. But triacylglycerols are not the structural components of biological membranes.

Structures of acylglycerols: Monoacylglycerols, diacylglycerols and triacylglycerols, respectively consisting of one, two and three molecules of fatty acids esterified to a molecule of glycerol. Among these, triacylglycerols are the most important biochemically.

Simple triacylglycerols:- contain the same type of fatty acid residue at all the three carbons e.g., tristearoyl glycerol or tristearin.

Mixed triacylglycerols:- are more common. They contain 2 or 3 different types of fatty acid residues. In general, fatty acid attached to C1 is saturated, that attached to C2 is unsaturated

while that on C3 can be either. Triacylglycerols are named according to placement of acyl radical on glycerol e.g., 1,3 –palmitoyl 2- linoleoyl glycerol.

Triacylglycerols of plants, in general, have higher content of unsaturated fatty acids compared to that of animals.

PROPERTIES OF TRIACYLGTYCEROLS

1.Hydrolysis:- Triacylglycerols undergo stepwise enzymatic hydrolysis to finally liberate free fatty acids and glycerol. The process of hydrolysis, catalysed by lipases is important for digestion of fat in the gastrointestinal tract and fat mobilization from the adipose tissues.

2. Saponification:- The hydrolysis of triacylglycerols by **alkali** to produce glycerol and soaps is known as saponification.

Triacylglycerol + 3 NaOH ⟶
Glycerol + 3 R-COONa (soaps)

3. **Rancidity:** Rancidity is the term used to represent the deterioration of fats and oils resulting in an unpleasant taste. Fats containing unsaturated fatty acids are more susceptible to rancidity.

Rancidity occurs when fats and oils are exposed to air, moisture, light, bacteria etc. Hydrolytic rancidity occurs due to partial hydrolysis of triacylglycerols by bacterial enzymes. Oxidative rancidity is due to oxidation of unsaturated fatty acids. This results in the formation of unpleasant products such as dicarboxylic acids, aldehydes, ketones etc. Rancid fats and oils are unsuitable for human consumotion.

Antioxidants: The substances which can prevent the occurrence of oxidative rancidity are known as antioxidants. Trace amounts of antioxidants such as tocopherols (vitamin E), hydroquinone, gallic acid and α-naphthol are added to the commercial preparations of fats and oils to prevent rancidity.

Propyl gallate, butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT) are the antioxidants used in food preservation.

4. Lipid peroxidation in vivo: In the living cells, lipids undergo oxidation to produce peroxides and free radicals which can damage the tissue. The free radicals are believed to cause inflammatory diseases, ageing, cancer, atherosclerosis etc. The body cells possess antioxidants such as vitamin E, urate and superoxide dismutase to prevent in vivo lipid peroxidation.

Lipid indices / Tests to check purity of fats and oils

1.Iodine number: It is defined as the grams (number) of iodine absorbed by 100 g of fat or oil. Iodine number is useful to know the relative unsaturation of fats, and is directly proportional to the content of unsaturated fatty acids.

2.Saponification number: It is defined as the mg (number) of KOH required to hydrolyse (saponify) one gram of fat or oil. Saponification number is a measure of the average molecular size of the fatty acids present. The value is higher for fats containing short chain fatty acids.

Fat/oil	*Iodine number*
Coconut oil	7 — 10
Butter	25 — 28
Palm oil	45 — 55
Olive oil	80 — 85
Groundnut oil	85 — 100
Cottonseed oil	100 — 110
Sunflower oil	125 — 135
Linseed oil	175 — 200

Saponification number

Human fat	: 195–200
Butter	: 230–240
Coconut oil	: 250–260

3.Reichert-Meissl (RM) number: It is defined as the number of ml 0.1 N KOH required to completely neutralize the soluble volatile fatty acids distilled from 5 g fat. RM number is useful in testing the purity of butter since it contains a good concentration of volatile fatty acids(butyric acid, caproic acid and caprylic acid). Other fats and oils which have a negligible amount of volatile fatty acids. Butter has a RM number in the range **25-30**, while it is less than 1 for most other edible oils. Thus any adulteration of butter can be easily tested by this **sensitive** RM number .

4.Acid number : It is defined as the number of mg of KOH required to completely neutralize free fatty acids present in one gram fat or oil. Refined oils should be free from any free fatty acids. Oils, on decomoosition-due to chemical or bacterial contamination-yield free fatty acids. Oils with **increased acid number are unsafe** for human consumption.

5.Polenske number: It is the number of milliliters of 0.1 N KOH required to neutralize the insoluble fatty acids from 5g of fat. It is a measure of non-volatile (long chain) fatty acids present in a fat.

Phospholipids

These are complex or compound lipids containing phosphoric acid, in addition to fatty acids, nitrogenous base and alcohol.

There are two classes of phospholipids-

1. Glycerophospholipids (or phosphoglycerides)
2. Sphingophospholipids (or sphingomyelins)

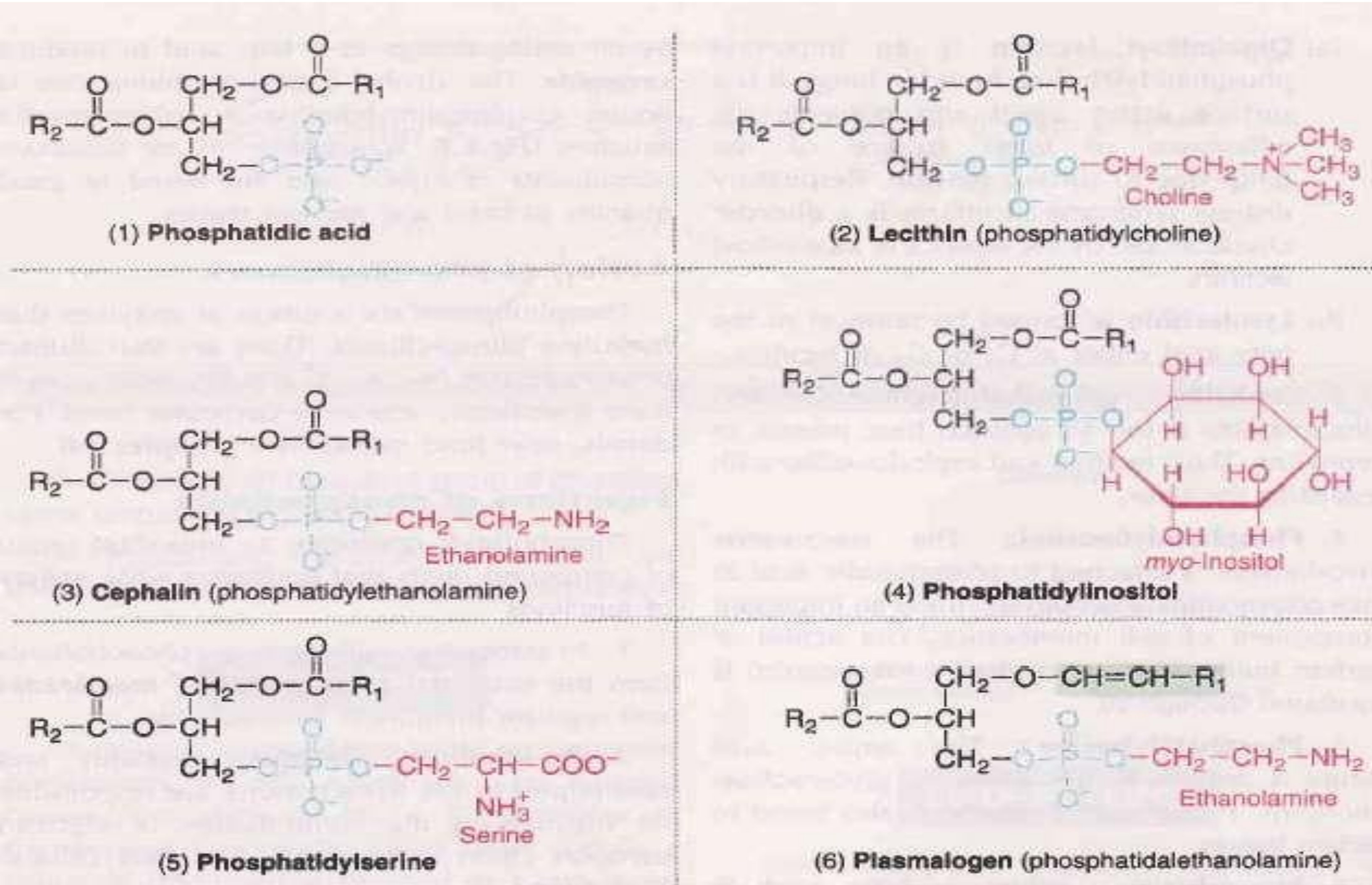
Glycerophospholipids are the major lipids that occur in biological membranes. They consist of glycerol 3- phosphate esterified at its C1 and C2 with fatty acids. Usually, C1 contains a saturated fatty acid while C2 contains an unsaturated fatty acid.

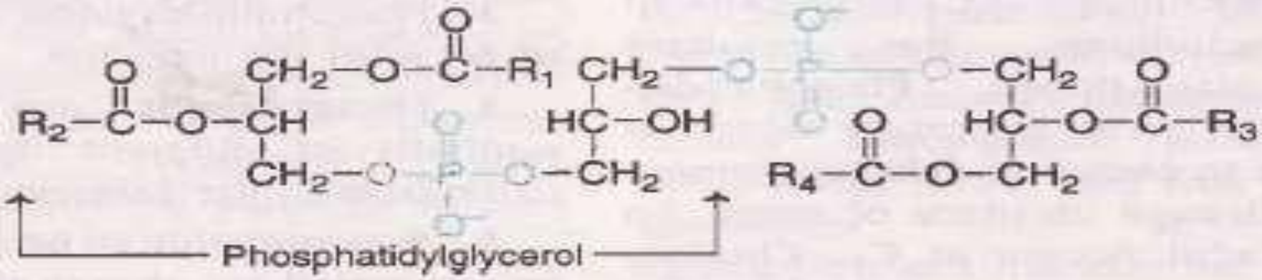
A.Phosphatidic acid : This is the simplest phospholipid. It does not occur in good concentration in the tissues. Basically, phosphatidic acid is an intermediate in the synthesis of triacylglycerols and phospholipids.

The other glycerophospholipids containing different nitrogenous bases or other groups may be regarded as the derivatives of phosphatidic acid.

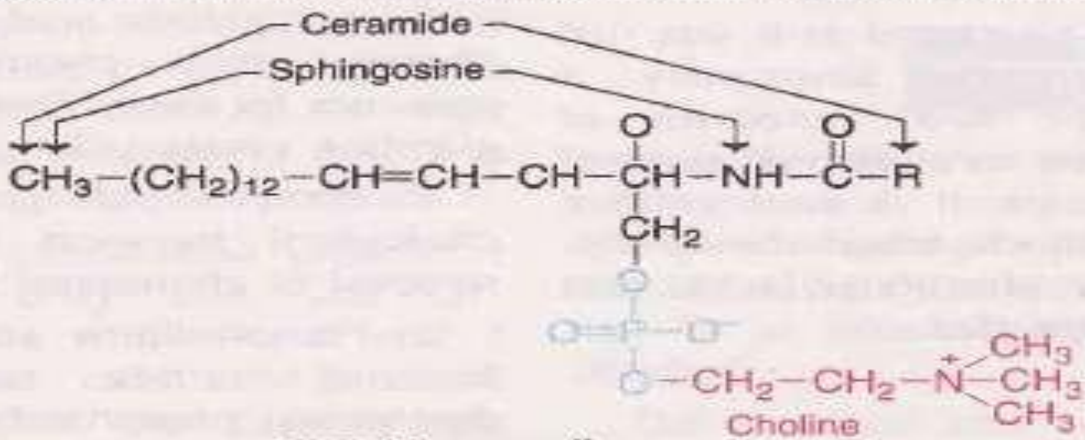
B.Lecithins (phosphatidylcholine)- These are the most abundant group of phospholipids in the cell membranes. Chemically, lecithin (Greek : lecithos-egg yolk) is a phosphatidic acid with choline as the base. Phosphatidylcholines represent the storage form of **body's choline.**

Structures of Phospholipids





(7) **Cardiolipin** (diphosphatidylglycerol)



(8) **Sphingomyelin**

(a) Dipalmitoyl lecithin- is an important phosphatidylcholine found in lungs, It is a surface active agent and prevents the adherence of inner surface of the lungs due to surface tension. Respiratory distress syndrome in infants is a disorder characterized by the absence of dipalmitoyl lecithin.

(b) Lysolecithin- is formed by removal of the fatty acid either at C1or C2 of lecithin.

C.Cephalins (phosphatidylethanolamine):- Ethanolamine is the nitrogenous base present in cephalins.

D.Phosphatidylinositol:- The steroisomer myo-inositol is attached to phosphatidic acid to give phosphatidylinositol (PI). This is an important component of cell membranes. The action of certain hormones (e.g. oxytocin, vasopressin) is mediated through Pl.

E. Phosphatidylserine: The amino acid serine is present in this group of glycerophospholipids.

F.Plasmalogens:- When a fatty acid is attached by an ether linkage at C1 of glycerol in the glycerophospholipids, the resultant compound is plasmalogen. Phosphatidalethanolamine is the most important which is similar in structure to phosphatidylethanolamine but for the ether linkage (in place of ester). An unsaturated fatty acid occurs at C1. Choline, inositol and serine may substitute ethanolamine to give other plasmalogens.

G. Cardiolipin: It is so named as it was first isolated from **heart muscle**. Structurally, a cardiolipin consists of two molecules of phosphatidic acid held by an additional glycerol through phosphate groups. It is an important component of inner mitochondrial membrane. Cardiolipin is the only phosphoglyceride that possesses **antigenic properties**.

Sphingomyelins:-

Sphingosine- is an amino alcohol present in sphingomyelin (sphingophospholipids). They do not contain glycerol at all. Sphingosine is attached by an amide linkage to a fatty acid to produce ceramide. The alcohol group of sphingosine is bound to phosphorylcholine in sphingomyelin structure. Sphingomyelins are important constituents of myelin and are found in good quantity in brain and nervous tissues.

Action of phospholipases:- Phospholipases are a group of enzymes that hydrolyse phospholipids.

Functions of phospholipids:-

1.In association with proteins, phospholipids form the structural components of membranes and regulate membrane permeability.

2.Phospholipids (lecithin, cephalin and cardiolipin) in the mitochondria are responsible for maintaining the conformation of electron transport chain components, and thus cellular respiration.

3. Phospholipids participate in the absorption of fat from the intestine.

4. Phospholipids are essential for the synthesis of different lipoproteins, and thus participate in the transport of lipids.

5. Accumulation of fat in liver (fatty liver) can be prevented by phospholipids, hence they are regarded as lipotropic factors.

6.Arachidonic acid, an unsaturated fatty acid liberated from phospholipids, serves as a precursor for the synthesis of eicosanoids (prostaglandins, prostacyclins, thromboxanes etc.).

7.Phospholipids participate in the reverse cholesterol transport and thus help in the removal of cholesterol from the body.

8.Phospholipids act as surfactants (agents lowering surface tension). For instance, dipalmitoyl phosphatidylcholine is an important lung surfactant. Respiratory distress syndrome infants is associated with insufficient production of this surfactant.

9. Cephalins, an important group of phospholipids participate in blood clotting.

10. Phospholipids (phosphatidylinositoal) are Involved in signal transmission across membranes.

Glycolipids-

Glycolipids (glycosphingolipids):- are important constituents of cell membrane and nervous tissues (particularly the brain). Cerebrosides are the simplest form of glycolipids. They contain a ceramide (sphingosine attached to a fatty acid) and one or more sugars. Galactocerebroside (galactosylceramide) and glucocerebroside are the most important glycolipids. It contains the fatty acid cerebronic acid. Sulfagalactosylceramide is the sulfatide derived from galactosylceramide.

Gangliosides: These are predominantly found in ganglions and are the most complex form of glycosphingolipids. They are the derivatives of cerebrosides and contain one or more molecules of N-acetylneuraminic acid (NANA) , the most important **sialic acid.**

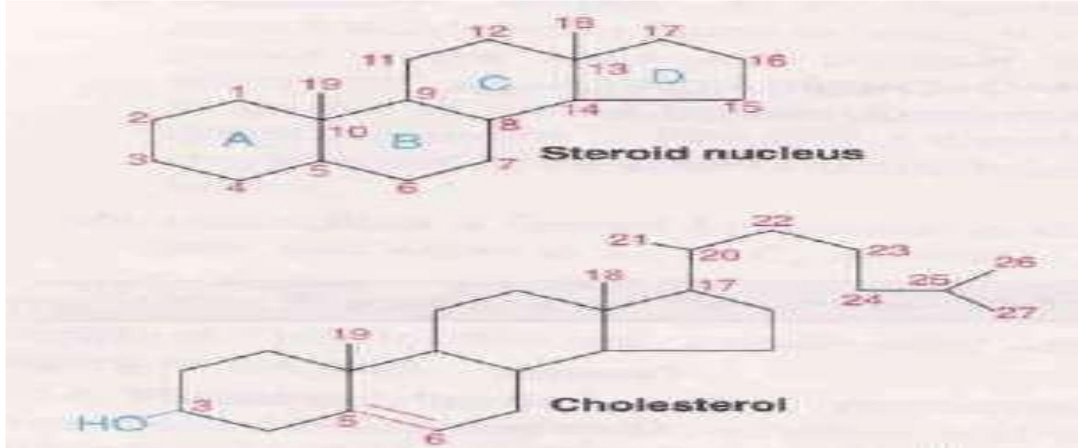
The most important gangliosides present in the brain are GM1, GM2, GD, and GT, (G represents ganglioside while M, D and T indicate mono-, di- or tri- sialic acid residues, and the number denotes the carbohydrate sequence attached to the ceramide).

Lipoproteins-

Lipoproteins are molecular complexes of lipids with proteins. They are the transport vehicles for lipids in the circulation. There are **five types** of lipoproteins, namely **chylomicrons**, very low density lipoproteins **(VLDL),** low density lipoproteins **(LDL),** high density lipoproteins **(HDL)** and **free fatty acid-albumin complexes**.

Steroids -

Steroids are the compounds containing a cyclic steroid nucleus (or ring) namely cyclopentanoperhydrophenanthrene (CPPP). It consists of a phenanthrene nucleus (rings A, B and C) to which a cyclopentane ring (D) is attached. The methyl side chains (19 and 18) attached to carbons 10 and 13 are shown as single bonds. At carbon 17, steroids usually contain a side chain. Ex. cholesterol, bile acids, vitamin D, sex hormones, adrenocortical hormones etc.



Cholesterol-

Cholesterol, exclusively found in animals, is the most abundant animal sterol. It is widely distributed in all cells and is a major component of cell membranes and lipoproteins. Cholesterol (Greek: chole-bile) was first isolated from bile.

Cholesterol literally means 'solid alcohol from bile.'

The structure of cholesterol is **($C_{27}H_{46}O$).**

It has one hydroxyl group at C3 and a double bond between C5 and C6. Cholesterol contains a total of 5 methyl groups.

Due to the presence of an -OH group, cholesterol is weakly amphiphilic. As a structural component of plasma membranes, cholesterol is an important determinant of membrane permeability properties. The occurrence of cholesterol is much higher in the membranes of sub-cellular organelles.

Cholesterol is found in association with fatty acids to- form cholesteryl esters (esterification occurs at the OH group of C3).

Properties and reactions:- Cholesterol is an yellowish crystalline solid. The crystals, under the microscope, show a notched appearance. Cholesterol is insoluble in water and soluble in organic solvents such as chloroform, benzene, ether etc. Salkowski's test, Liebermann-Burchard reaction and Zak's test are useful for its qualitative identification and quantitative estimation.

Functions of cholesterol:- It is present in abundance in nervous tissues. It appears that cholesterol functions as an insulating cover for the transmission of electrical impulses in the nervous tissue. Cholesterol performs several other biochemical functions which include its role in membrane structure and function, in the synthesis of bile acids, hormones (sex and cortical) and vitamin D.

ERGOSTEROL:-

Ergosterol occurs in plants. It is also found as a structural constituent of membranes in yeast and fungi and important precursor for vitamin D. When exposed to light, the ring B of ergosterol opens and it is converted to ergocalciferol, a compound containing vitamin D activity.

Amphipathic lipids

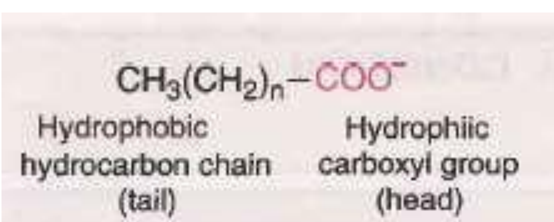
Lipids are insoluble (hydrophobic) in water. This is primarily due to the predominant presence of hydrocarbon groups. Some of the lipids possess polar or hydrophilic groups which tend to be soluble in water.

Molecules which contain both hydrophobic and hydrophilic groups are known as amphipathic (Greek: amphi-both, pathos-passion).

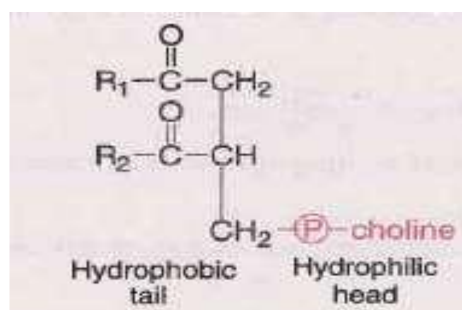
Examples of amphipathic lipids are fatty acids, phospholipids, sphingolipids, bile salts and cholesterol.

Phospholipid have a hydrophilic head (phosphate group attached to choline, ethanolamine, inositol etc.) and a long hydrophobic tail.

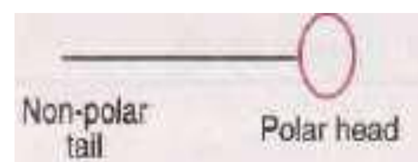
Fatty acids contain a hydrocarbon chain with a carboxyl (COO-) group at physiological pH. The carboxyl group is polar in nature with affinity to water (hydrophilic) while hydrocarbon chain of fatty acid is hydrophobic.



(A) Fatty acid



(B) Phospholipid

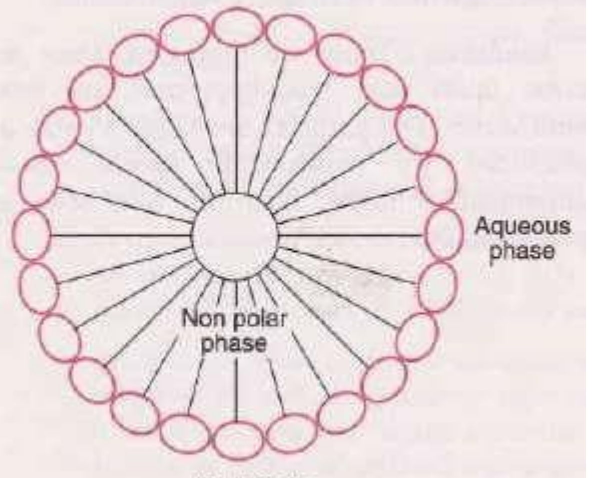


(C) Amphipathic lipid

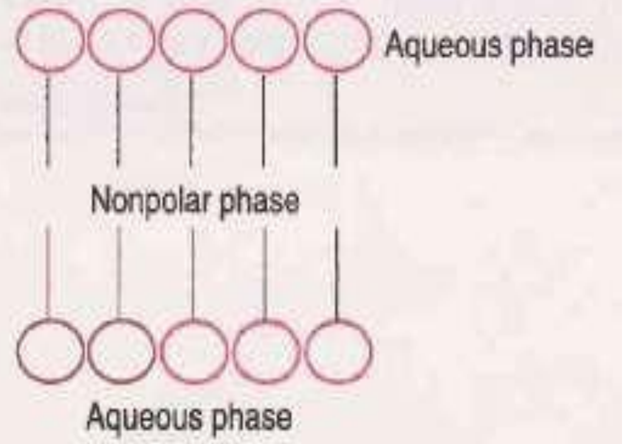
Orientation amphipathic lipids: When the amphipathic lipids are mixed in water (aqueous phase), the polar groups (heads) orient themselves towards aqueous phase while the non-polar (tails) orient towards the opposite directions. This leads to the formation of micelles. Micelle formation, facilitated by bile salts is very important for lipid digestion and absorption.

Membrane bilayers:-

In case of biological membranes, a bilayer of lipids is formed orienting the polar heads to the outer aqueous phase on either side and the nonpolar tails into the interior. The formation of a lipid bilayer is the basis of membrane structure.



(D) Micelle



(E) Lipid bilayer

Liposomes: A minute spherical sac of phospholipid molecules enclosing a water droplet, especially as formed artificially to carry drugs or other substances into the tissues.

Emulsions: These are produced when nonpolar lipids (e.g. triacylglycerols) are mixed with water. The particles are larger in size and stabilized by emulsifying agents (usually amphipathic lipids), such as bile salts and phospholipids.

Prostaglandins

Prostaglandins (PG) and their related compounds-prostacyclins (PGI), thromboxanes (TXA), leukotrienes (LT) and lipoxins are collectively known as eicosaniods, since they all contain **20 carbons (Greek: eikosi-twenty)**.

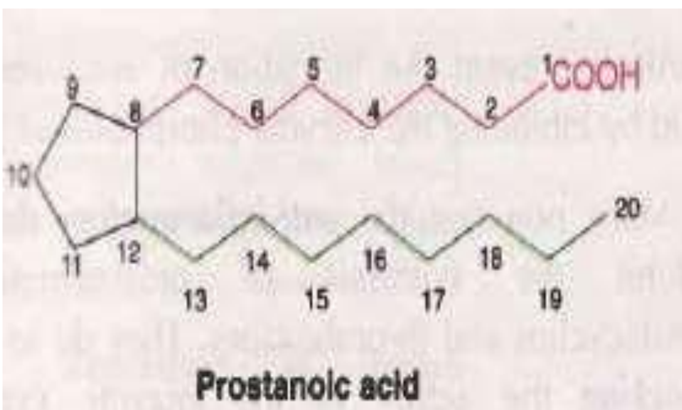
Eicosanoids are considered as locally acting hormones with a wide range of biochemical functions. The prostaglandins E and F were first isolated from the biological fluids. They were so named due to their solubility in ether (PGE) and phosphate buffer (PGF, F for fosfat, in Swedish).

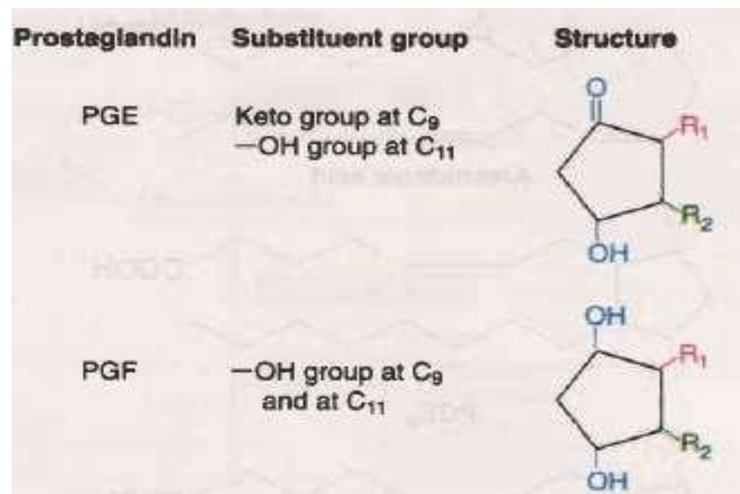
All other prostaglandins discovered later were denoted by a letter-PGA, PGH etc.

Structure of prostaglandins:-

Prostaglandins are derivatives of a 20-carbon fatty acid namely prostanoic acid hence known as prostanoids.

This has a cyclopentane ring (formed by carbon atoms 8 to 12) and two side chains, with carboxyl group on one side. Prostaglandinds differ in their structure due to substituent group and double bond on cyclopentane ring.





Functions:-

1.Regulation of blood pressure: The prostaglandins (PGE, PGA and PGI2) are vasodilator in function. This results in increased blood flow and decreased peripheral resistance to lower the blood pressure. PGs serve as agents in the treatment of hypertension.

2.Pain, Fever & Inflammation : The prostaglandins PGE1 and PGE2 induce the symptoms of inflammation (redness, swelling, edema etc.) due to arteriolar vasodilation. This led to the belief that PGs are natural mediators of inflammatory reactions.

3.Reproduction: Prostaglandins have widespread applications in the field of reproduction. PGE2 and PGF2 are used for the medical termination of pregnancy and induction of labor. Prostaglandins are administered to cattle to induce estrus and achieve better rate of fertilization.

4.Regulation of gastric secretion : In general , prostaglandins(PGE) inhibit gastric secretion. PGs are used for the treatment of gastric ulcers. However, PGs stimulate pancreatic secretion and increase the motility of intestine which often causes diarrhea.

5. Influence on immune system:- Macrophages secrete PGE which decreases the immunological functions of B-and T -lymphocytes.

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6.Effects on respiratory function:- PGE is a bronchodilator where as PGF acts as a constrictor of bronchial smooth muscles. Thus, PGE and PGF oppose the actions of each other in the lungs. PGE1 and PGE2 are used in the treatment of asthma.

7.Influence on renal functions:- PGE increases glomerular filtration rate (GFR) and promotes urine output.

8.Effects on metabolism:- Prostaglandins influence certain metabolic reactions like lipolysis, increases glycogen formation and promotes calcium mobilization from the bone.

9. Platelet aggregation and thrombosis:- The prostaglandins, namely prostacyclins (PGI2), inhihit platelet aggregation. Thromboxanes (TXA2) and prostaglandin E2 promote platelet

aggregation and blood clotting that might lead to thrombosis.

THANKS