Lipids

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Lipids

Lipids are a heterogeneous group of compound related to fatty acids. Lipids are relatively insoluble in water. They are soluble In nonpolar solvents such as ether, chloroform or benzene.

Functions (biomedical Importance):

1. In diet : Lipids are important constituent of diet due to:

a) They are a source of high energy value.

b) They contain fat soluble vitamins.

c) They contain essential fatty acids.

2. In the body :

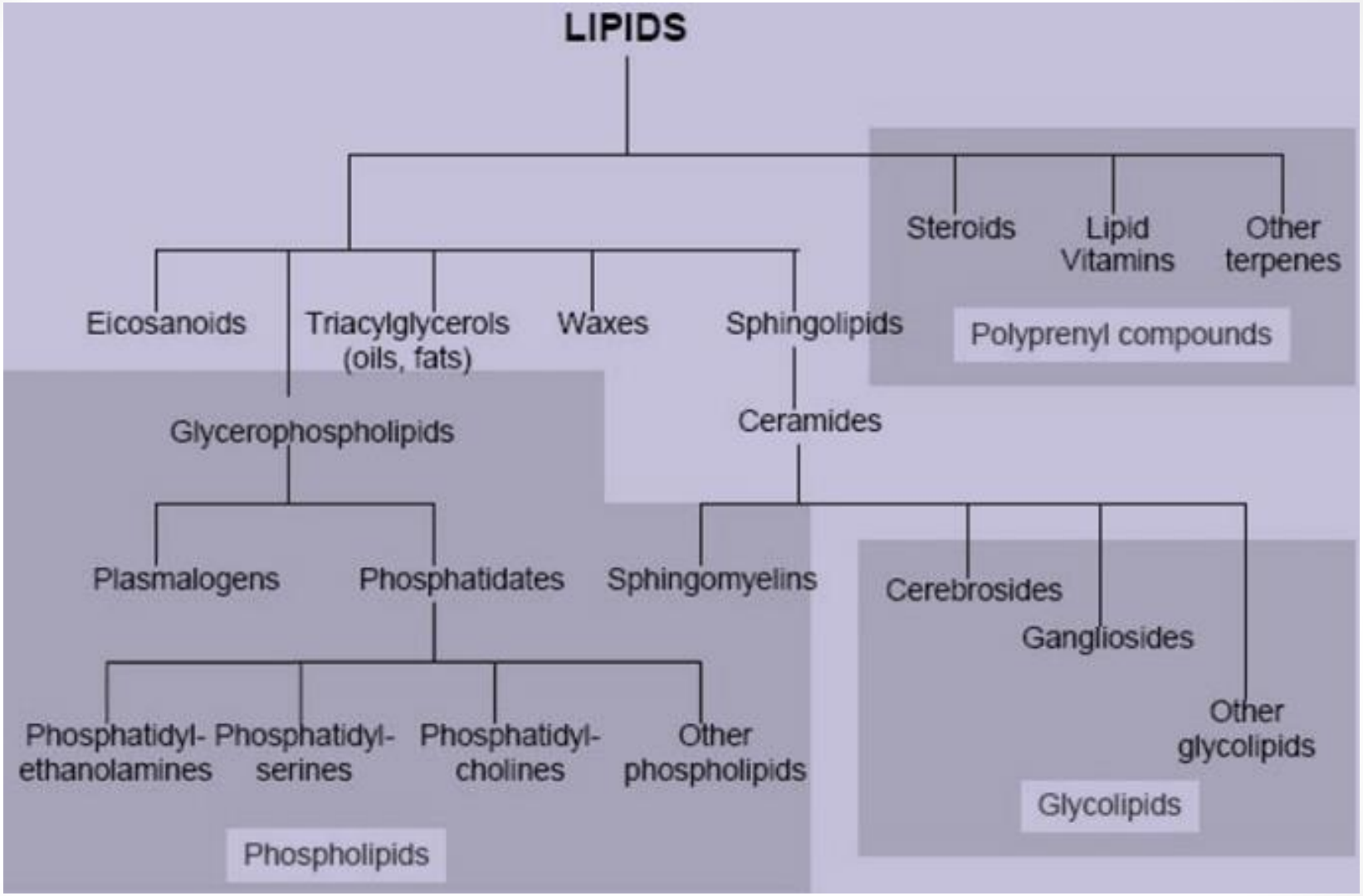
a) Lipids in adipose tissue serve as storage form of energy.

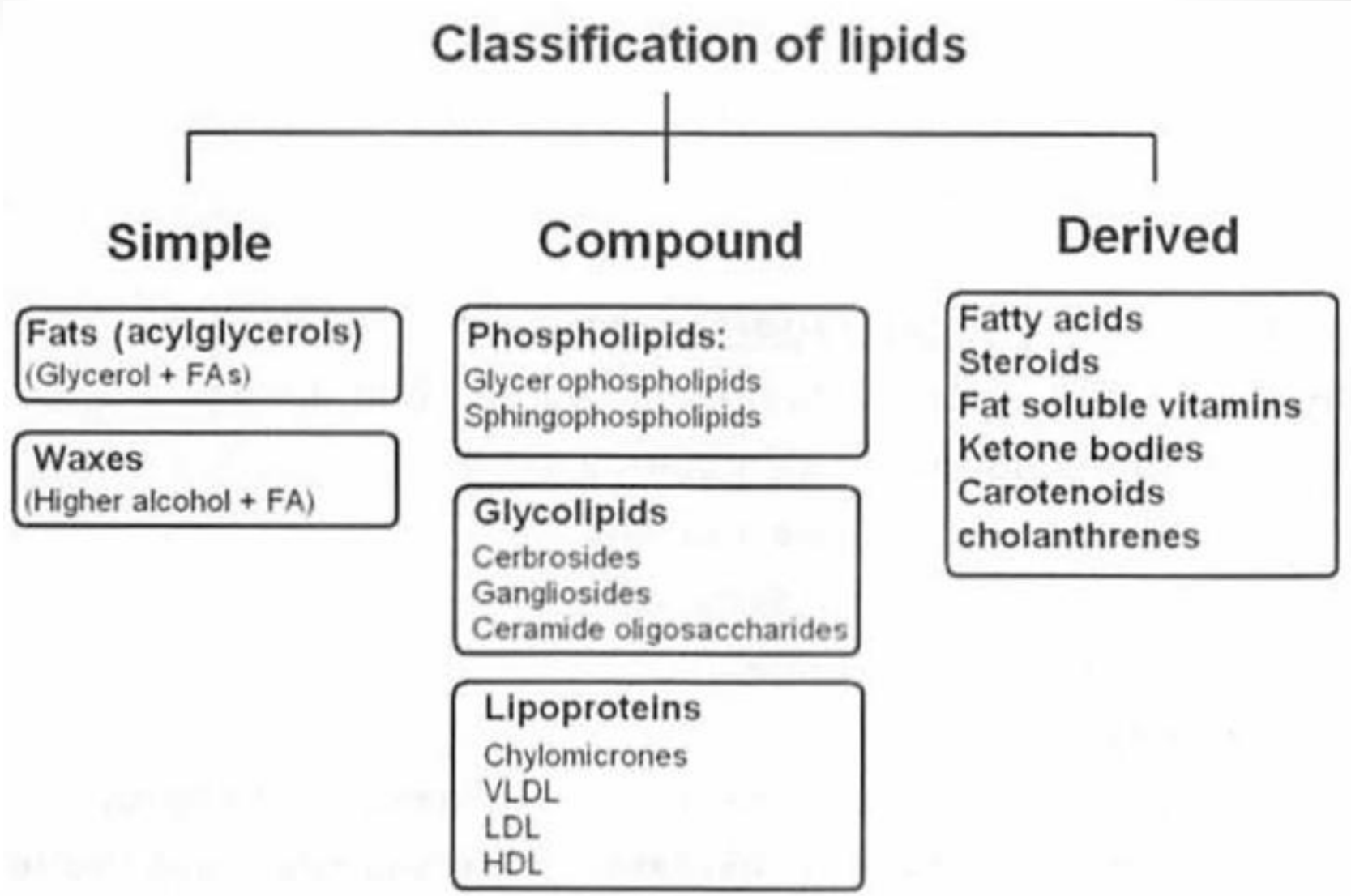
b) They serve as thermal insulator in the subcutaneous tissues.

c) Lipoproteins (a combination of fat and proteins) are important because :

1) They enter In the structure of cell membranes.

2) They serve as a transport form of energy in the blood.


LIPIDS
Steroids
Lipid Vitamins
Other terpenes
Eicosanoids
Triacylglycerols (oils, fats)
Waxes
Sphingolipids
Polyprenyl compounds
Glycerophospholipids
Ceramides
Plasmalogens
Phosphatidates
Sphingomyelins
Cerebrosides
Gangliosides
Other glycolipids
Phosphatidyl-ethanolamines
Phosphatidyl-serines
Phosphatidyl-cholines
Other phospholipids
Glycolipids
Phospholipids


Classification of lipids
Simple
Compound
Derived
Fats (acylglycerols)
(Glycerol + FAs)
Waxes
(Higher alcohol + FA)
Phospholipids:
Glycerophospholipids
Sphingophospholipids
Glycolipids
Cerbrosides
Gangliosides
Ceramide oligosaccharides
Lipoproteins
Chylomicrones
VLDL
LDL
HDL
Fatty acids
Steroids
Fat soluble vitamins
Ketone bodies
Carotenoids
cholanthrenes

CLASSIFICATION OF LIPIDS:

1. Simple Lipids

Esters of fatty acids with different alcohols:

(a) Neutral fats (Triacylglycerol, TG): These are triesters of fatty acids with glycerol.

(b) Waxes are esters of fatty acids with higher alcohols (higher monohydroxy aliphatic alcohols).

CLASSIFICATION OF LIPIDS:

2. Compound Lipids

Esters of fatty acids containing groups, other than, and in addition, to an alcohol and fatty acids.

(a) Phospholipids: They are substituted fats containing in addition to fatty acid and glycerol, a phosphoric acid residue, a nitrogenous base and other substituents.

Examples: phosphatidyl choline (Lecithin), phosphatidyl ethanolamine (Cephalin), phosphatidyl inositols (Lipositols), phosphatidyl serine, plasmalogens, sphingomyelins, etc.

(b) Glycolipids: Lipids containing carbohydrate moiety are called glycolipids. They contain a special alcohol called sphingosine or sphingol and nitrogenous base in addition to fatty acids but does not contain phosphoric acid or glycerol. These are of two types:

- Cerebrosides
- Gangliosides

(c) Sulpholipids: Lipids characterised by possessing sulphate groups.

(d) Aminolipids (Proteolipids)

(e) Lipoproteins: Lipids as prosthetic group to proteins.

CLASSIFICATION OF LIPIDS:

3. Derived Lipids

Derivatives obtained by hydrolysis of those given in group I and II, which still possess the general characteristics of lipids.

Substances which are insoluble In water but soluble in nonpolar solvents as :

1) Steroids.

2) Carotenoids.

3) Cholanthrenes.

4) Ketone bodies.

5) Fat soluble vitamins

(a) Fatty acids may be saturated, unsaturated or cyclic.

(b) Monoglycerides (Monoacylglycerol) and Diglycerides (Diacylglycerol).

(c) Alcohols:

• Straight chain alcohols are water insoluble alcohols of higher molecular weight obtained on hydrolysis of waxes.

• Cholesterol and other steroids

• Alcohols containing ring and certain carotenoids.

• Glycerol.

FATTY ACIDS (RCOOH) :

1) Fatty acids are water-insoluble long chain hydrocarbons.

2) Fatty acids may be saturated (containing no double bonds) or unsaturated (containing one or more double bonds).

3) They are mostly monocarboxylic i.e. having one carboxyl group at the end of the chain (-COOH).

4) They are mostly aliphatic (i.e. not branched). A few branched chain fatty acids are present in animals and plants.

5) Fatty acids occur mainly as esters in natural fats and oils.

6) Fatty acids may also present as free fatty acids in the plasma.

Types of fatty acids:

Straight chain FA: These may be:

- Saturated FA: Those which contain no double bonds.
- Unsaturated FA: Those which contain one or more double bonds.

(a) Saturated FA: Their general formula is C_nH_{2n+1} COOH

Examples:

1. Butyric acid (4C) = CH_3 - CH_2 - CH_2 -COOH.
2. Caproic acid (6C) = CH_3- CH_2- CH_2- CH_2- CH_2- COOH.
3. Palmitic acid (16C) = CH_3- $(CH_2)_{14}$- COOH.
4. Stearic acid (18C) = CH_3- $(CH_2)_{16}$- COOH.

Saturated fatty acids having 10 carbon or less number of carbon atoms are called as lower fatty acids, e.g. acetic acid, butyric acid, etc. Saturated fatty acids having more than 10 carbon atoms are called higher fatty acids, e.g. palmitic acid, stearic acid, etc. Milk contains significant amount of lower fatty acids.

Types of fatty acids:

(b) Unsaturated FA: They are classified further according to degree of unsaturation.

(1) Mono unsaturated (Monoethenoid) fatty acids: They contain one double bond.

Their general formula is $C_n H_{2n-1} COOH$

(2) Polyunsaturated (Polyethenoid) fatty acids: There are three polyunsaturated fatty acids of biological importance.

• Linoleic acid series (18 : 2; 9, 12): It contains two double bonds between C_9 and C_{10}; and between C_{12} and C_{13}. Their general formula is $C_nH_{2n-3}COOH$.

$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$

Dietary sources: Linoleic acid is present in sufficient amounts in peanut oil, corn oil, cottonseed oil, soyabean oil and egg yolk.

Types of fatty acids:

• Linolenic acid series (18 : 3; 9, 12, 15): It contains three double bonds between 9 and 10; 12 and 13; and 15 and 16. Their general formula is CnH2n–5 COOH.

CH3CH2CH=CHCH2CH=CHCH2CH=CH(CH2)7COOH

Dietary Source: Found frequently with linoleic acid, but particularly present in linseed oil, rapeseed oil, soybean oil, fish visceras and liver oil (cod liver oil).

• Arachidonic acid series (20 : 4; 5, 8, 11, 14): It contains four double bonds. Their general formula: CnH2n–7 COOH

CH3(CH2)4CH=CHCH2CH=CHCH2CH=CHCH2CH=CH(CH2)3COOH

Dietary source: Found in small quantities with linoleic acid and linolenic acid but particularly found in peanut oil. Also found in animal fats including Liver fats.

Note: These three polyunsaturated fatty acids, viz. linoleic acid, linolenic acid and arachidonic acid are called as “Essential fatty acids (EFA)”. They have to be provided in the diet, as they cannot be synthesised in the body.

Types of fatty acids:

(c) Branched chain FA: Odd and even carbon branched chain fatty acids occur in animal and plant lipids, e.g.

- Sebaceous glands: Sebum contain branched chain FA
- Branched chain FA is present in certain foods, e.g. phytanic acid in butter.

(d) Substituted fatty acids: In hydroxy fatty acid and methyl fatty acid, one or more of the hydrogen atoms have been replaced by – OH group or – CH_3 group respectively. Both saturated and unsaturated hydroxyl fatty acids, particularly with long chains, are found in nature, e.g. cerebronic acid of brain glycolipids, Ricinoleic acid in castor oil.

(e) Cyclic fatty acids: Fatty acids bearing cyclic groups are present in some seeds,e.g.

- Chaulmoogric acid obtained from chaulmoogra seeds,
- Hydnocarpic acid.

Types of fatty acids:

(f) Eicosanoids: These are cyclic compounds that derived from arachidonic acid (eicosatetraenoic) (20 C) after cyclization of its carbons chain to form a ring. Components of eicosanoids:

1. Prostanoids : which comprice prostaglandins, prostacyclins and thromboxanes:

a) Prostaglandins (PG):

- They have hormonal like action.
- They cause vasodilatation, contraction of the uterus and intestine.
- Contribute to the healing process when tissue damage or infection By activating the reaction Inflammatory and causing pain and high temperature.
- Increasing mucus secretion and preventing acid production in the gut to treat Gastric ulcer
- Increased blood flow to the kidneys.

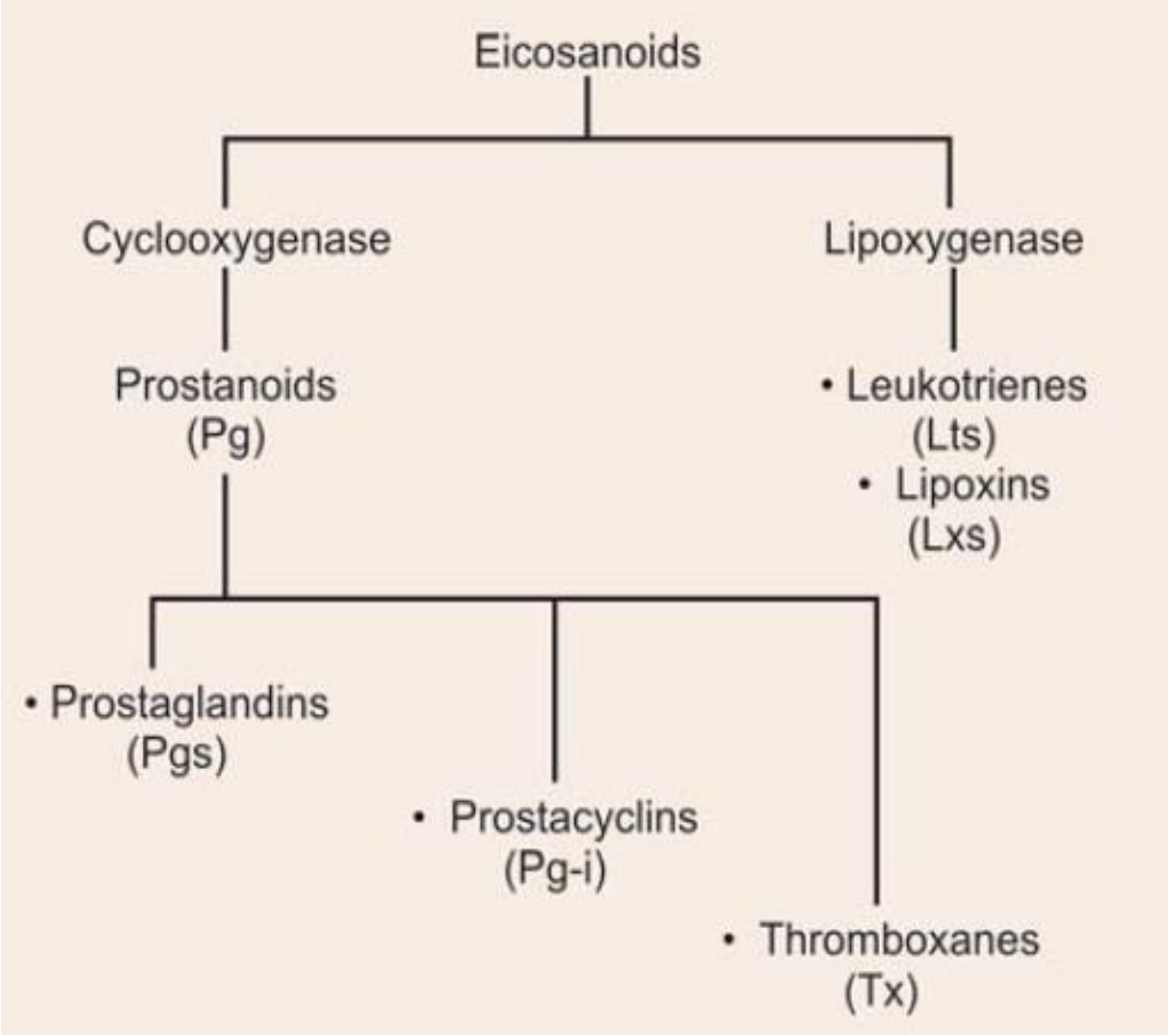
b) Prostacyclines: They cause vasodilatation and inhibit platelets aggregation.

c) Thromboxanes: They cause aggregation of platelets.

2. Leukotriens (LT):

a) They are present in leucocytes, platelets and mast cells.

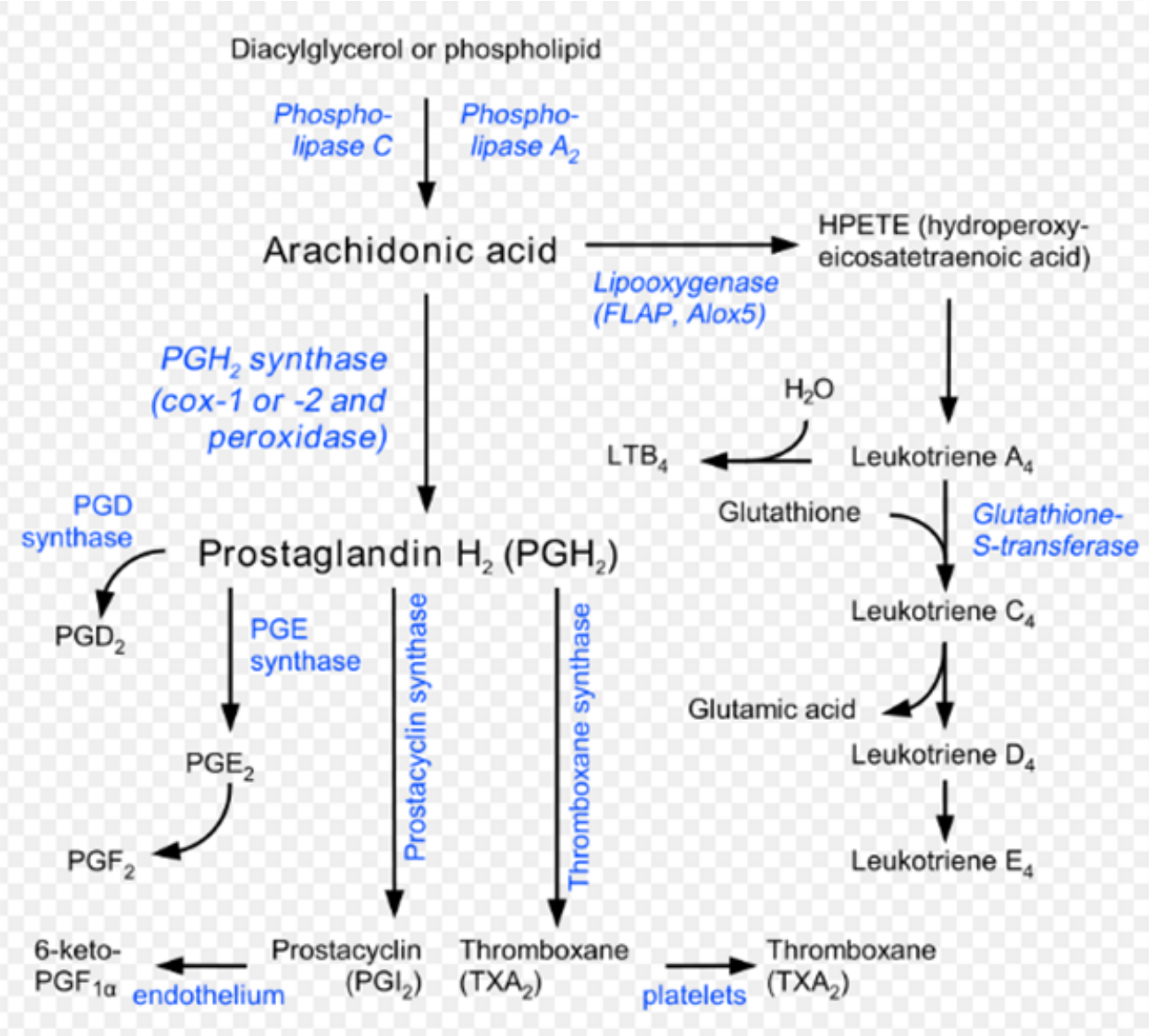
b) They cause chemotaxis i.e. Collection of white blood cells at the site of inflammation.



Classification of Eicosanoids

Biosynthesis of eicosanoids

Prostaglandins are found in most tissues and organs. They are produced by almost all nucleated cells. They are autocrine and paracrine lipid mediators that act upon platelets, endothelium, uterine and mast cells. They are synthesized in the cell from the fatty acid arachidonic acid. Arachidonic acid is created from diacylglycerol via phospholipase-A_2 , then brought to either the cyclooxygenase pathway or the lipoxygenase pathway. The cyclooxygenase pathway produces thromboxane, prostacyclin and prostaglandin D, E and F. Alternatively, the lipoxygenase enzyme pathway is active in leukocytes and in macrophages and synthesizes leukotrienes.



Biosynthesis of eicosanoids

Types of fatty acids:

g) Essential and Nonessential fatty acids:

Nonessential fatty acids : These are fatty acids which can be synthesized in the body. Thus they are not necessary to be obtained from the diet .They include all saturated and monounsaturated (one double bond) fatty acids as palmitoleic and oleic acid.

Essential fatty acids : Three polyunsaturated fatty acids, linoleic acid, linolenic acid and arachidonic acid are called "essential fatty acids" (EFA). They cannot be synthesised in the body and must be provided in the diet. They include fatty acids that contain more than one double bond (polyunsaturated fatty acids), e.g. lenoleic, lenolenic and arachidonic acids.

Sources: Plant oils , Fish oils

Importance (functions):

a) Normal growth.

b) They enter in the structure of phospholipids and cholesterol esters.

c) They enter in the structure of cell membranes

d) They protect against atherosclerosis and coronary heart disease

ALCOHOLS (ROH):

Alcohols contained in the lipid molecule includes glycerol, cholesterol and the higher alcohols, e.g. cetylalcohol, $C_{16}H_{33}COOH$ (usually found in waxes).

Glycerol: It is polyhydric alcohol containing 3 (-OH) groups

Properties:

1. Glycerol is colorless, odorless, hygroscopic and has sweet taste.

2. It is soluble In water and alcohol, insoluble in nonpolar solvents.

3. It combines with one fatty acid to form monoacylglycerol, two fatty acids to form diacylglycerols and three fatty acids to form triacylglycerols. This combination Is through ester linkage.

Uses of glycerol:

1. Nitroglycerol is used - as a drug - for dilatation of coronary artery.

2. Glycerol enters In manufacturing of creams and lotions for dry skin.

Cholesterol: is an alcohol and derived lipids

Higher alcohol: They contain one (-OH) group i.e. monohydric alcohols.

SIMPLE LIPIDS :

They are called simple because they are formed only from alcohols and Fatty acids. There are two classes of simple lipids (according to the type of alcohol): acylglycerols and waxes.

Acylglycerols are esters of one, two or three fatty glycerol.

Triacylglycerols (triglycerides):

They are called neutral fats because they carry no charge.

Body triacylglycerols:

1. Location: They are stored mainly In cytoplasm of adipose tissue cells (which Is located subcutaneously and around kidney and other organs).

2. Body fat is important source of energy. Each gram fat gives 9.3 kcal.

3. Human fat is liquid at room temperature and contains high contents of oleic acid.

Dietary sources of triacylglycerols:

1. In animals e.g. butter and lards.

2. In plants e.g. cotton seed oil, linseed oil, sesame oil and olive oil.

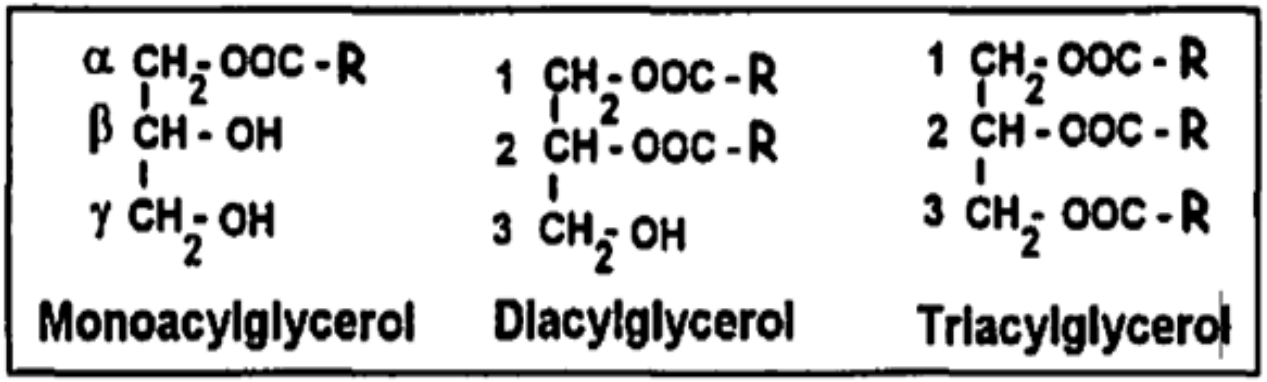
3. Marine oils e.g. cod liver oil and shark liver oil.

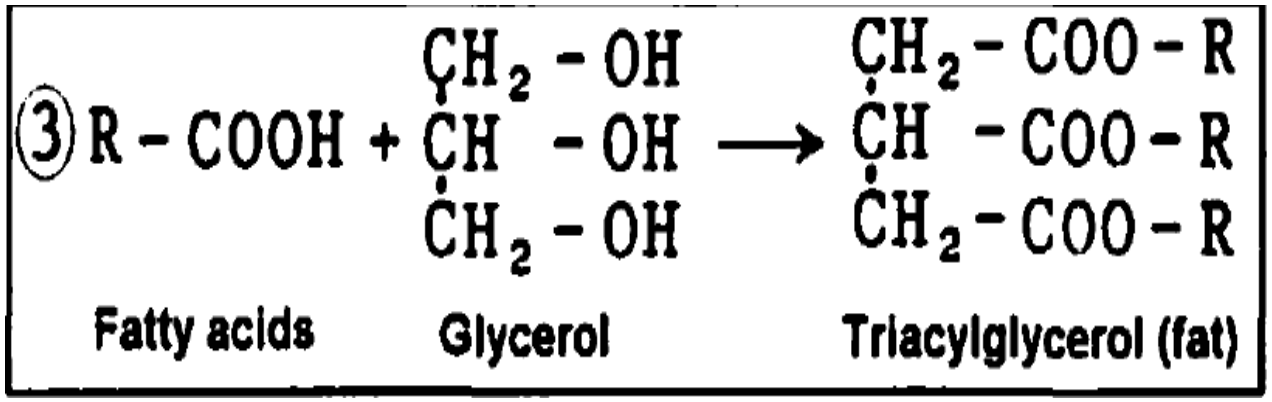
Types of triacylglycerols: simple or mixed.

1. Simple triacylglycerols: similar 3 fatty acids are attached to glycerol.

2. Mixed triacylglycerols: 3 different fatty acids are attached to glycerol.

SIMPLE LIPIDS





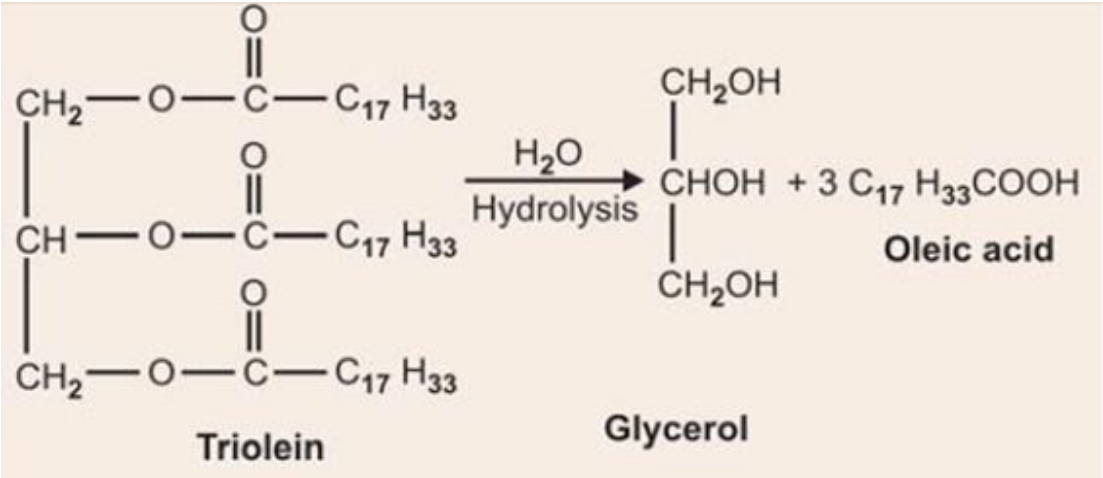
SIMPLE LIPIDS

The fats may be hydrolysed with:

Super heated steam,

By acids or alkalies

By the specific fat spliting enzymes lipases



Hydrolysis of Triolein

SIMPLE LIPIDS

Waxes:

These are esters of fatty acids with long chain alcohol other than glycerol. These alcohols contain one (-OH) group, i.e., monohydric alcohols e.g. bee wax.

Beeswax consists of palmitic acid ester for a long chain of fatty alcohol

Waxes are excreted extracellularly In some plants and animals and has a protective function as in:

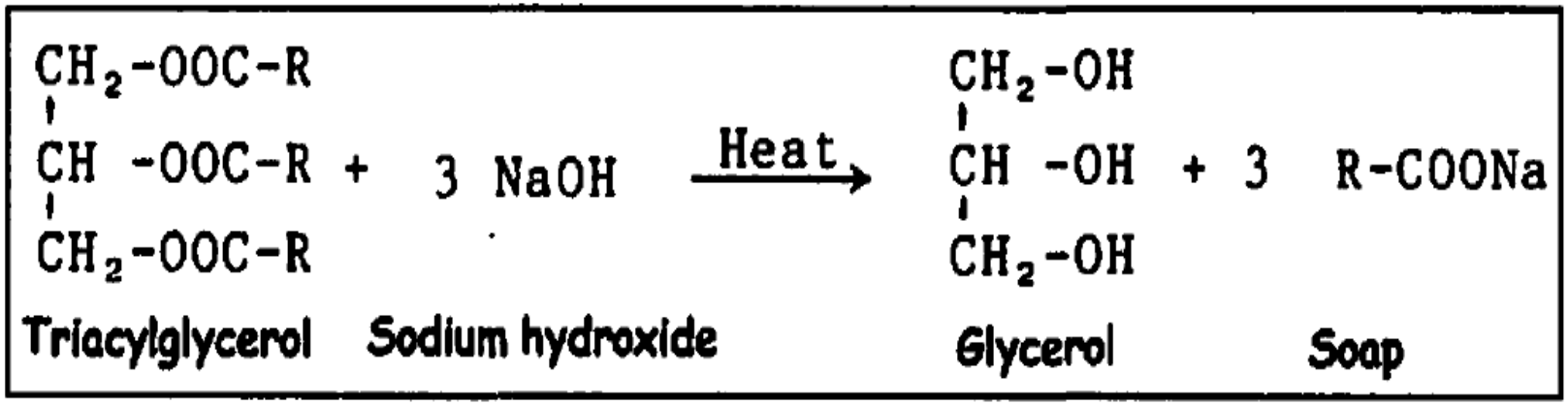
1. Bee wax.

2. Sebaceous secretions.

3. Cuticles of leaves.

Saponification:

Hydrolysis of a fat by an alkali is called saponification. The resultant products are glycerol and the alkali salts of the fatty acids, which are called “soaps”.



COMPOUND LIPIDS

1-Phospholipids : are compound lipids, they contain in addition to fatty acids and glycerol/or other alcohol, a phosphoric acid residue, nitrogen containing base and other substituents.

Classification given by Celmer and Carter is used, which is based on the type of alcohol present in the phospholipids. Thus they are classified mainly into following three groups:

Classification of Phospholipids

- **Glycerophosphatides:** In this glycerol is the alcohol group.

Examples: Phosphatidylethanolamine (cephalin), phosphatidylcholine (Lecithin), phospatidylserine, plasmalogens, phosphatidic acid and phosphatides.

- **Phosphoinositides:** In this group, inositol is the alcohol, e.g. phosphatidyl inositol (lipositol).
- **Phosphosphingosides:** Alcohol present is sphingosine (also called as sphingol), an unsaturated amino alcohol, e.g. sphingomyelin.

COMPOUND LIPIDS

Phosphatidyl Choline (Lecithin) :

It is widely distributed in animals in liver, brain, nerve tissues, sperm and egg-yolk, In plants, particularly abundant in seeds and sprouts. On hydrolysis, lecithin yields:

(a) glycerol (b) fatty acids

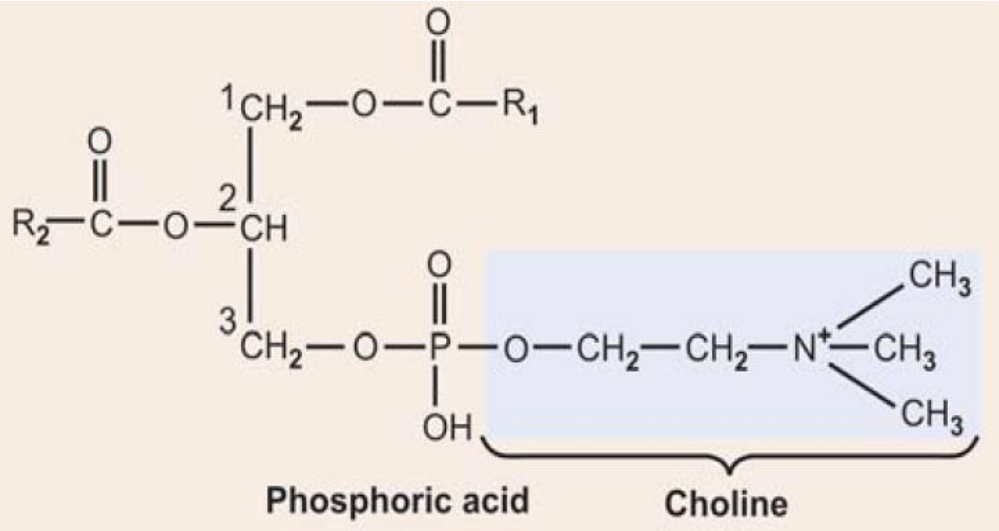
(c) phosphoric acid (d) nitrogenous base choline.

Functions:

1) Metabolic and structural

2) Nerve transmission .

3) Lecithin prevents gall stones



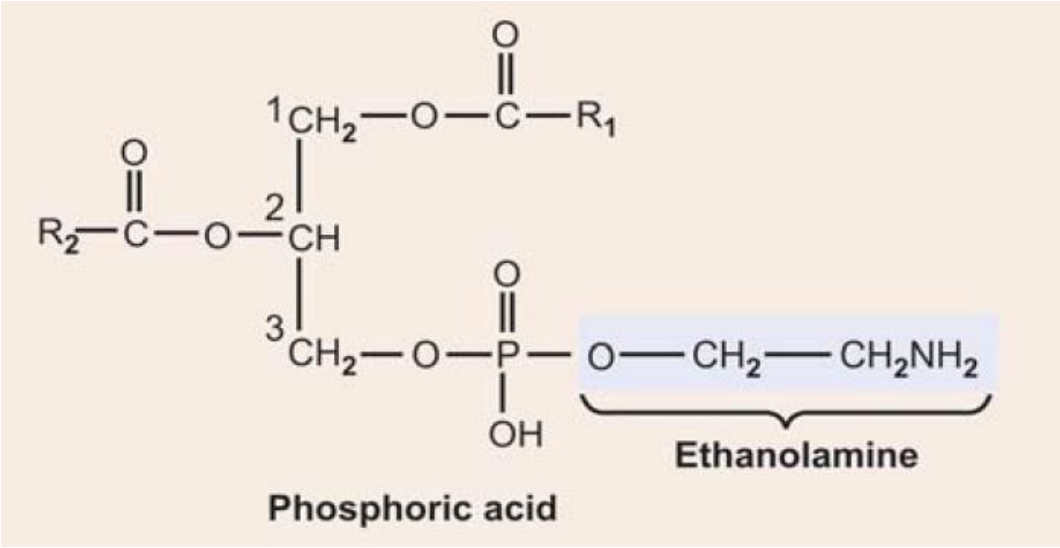
Lecithin (Phosphatidylcholine)

COMPOUND LIPIDS

Phosphatidyl Ethanolamine (Cephalin):

Cephalin are structurally identical with Lecithin, with the exception that the base ethanolamine replaces choline. particularly rich in brain and nervous tissues.

Function: It is one of activating factors of coagulation mechanism.

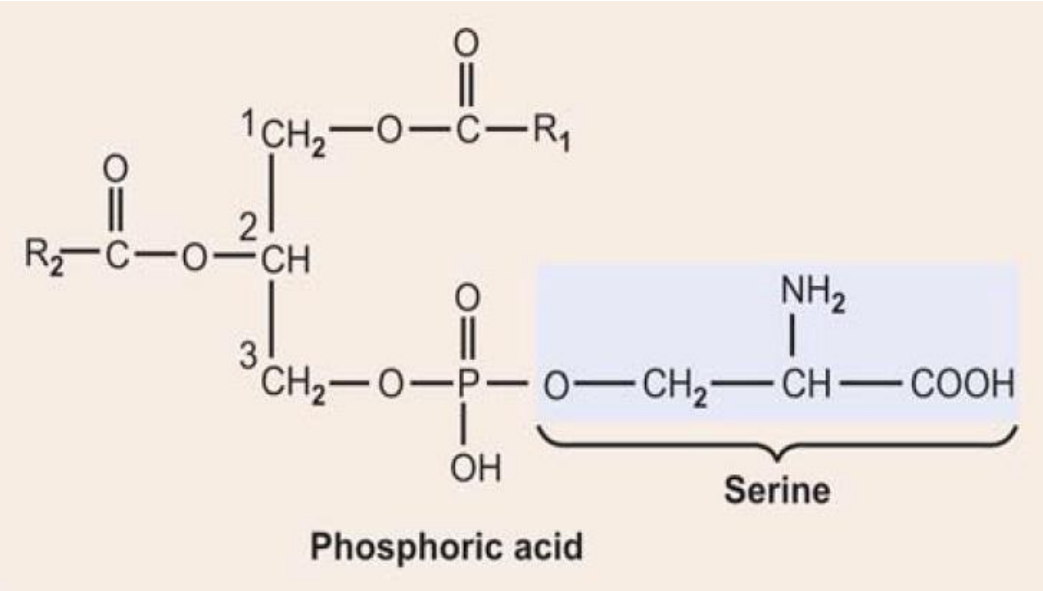


Cephalin

COMPOUND LIPIDS

Phosphatidyl Serine :

A cephalin like phospholipid contains amino acid serine in place of ethanolamine found in brain and nervous tissues and small amount in other tissues. Also found in blood.

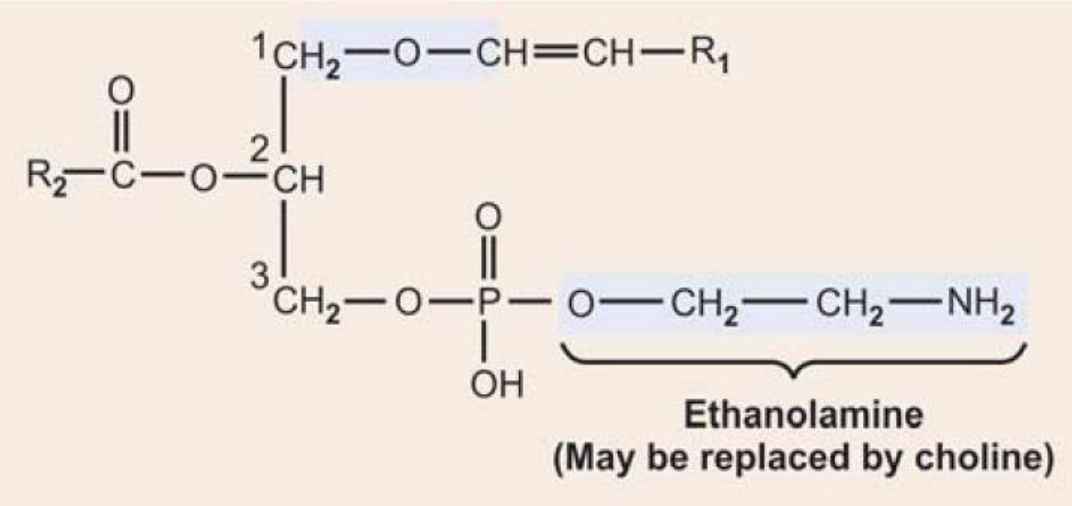


Phosphatidylserine

COMPOUND LIPIDS

Plasmalogens :

The plasmalogens make up an appreciable amount, about 10 per cent of total phospholipids of brain and nervous tissue, muscle and mitochondria. These compounds yield on hydrolysis (a) one molecule each of long chain aliphatic aldehyde, (b) a fatty acid, (c) glycerol –PO4, and (d) a nitrogenous base which is usually ethanolamine, but may be sometimes choline.



Plasmalogens

COMPOUND LIPIDS

Lipositol:

a) Structure: Like lecithin but it contains inositol instead of choline.

b) Function: it is present in cell membrane. it acts as precursor of second messenger (inositol triphosphate), mediating hormonal action inside cells

COMPOUND LIPIDS

Sphingomyelins :

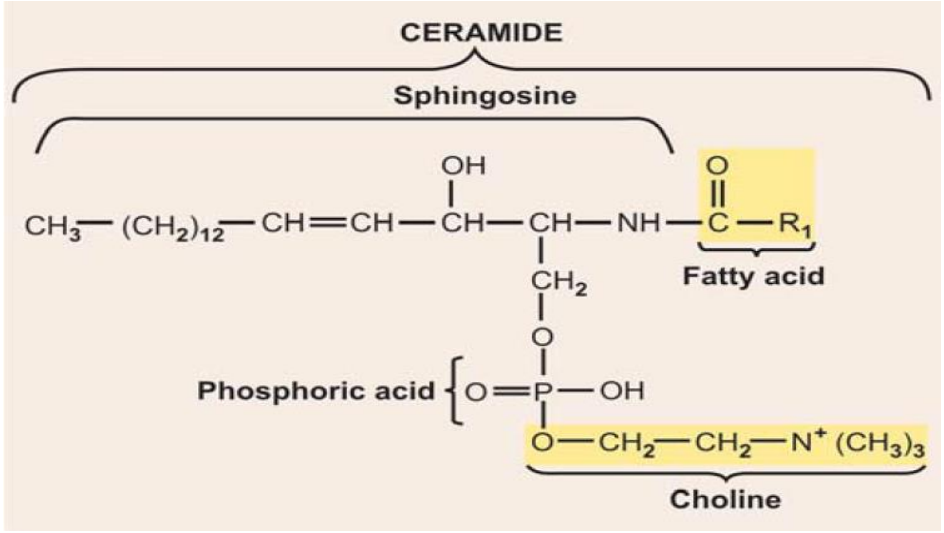
a) Structure: Sphingosine , Fatty acid (attached to amino group), Phosphoric acid residue, Choline base (attached to phosphoric acid).

b) Function: It is present in high concentrations in brain and nerve tissue.

c) Niemann Pick's disease:

1) It is accumulation of large amounts of sphingomyelin in liver due to deficiency of sphingomyelinase enzyme.

2) It leads to mental retardation and death in early life.



Sphingomyelins

COMPOUND LIPIDS

Glycolipids : These are complex lipids containing carbohydrate They also contain sphingosine (therefore, glycolipids together with sphingomyeltn may be classified as sphingoliplds). Glycolipids include **cerebrosldes , gangliosides.**

Cerebrosides:

They are called simple glycolipids.Upon hydrolysis ,they give:

1) Sphingosine

2) Fatty acid

3) Sugar (usually galactose or glucose)

There are present in many tissues especially in the brain and myelin of nerve fibres.

Gangliosides:

They are called complex glycolipids, because they contain in addition to hexose, one or more sialic acid molecules. Upon hydrolysis they give:

1) Ceramide (sphingosine and fatty acid).

Ceramide oligosaccharide: They contain sphingosine base, fatty acid (C_{24}) and many glucose and galactose units. They are present in heart and kidney.

2) Hexoses (glucose and galactose).

3) Hexosamines:

a) Sialic acid (N-acetylneuraminic acid).

b) N-acetylgalactosamine.

It is usually found on the outer surface of the cell envelopes especially the covers of neurons.

COMPOUND LIPIDS

Sulpholipids: Lipids material containing sulphur has long been known to be present in various tissues and has been found in liver, kidney, testes, brains and certain tumours.

Lipoproteins: These are complex lipids formed of lipids conjugated with protein.

1) They are present in cell membrane. mitochondria. and plasma (plasma lipoproteins).

2) Plasma lipoproteins convert water insoluble lipids into water soluble complexes. This facilitates transport of lipids between blood and different tissues

3) The plasma lipids are triacylglycerols, phospholipids, cholesterol (free and esterified) and free fatty acids.

Lipoproteins are classified based on their density, electrophoretic mobility, and nature of apoprotein content.

Based on their density, lipoproteins can be classified into chylomicrons, very low-density lipoproteins (VLDL), intermediate density lipoproteins (IDL), low-density lipoproteins (LDL), and high-density lipoproteins (HDL).

DERIVED LIPIDS:

Substances which are insoluble in water but soluble in nonpolar solvents. They include:

1. Steroids and sterols.

2. Carotenoids

3. Cholanthrenes

4. Ketone bodies.

5. Fatty aldehydes.

DERIVED LIPIDS:

1.Steroids and sterols: These are a group of compounds that contain ring called **cyclopentanoperhydrophenanthrene** ring.

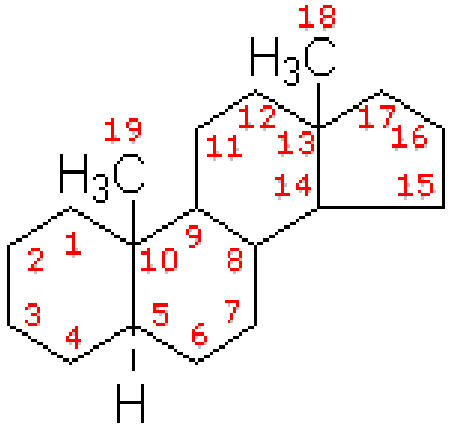
Types of steroids and sterols are:

1. Cholesterol (animal origin).
2. Ergosterol (plant origin).
3. Vitamin D group (D_2 and D_3).
4. Steroid hormones:

a) Male sex hormones. **b)** Female sex horn

c) Adrenocortical hormones.

5. Bile salts.
6. Digitalis glycosides.
7. Some carcinogenic substances



Cyclopentanoperhydro phenanthrene

Cholesterol :

1. Structure: It contains:

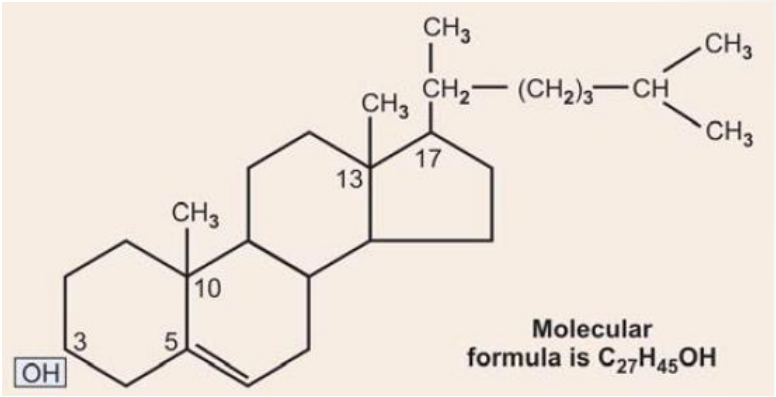
a) Cyclopentanoperhydrophenanthrene ring

b) -OH group at C_3 (so it is an alcohol).

c) 2 methyl groups at C_{10} , C_{13}

d) Long side chain at C_{17}.

Its molecular formula is $C_{27}H_{45}OH$



Cholesterol

2. Body cholesterol:

It is present in every body cell (cell membrane) especially in:

1) Adrenal cortex.

2) Gonads.

3) Liver and kidney.

4) Brain and nerve tissue.

b) Blood cholesterol:

1) It occurs in the blood in 2 forms: free form and esterified form (combined to fatty acids to form ester).

2) The level of blood cholesterol is normally less than 220 mg/dl. Any increase above this level is called: hypercholesterolemia.

Cholesterol :

The importance of cholesterol for humans:

1) It is present In every body cell (cell membrane) especially In Adrenal cortex, Gonads, Liver and kidney, Brain and nerve tissue and is involved in the formation of hormones such as adrenal cortical hormones such as aldosterone.

2) It regulates the balance of water and salt and is included in the composition of testosterone, which is a male hormone and in the composition of vitamin D_3

3) He production of bile acids such as **Cholic Acid**

Cholic acid contributes to the formation of important bile salts For the processes of digestion and absorption of fatty substances in the body.