PHYSICAL PROPERTIES

1. State

- Fats containing saturated fatty acids are solid at ordinary room temperature.
- The *animal fats* belong to this category.
- Most *plant fats*, on the contrary, possess unsaturated fatty acids and are, henceforth, liquid at room temperature.

2. Colour, Odour and Taste

- When pure, the fats are *colourless,* virtually *odourless* and *possess* an extremely *bland taste*.
- They are capable of absorbing a variety of odours and hence flavour during storage. For the same reason, a house wife knows that the flavour of an onion quickly permeates butter that is stored with it in a refrigerator. In some cases, however, this absorbing property of fats is of advantage. For example, the perfumes of some flowers can be isolated by placing their petals in contact with the fat for a certain period, then extracting the fat with alcohol and concentrating the essence.

3. Solubility

- The fats are, however, only sparingly soluble in water. These are, therefore, described as *hydrophobic* in contrast to the water-soluble or hydrophilic substances like many carbohydrates and proteins.
- However, these are freely soluble in organic solvents like chloroform, ether, acetone and benzene. These solvents, as they dissolve fats in them, are also known as' *fat solvents*'.
- The solubility of the fatty acids in organic solvents, in fact, decreases with the increase of chain length.

4. Melting point. The melting point of fats depends on the chain length of the constituent fatty acid and the degree of unsaturation. Fats containing saturated fatty acids from C 4 to C 8 are liquid at room temperature but those containing C 10 or higher saturated fatty acids are solid and their melting points increase with increasing chain length. With the introduction of double bond in the fat molecule, the melting point lowers considerably. It may be stated, in general, that *greater the degree of unsaturation (or higher the number of double bonds) of the constituent fatty acid, the lower is the melting point of the fat*. This may be easily visualized in terms of constituent fatty acids from the Table 14–1. In fact, short chain length and unsaturation enhance the fluidity of fatty acids and of their derivatives.

Table 14–1. Melting points of the common fatty acids*

Fatty acid	*No. of carbon atoms*	*No. of double bonds*	*M.P. (in °C)*
Saturated			
Caprylic	8	0	16.0
Capric	10	0	31.0
Lauric	12	0	44.2
Myristic	14	0	53.9
Palmitic	16	0	63.1
Stearic	18	0	69.6
Arachidic	20	0	76.5
Behenic	22	0	79.9
Lignoceric	24	0	86.0
Unsaturated			
Palmitoleic	16	1	11.0
Oleic	18	1	13.4
Linoleic	18	2	– 5.0
Linolenic	18	3	–11.0
Arachidonic	20	4	– 49.5

5. Specific gravity. The specific gravity of the fats is less than 1 (about 0.86) and, therefore, they float on water surface. Solid fats are lighter than the liquid fats. Oils spread on water to form thin monomolecular layers. In general, either unsaturation of the fatty acid chains increase or increase in chain length of the fatty acid residues tend to increase the specific gravity.

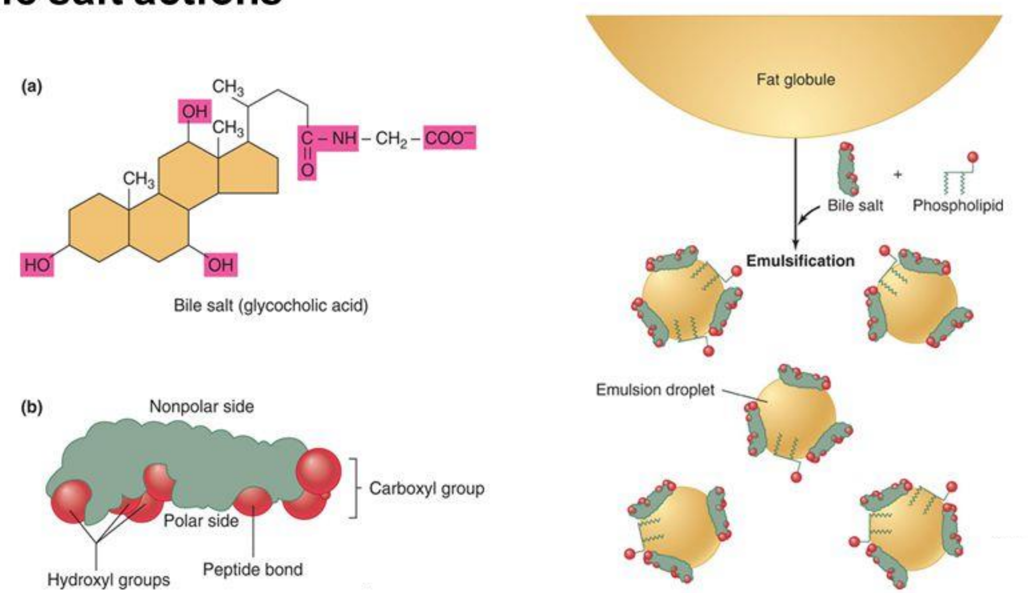
6. Geometric isomerism. As stated earlier, the presence of double bond (*s*) in the unsaturated fatty acid part of the fat molecule produces geometric (or *cis-trans*) isomerism.

7. Insulation. The fats possess *high insulating power*, *i.e.*, they are bad conductor of heat. A layer of fat below the skin provides a sort of blanket for warm-blooded animals (or *homoiotherms*). This is especially important for whales and seals which have to maintain a high temperature in cold waters. The fishes are cold-blooded animals (*or poikilotherms*) and, therfore, do not require maintenance of high temperature and so have very little subcutaneous fat.

8. Emulsification. It is the process by which a lipid mass is converted into a number of small lipid droplets. The fats may be emulsified by shaking either with water or with emulsifying agents like soaps, gums, proteins etc. An emulsifying agent helps in the production of a finely divided suspension of a fat in an aqueous medium. The hydrocarbon portions of the two (the emulsifier and the fat) tend to aggregate. This leaves the water-soluble group of the emulsifier projecting into the aqueous phase. A fat droplet will associate with a number of molecules of the emulsifier, thus producing a new water-soluble surface. Water molecules, henceforth, tend to be held in a layer or '*cloud*' around each droplet, thus disallowing the aggregation of the fat droplets

The process of emulsification is of great metabolic significance. In fact, *the fats have to be emulsified before they can be absorbed by the intestinal wall.* The process is accomplished by the bile juice secreted from liver.

Bile salt actions

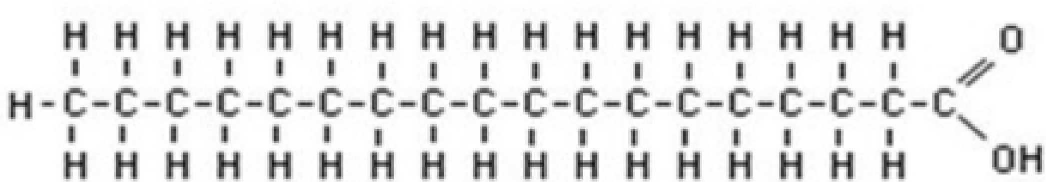


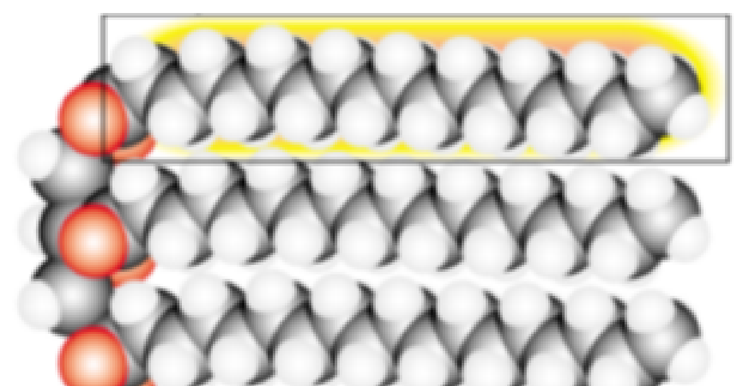
Bile: produced in liver, stored in gall bladder
Emulsification in duodenum & upper intestine

Saturated and Unsaturated Fatty Acids

Saturated Fatty acids

- The terms **saturated**, **mono-unsaturated**, and **poly-unsaturated** refer to the **number of hydrogen** attached to the hydrocarbon tails of the fatty acids as compared to the number of double bonds between carbon atoms in the tail.
- **Saturated fats** have all **single bonds** between the carbons in their fatty acid tails, thus all the carbons are also bonded to the maximum number of hydrogen possible…maximum possible amount of hydrogen → ***saturated* fats**.
- The hydrocarbon chains in these fatty acids are, thus, fairly straight and can pack closely together. There are strong attractions between the fatty acids in triglycerides with saturated fatty acids. These fats are **solid at room temperature.**



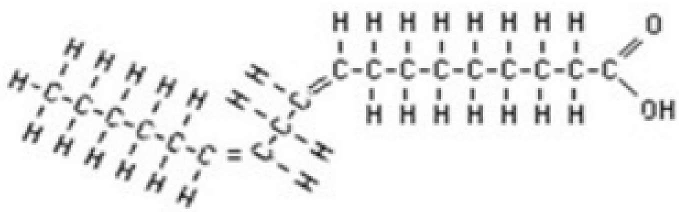


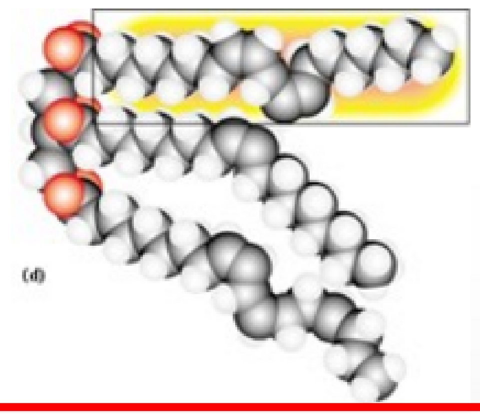
Saturated and Unsaturated Fatty Acids

Unsaturated Fatty acids

- Oils have some double bonds between some of the carbons in the hydrocarbon tail, causing bends or "kinks" in the shape of the molecules.
- Because some of the carbons share double bonds, they're not bonded to as many hydrogen as they could if they weren't double bonded to each other. These oils are called **unsaturated fats** .
- Because of the kinks in the hydrocarbon tails, unsaturated fats can't pack as closely together, making them **liquid at room temperature** .
- unsaturated fats are "healthier"

  than the saturated ones.





1. **Hydrolysis**

The fats are hydrolyzed by the enzymes *lipases* to yield fatty acids and glycerol. The lipases catalyze this reaction at a slightly alkaline *p*H (7.5 – 8.5) in a stepwise manner. The fats first split to produce *diglycerides*, part of these are then split to *monoglycerides*. Finally, part of the monoglycerides split to yield *fatty acid* and *glycerol.*

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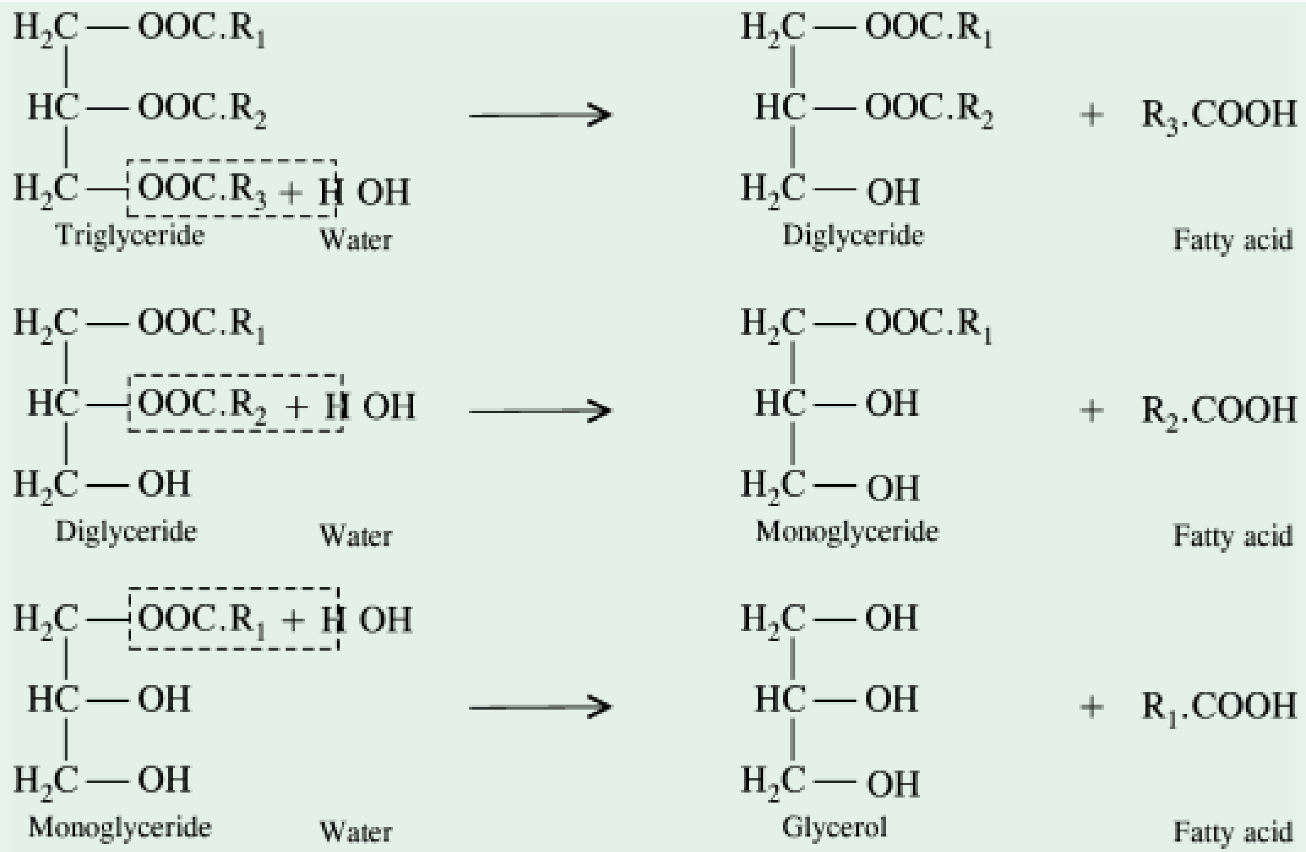


[Radicals R_1, R_2 and R_3 may be similar or dissimilar.]

2. Saponification

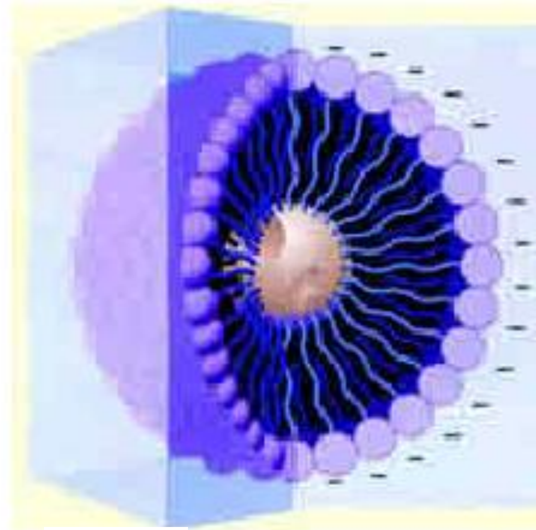
- ***The hydrolysis of fats by alkali is called saponification.*** This reaction results in the formation of glycerol and salts of fatty acids which are called *soaps.*

  The soaps are of two types : hard and soft.

  Hard soaps
  such as the common bar soaps are the sodium salts of the higher fatty acids.

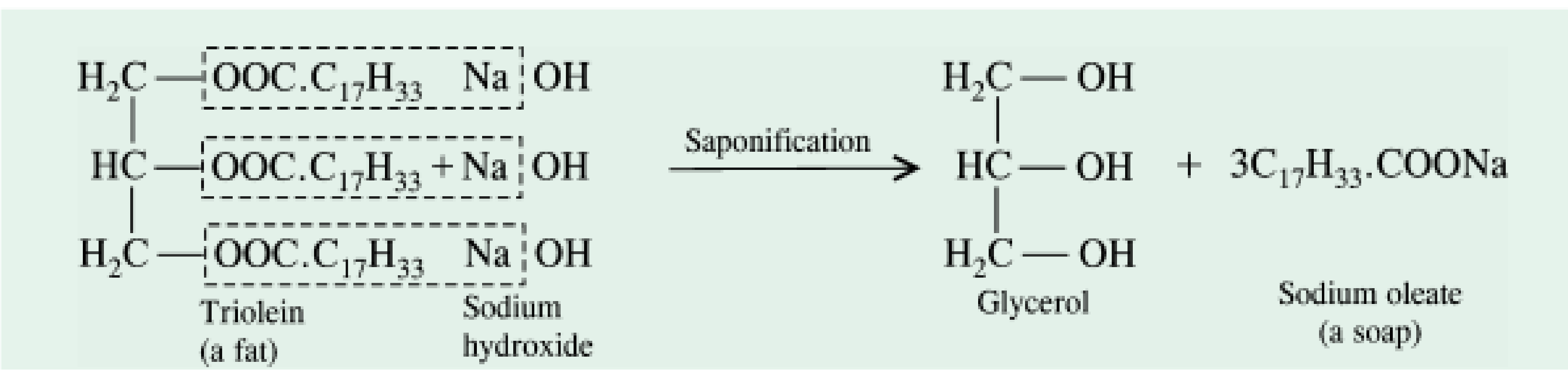
  Soft soaps
  are the potassium salts of higher fatty acids and are market as semisolids or pastes.

- The fatty acid salts of calcium, magnesium, zinc and lead are, however, insoluble in water. Calcium soaps are used industrially as lubricating greases. Zinc soaps are employed in the manufacture of talcum powder and other cosmetics. Lead and magnesium soaps are used in paints industry to hasten the process of drying



Soaps consist of fatty acids

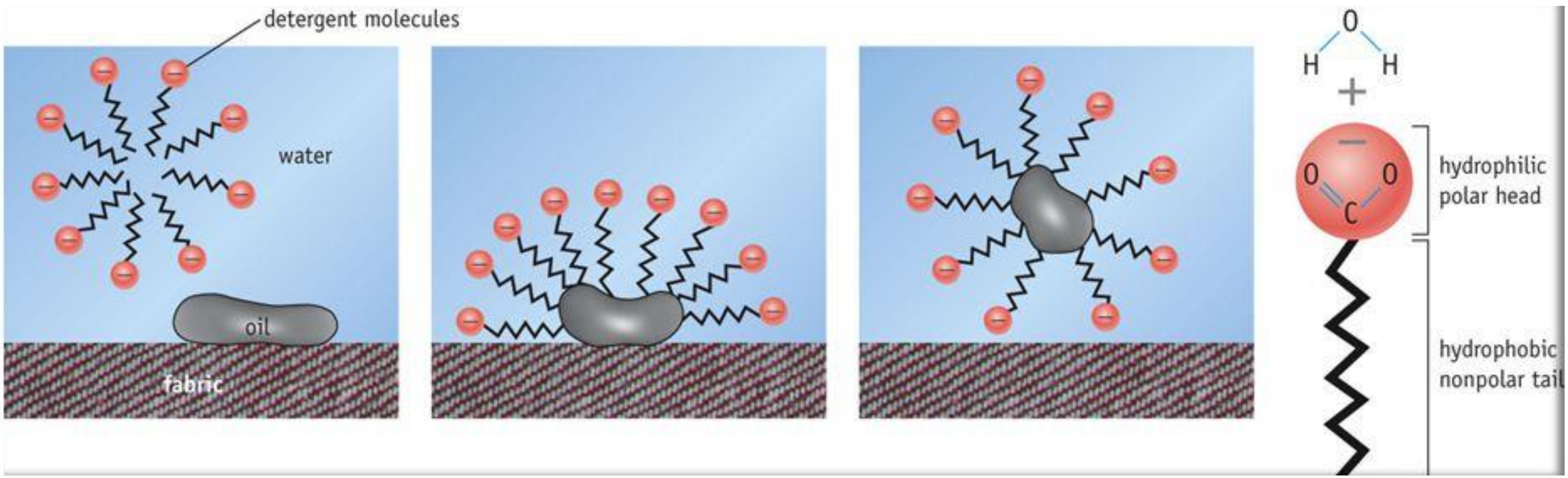
In this schematic drawing of a soap micelle, the nonpolar tails of the fatty acids are directed inward, where they interact with the greasy matter to be dissolved. The negatively-charged heads are located at the surface of the micelle, where they interact with the surrounding water. Membrane proteins, which also tend to be insoluble in water, can also be solubilized in this way by extraction of membranes with detergents.

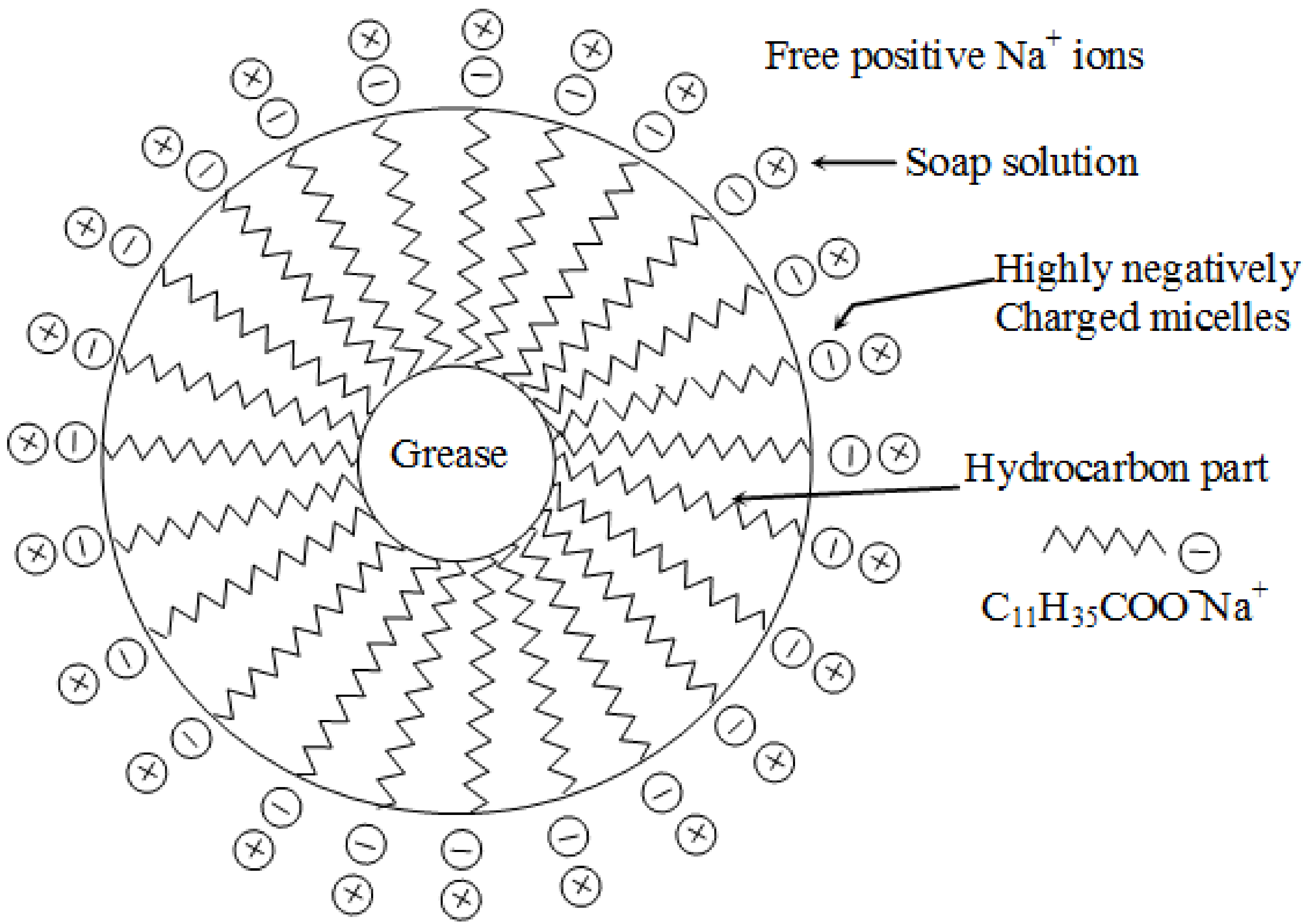


When greasy dirt is mixed with soapy water, the soap molecules arrange themselves into tiny clusters called micelles.

The water-loving (hydrophilic) part of the soap molecules sticks to the water and points outwards, forming the outer surface of the micelle.

The oil-loving (hydrophobic) parts stick to the oil and trap oil in the center where it can't come into contact with the water. With the oil tucked safely in the center, the micelle is soluble in water. As the soapy water is rinsed away the greasy dirt goes along with it.





Cleansing action of soap. Soap micelle entraps the oily dirt particle

Rancidity

Definition:

- It is a physico-chemical change in the natural properties of the fat leading to the development of **unpleasant odor or taste or abnormal color** particularly on aging after exposure to atmospheric oxygen, light, moisture, bacterial or fungal contamination and/or heat.

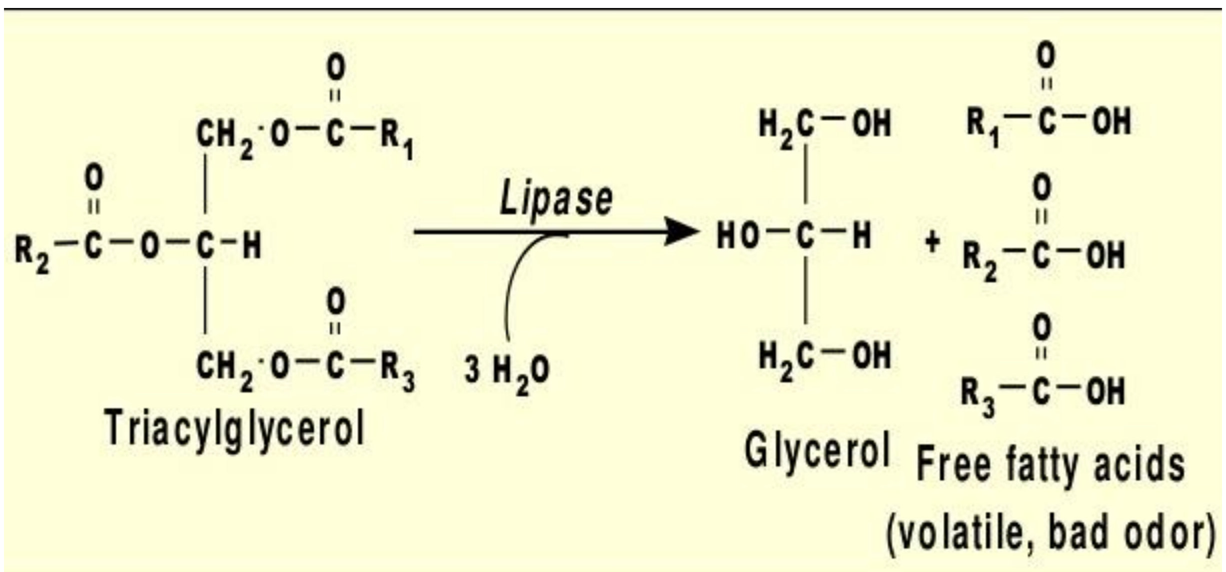
- Saturated fats resist rancidity more than unsaturated fats that have unsaturated double bonds.

Types and causes of Rancidity:

1. Hydrolytic rancidity
2. Oxidative rancidity
3. Ketonic rancidity

1-Hydrolytic rancidity:

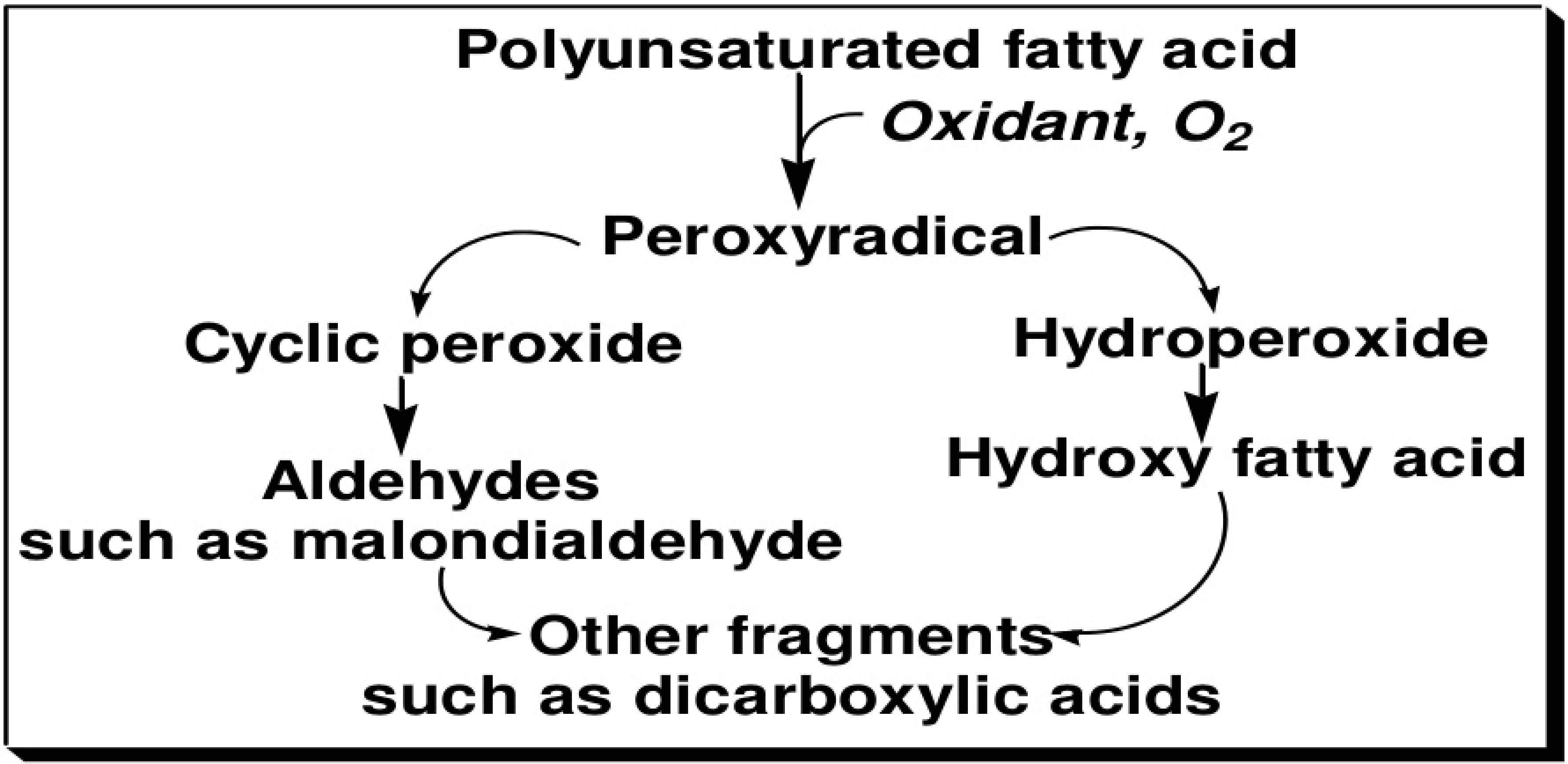
- It results from slight hydrolysis of the fat by lipase from bacterial contamination leading to the liberation of free fatty acids and glycerol at high temperature and moisture.
- Volatile short-chain fatty acids have unpleasant odor.



2-Oxidative Rancidity:

- **It is oxidation of fat or oil catalyzed by exposure to oxygen, light and/or heat producing peroxide derivatives which on decomposition give substances, e.g., peroxides, aldehydes, ketones and dicarboxylic acids that are toxic and have bad odor.**

- **This occurs due to oxidative addition of oxygen at the unsaturated double bond of unsaturated fatty acid of oils.**


Polyunsaturated fatty acid
Oxidant, O2
Peroxyradical
Cyclic peroxide
Hydroperoxide
Aldehydes
such as malondialdehyde
Hydroxy fatty acid
Other fragments
such as dicarboxylic acids

3-Ketonic Rancidity:

- It is due to the contamination with certain fungi such as Asperigillus Niger on fats such as coconut oil.

- Ketones, fatty aldehydes, short chain fatty acids and fatty alcohols are formed.
- Moisture accelerates ketonic rancidity.

- **Prevention of rancidity is achieved by:**

1. Avoidance of the causes (exposure to light, oxygen, moisture, high temperature and bacteria or fungal contamination). By keeping fats or oils in well-closed containers in cold, dark and dry place (i.e., good storage conditions).
2. Removal of catalysts such as lead and copper that catalyze rancidity.
3. Addition of anti-oxidants to prevent peroxidation in fat (i.e., rancidity). They include phenols, naphthols, tannins and hydroquinones. The most common natural antioxidant is vitamin E that is important *in vitro* and *in vivo*.

Hazards of Rancid Fats:

1. The products of rancidity are toxic, i.e., causes food poisoning and cancer.
2. Rancidity destroys the fat-soluble vitamins (vitamins A, D, K and E).
3. Rancidity destroys the polyunsaturated essential fatty acids.
4. Rancidity causes economical loss because rancid fat is inedible.

REACTIONS INVOLVING DOUBLE BOND

1. Hydrogenation

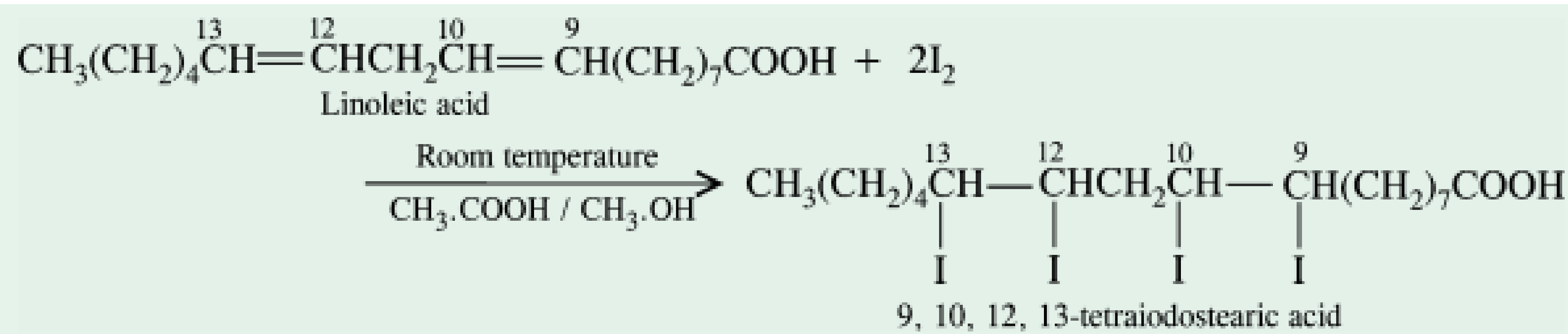
- Unsaturated fatty acids, either free or combined in lipids, react with gaseous hydrogen to yield the *saturated fatty acids.*
- The reaction is catalyzed by platinum, palladium or nickel. The addition of hydrogen takes place at the C—C double bond (*s*).
- Thus, 1 mole of oleic, linoleic or linolenic acid reacts with 1, 2 or 3 moles of hydrogen respectively to form stearic acid.

$$\underset{\text{Oleic acid}}{CH_3(CH_2)_7\overset{10}{C}H=\overset{9}{C}H(CH_2)_7COOH} + H_2 \xrightarrow[\text{as catalyst}]{\text{Pt, Pd or Ni}} \underset{\text{Stearic acid}}{CH_3(CH_2)_7\overset{10}{C}H_2-\overset{9}{C}H_2(CH_2)_7COOH}$$

This reaction is of great commercial importance since it permits transformation of inexpensive and unsaturated liquid vegetable fats into solid fats. The latter are used in the manufacture of candles, vegetable shortenings and of oleomargarine.

2. Halogenation

Unsaturated fatty acids and their esters can take up halogens like Br_2 and I_2 at their double bond (*s*) at room temperature in acetic acid or methanol solution.

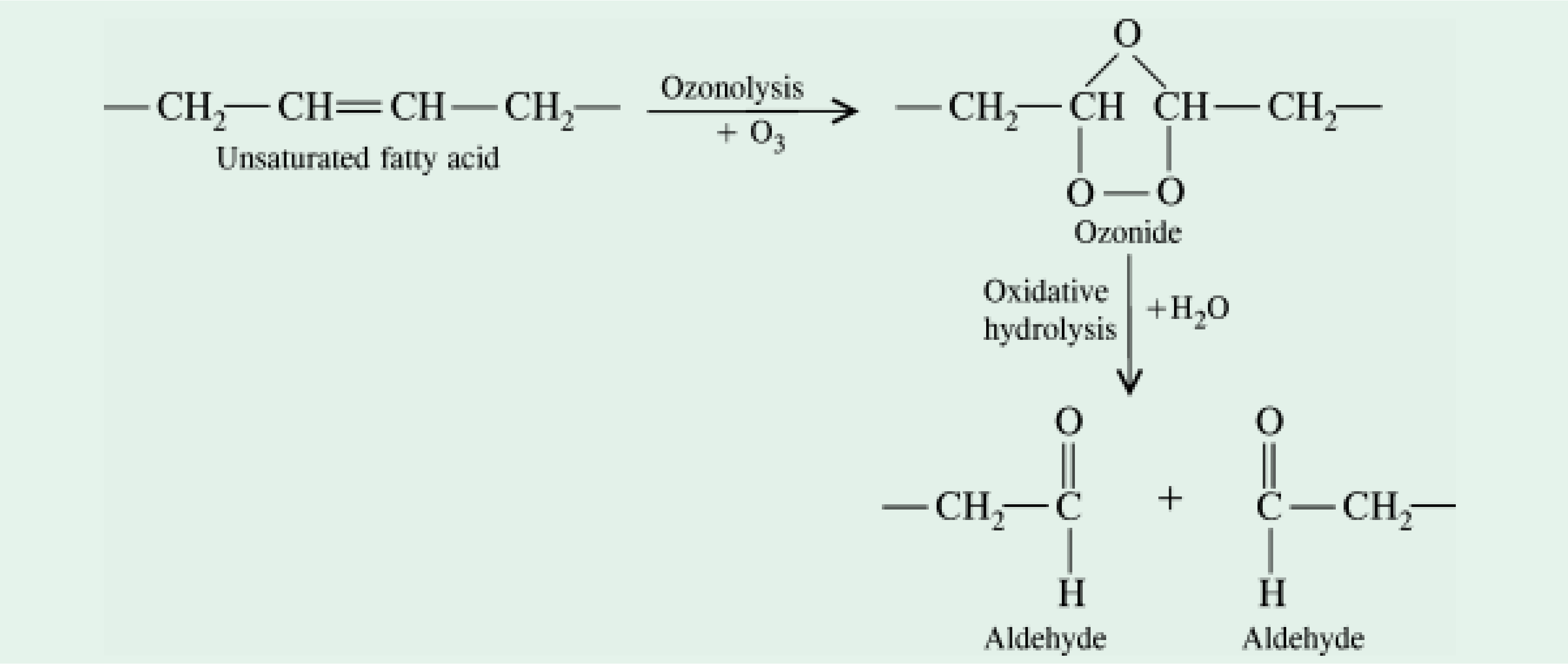


3. Oxidation

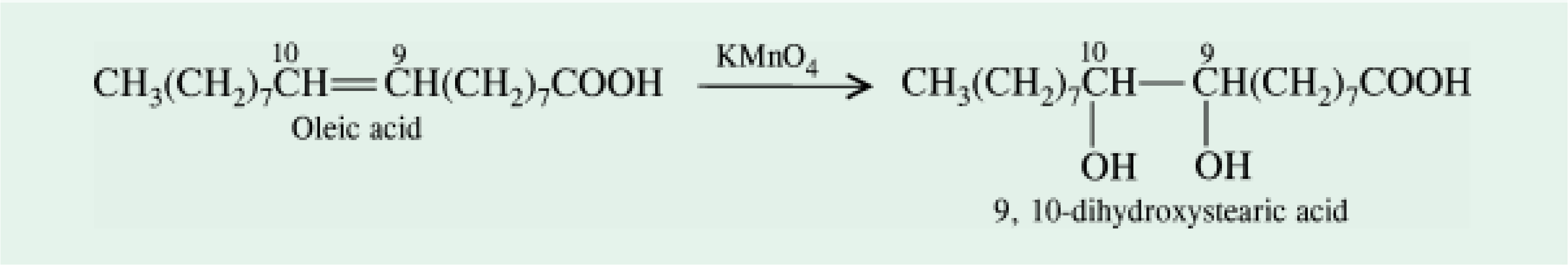
Unsaturated fatty acids are susceptible to oxidation at their double bonds. Oxidation may be carried with **ozone** or **$KMnO_4$.**

(*a*) **With ozone** – An unstable ***ozonide*** is formed which later cleaves by water to give rise to 2 *aldehydic groups*

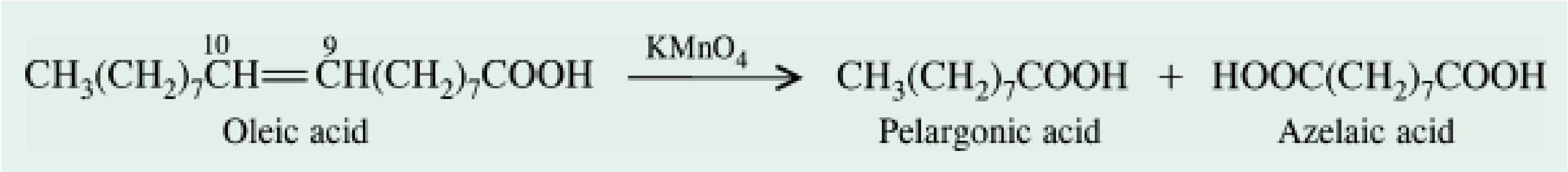
.



(b) **With $KMnO_4$** – Under mild conditions, the ***glycols*** are formed at the sites of double bonds.

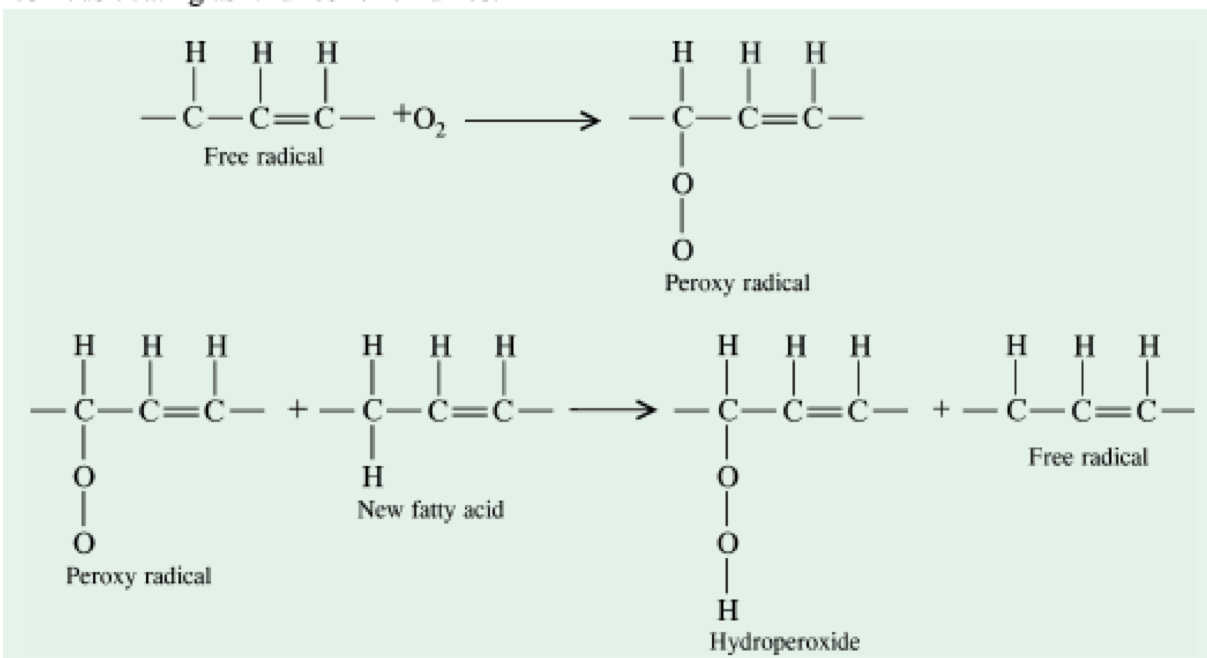


Under vigorous conditions, the same reagent cleaves the molecule at the double bond and oxidizes the terminal portions to the *carboxyl group*



4. Oxidative rancidity. Oils containing highly unsaturated fatty acids are spontaneously oxidized by atmospheric oxygen at ordinary temperatures. The oxidation takes place slowly and results in the formation of *short chain fatty acids* (*C_4 to C_{10}*) and *aldehydes* which give a rancid taste and odour to the fats. This type of rancidity or rancidification is called 'oxidative rancidity' and is due to a reaction called `*autoxidation*'. Autoxidation proceeds by a free radical mechanism in which the a- methylene group is primarily attacked. A hydrogen atom is removed from an α-methylene group. This initiates a chain of reactions leading to oxidation (Holman, 1954).

Oxidative rancidity is observed more frequently in animal fats than in vegetable fats. This is due to the presence, in the vegetable oils, of natural **'antioxidants'** such as tocopherols (= vitamin E), phenols, naphthols etc., which check autoxidation. Vitamin E is, therefore, some-times added to foods to prevent rancidity. Animal shortenings such as lard are nowadays protected against oxidative rancidity by the addition of synthetic antioxidants such as nordihydroguiaretic acid (NDGA), tertiary butyl hydroxy anisole (BHA) etc. Linseed oil, a plant oil used as a base for paints, is highly rich in unsaturated fatty acids. It undergoes autoxidation when exposed to air, followed by polymerization to a hard, resinous coating as it 'dries' or oxidizes.



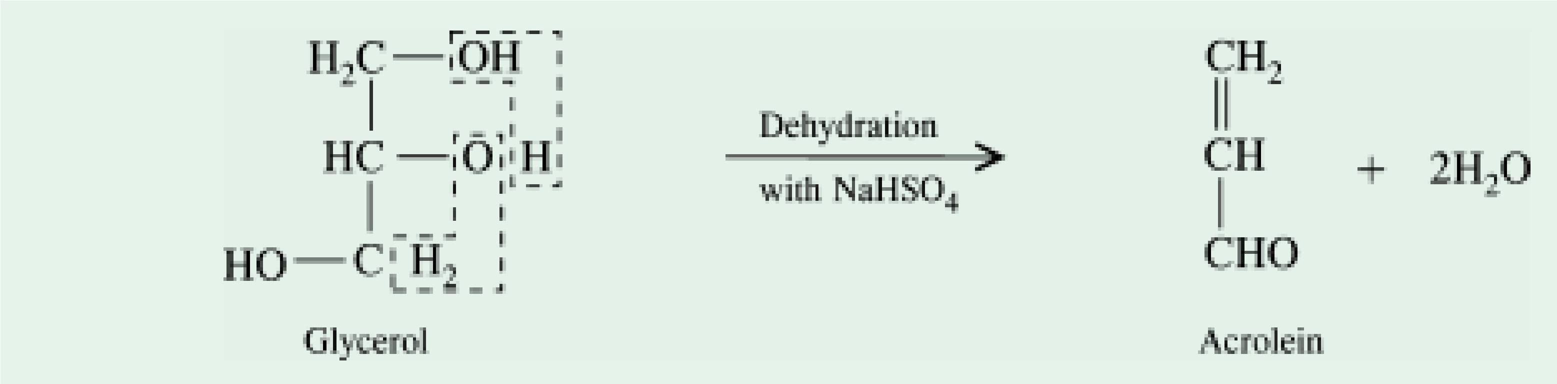
The action of antioxidants is opposed by a group of compounds present in the fats and oils. These accelerate the oxidation of the parent compound and are called *pro-oxidants.* Majority of these substances are formed during the processing and refining of fats. Among the noteworthy pro-oxidants are the copper, iron and nickel salts of organic acids like lactic, etc.

REACTION INVOLVING OH GROUPS

Dehydration (Acrolein test)

Fats, when heated in the presence of a dehydrating agent, $NaHSO_4$ or $KHSO_4$ produce an unsaturated aldehyde called **acrolein** from the glycerol moiety.

Acrolein is easily recognized by its pungent odour and thus forms the basis of the test for the presence of glycerol in fat molecule



QUANTITATIVE TESTS

The reactions described above give valuable information about the chemical nature of fatty acids and the number of hydroxyl groups present in the fat molecule. Such chemical determinations involve various analytical tests. These are called *chemical constants* and include the following:

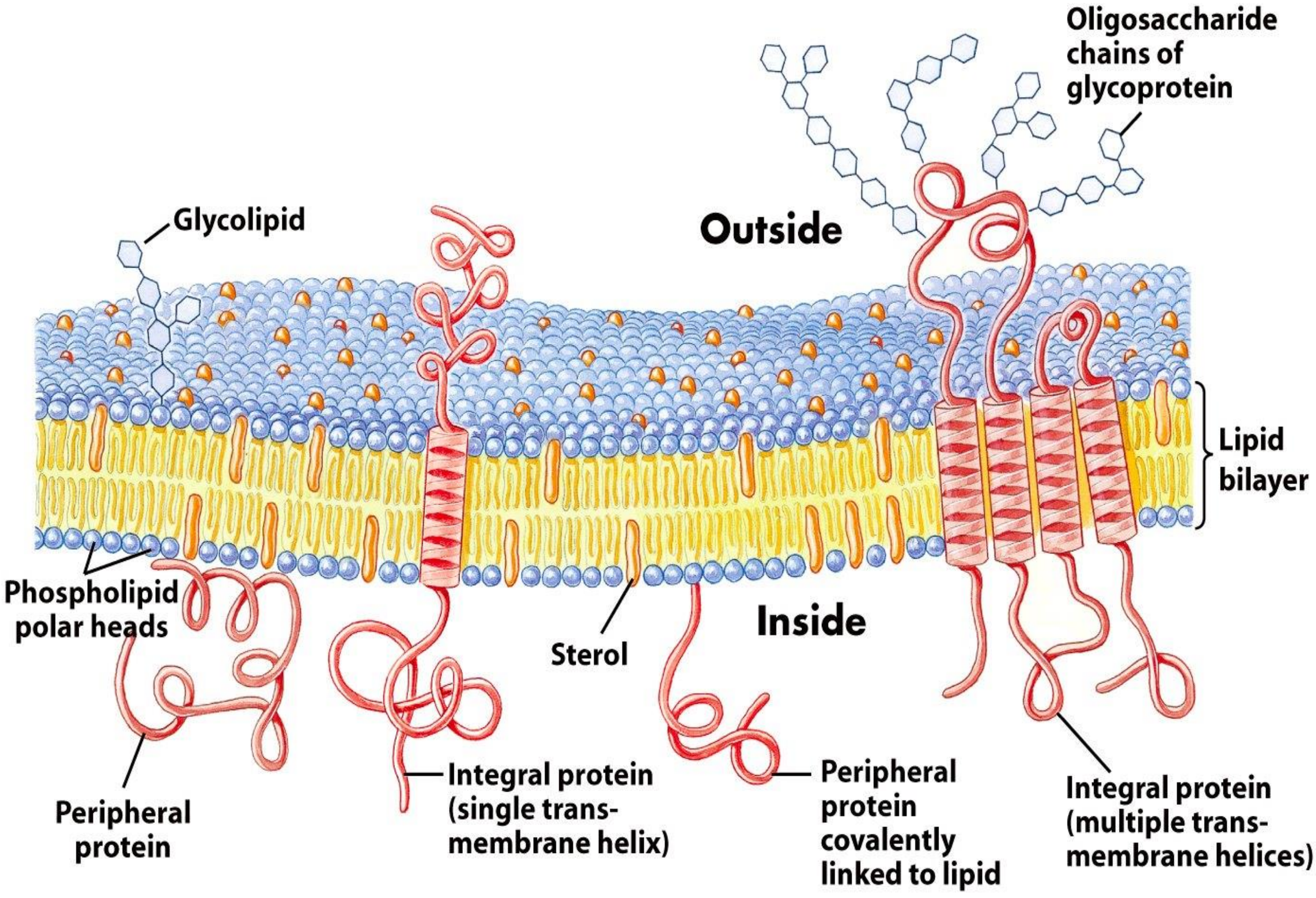
1. Acid value. It is the number of milligrams of KOH required to neutralize the free fatty acids present in 1 gm of fat. The acid number, thus, tells us of the quantity of free fatty acid present in a fat. Obviously, a fat which has been both processed and stored properly has a very low acid number.

2. Saponification number. It is the number of milligrams of KOH required to saponify 1 gm of fat. The saponification number, thus, provides information of the average chain length of the fatty acids in the fat. It varies inversely with the chain length of the fatty acids. *The shorter the average chain length of the fatty acids, the higher is the saponification number.*

3. Iodine value (or Koettstorfer numb … number of grams of iodine absorbed by 100 g of fat. T … saturation of the fatty acids in the fat. Oils l … s (133, 127 and 109, respectively) than the … er possess more unsaturated fatty acids in t … cation as to the number of double bonds pr …

6. A … red to neutralize the acetic acid obtained … The treatment of fat or fatty acid mixture … OH groups). The acetyl number is, thus, a … e, the castor oil has a high acetyl number (146) … acid, in it.

Acid value refers to the amount of "free" fatty acids in the oil/fat.
Saponification value refers to the amount of esters that can be hydrolysed and turned into soap.
Both these values are given as mg KOH per g of oil or fat


Oligosaccharide chains of glycoprotein
Glycolipid
Outside
Lipid bilayer
Phospholipid polar heads
Inside
Sterol
Peripheral protein
Integral protein (single trans-membrane helix)
Peripheral protein covalently linked to lipid
Integral protein (multiple trans-membrane helices)

MEMBRANE LIPIDS

Properties, Structure & Classification

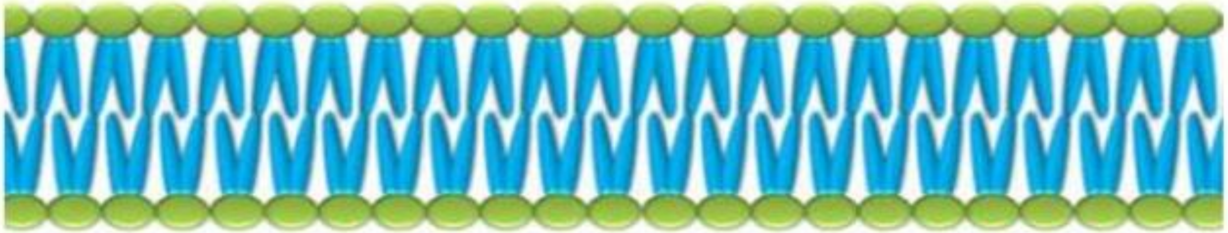
"Good fences make good neighbors"

Robert Frost, *"Mending Wall,"*
In North of Boston, 1914

MEMBRANE LIPIDS

Biological membrane system:

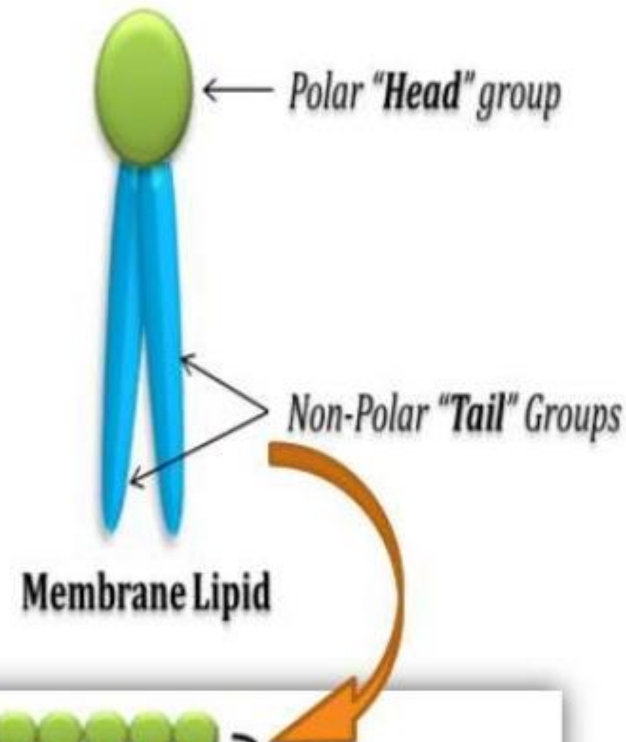
- Membranes are two layers thick sheath like structures
- Formed by ***non-covalent assemblage*** of lipids and proteins
- Mainly consists of **Lipids**, **Proteins** and **Carbohydrates**
- Thickness of membrane: 60 Å (6 nm) to 100 Å (10 nm)
- Membrane forms closed boundaries between different compartments
- Act as barriers to the passage of **polar molecules** and **ions**

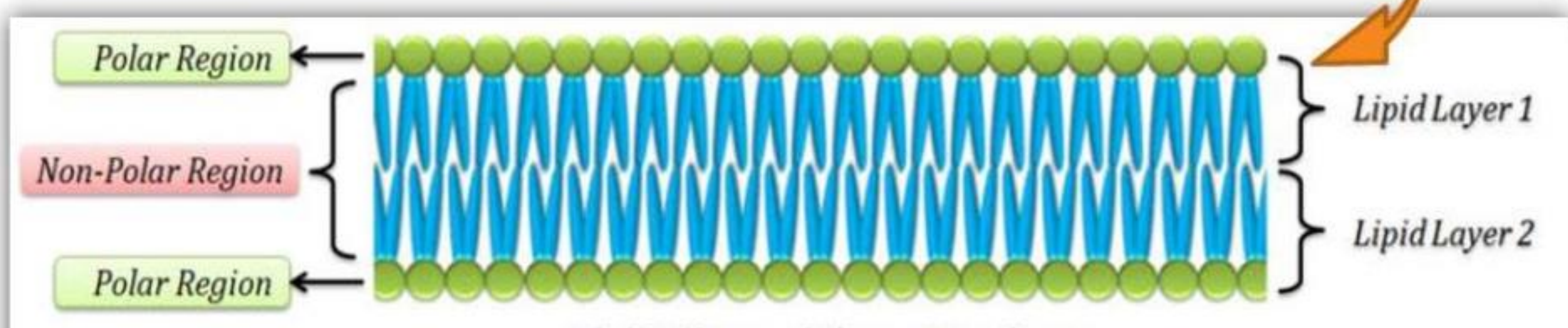


Plasma membrane

MEMBRANE LIPIDS

- Membrane lipids have **hydrophilic** (polar) & **hydrophobic** (non-polar) parts
- One end is hydrophilic and the other end is hydrophobic (**amphipathic**)
- *Their **hydrophobic** interactions with each other and their **hydrophilic** interaction with **water** direct the **packing** of lipids in the membrane*





Lipid Bilayer of Plasma Membrane

MEMBRANE LIPIDS

- Bio-membranes are asymmetric
- Components of two faces always differ from each other
- Long hydrocarbon chains of fatty acid forms the hydrophobic part
- ***Hydrophilic*** *moieties of the membrane lipids may be* ***as simple as single –OH*** *at one end of the sterol ring system or they may be* ***much complex***
- We commonly represent the polar part of membrane lipid as '**Head**' and the non-polar part as '**Tail**'

MEMBRANE LIPIDS

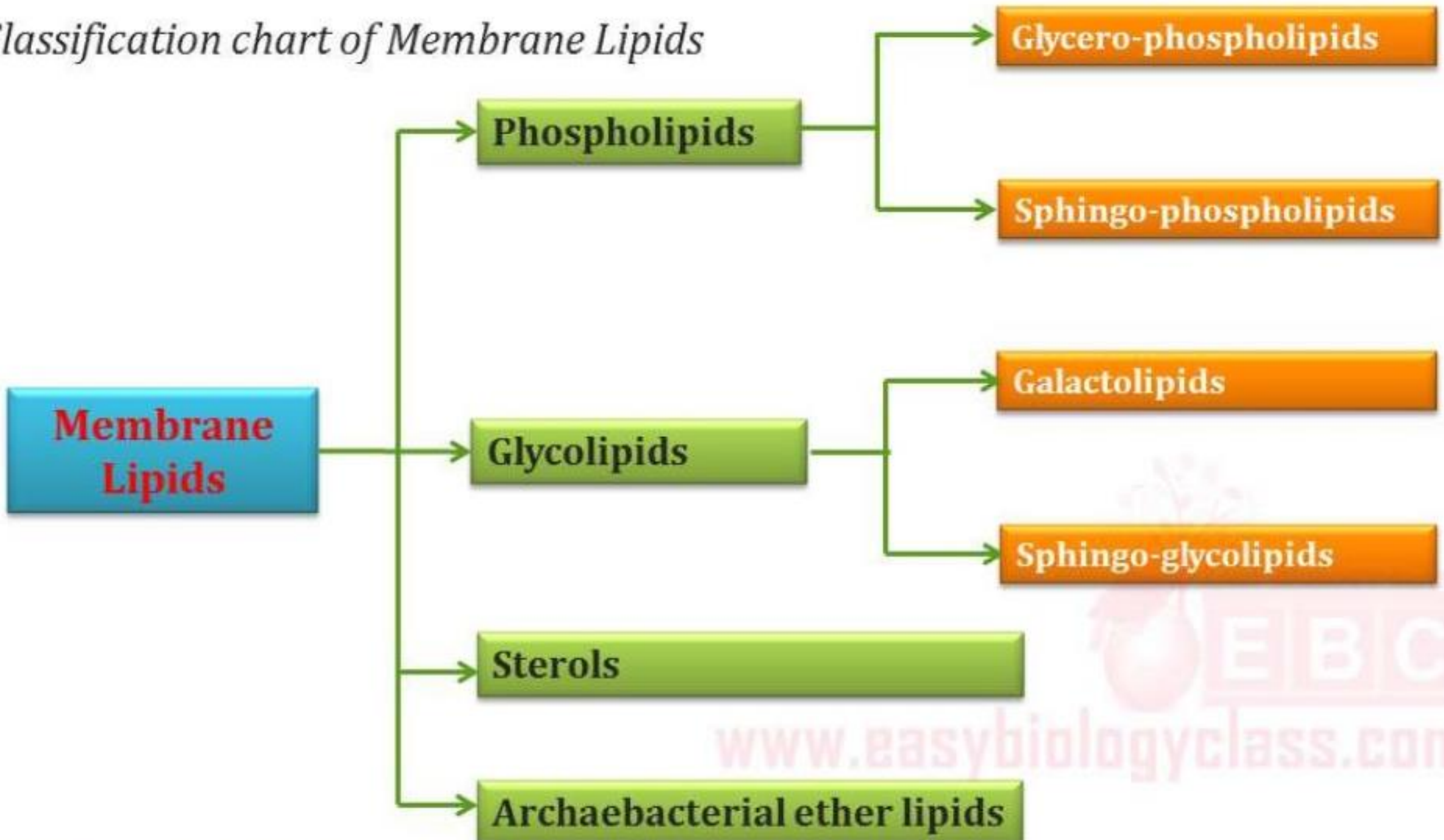
- Membrane lipids are classified based on the properties of '**head**' group
- Membrane lipids of **Prokaryotes**, **Eukaryotes** and **Archaebacteria** are grouped into **Four** major categories:

1. *Phospholipids*
2. *Glycolipids*
3. *Sterols*
4. *Archaebacterial ether lipids*

MEMBRANE LIPIDS

Mind-Map:

Classification chart of Membrane Lipids



MEMBRANE LIPIDS

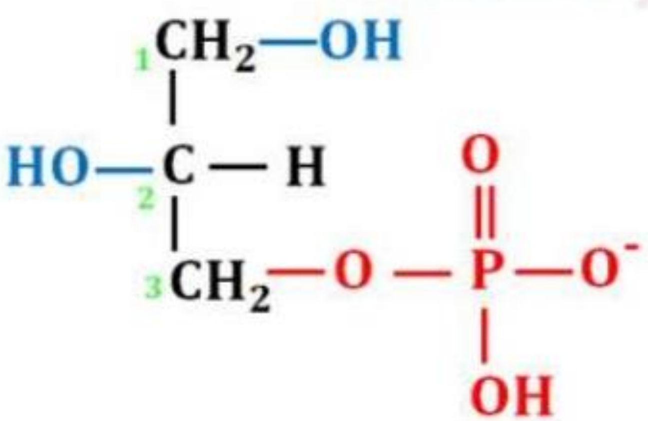
Membrane lipids classification:

1. ***Phospholipids***
   - Glycerophospholipids
   - Sphingo-phospholipids
2. ***Glycolipids***
   - Galactolipids (sulfolipids)
   - Sphingo-glycolipids
3. ***Sterols***
4. ***Archaebacterial ether lipids***

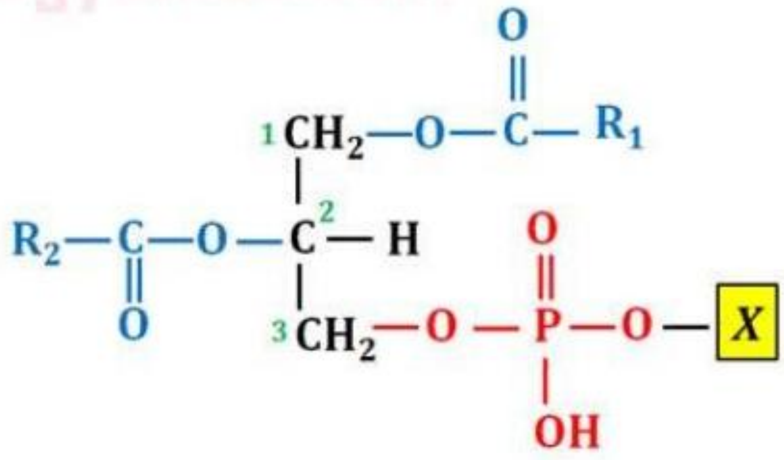
MEMBRANE LIPIDS

(1). Phospholipids:

- **Glycerol-3-phosphate** is the backbone of all phospholipids
- Here a polar head group is joined to the hydrophobic moiety by a **phosphodiester linkage**
- Other two –**OH** groups (C1 and C2) are esterified by fatty acids ($\mathbf{R_1}$ & $\mathbf{R_2}$)



Glycerol-3-Phosphate



Glycerophospholipid

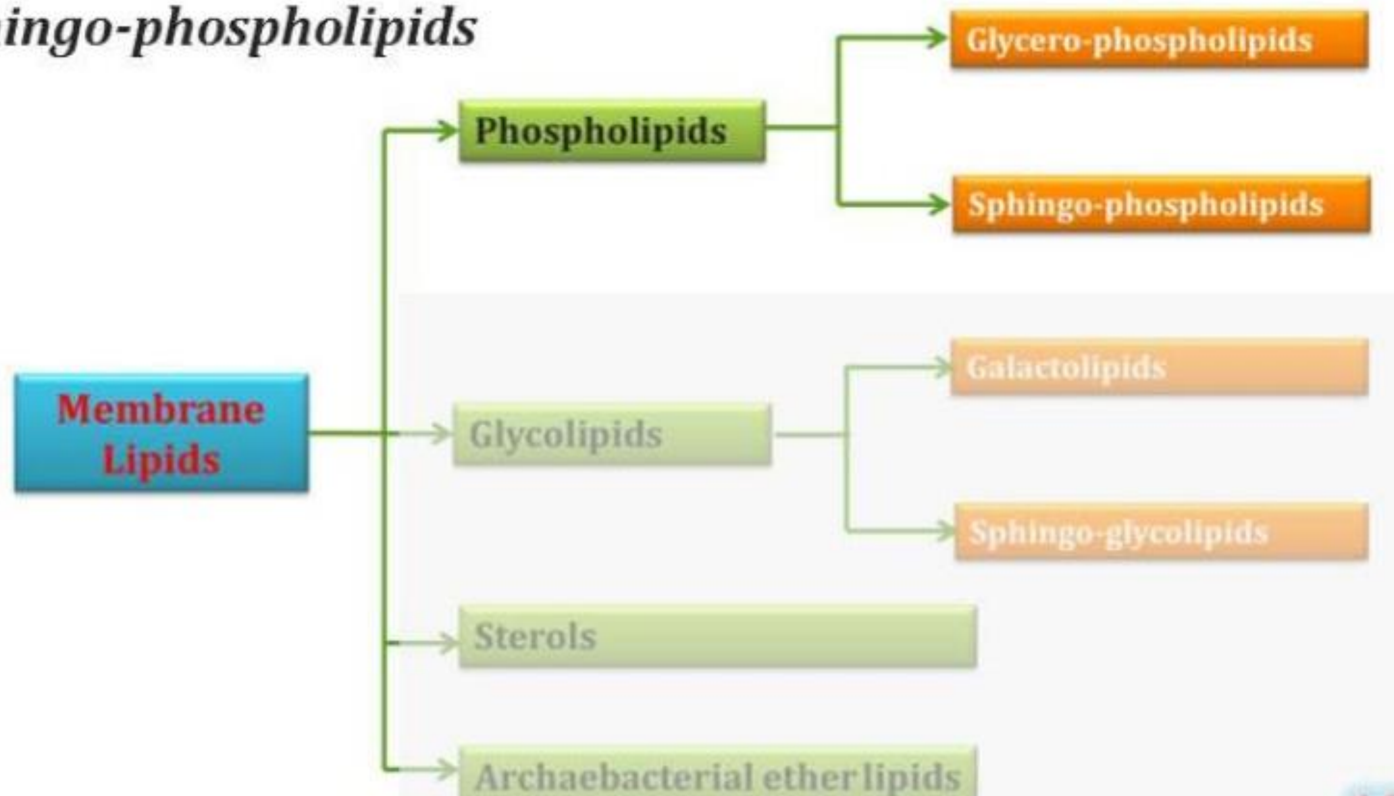
MEMBRANE LIPIDS

(1). Phospholipids:

- There are two major class of Phospholipids:

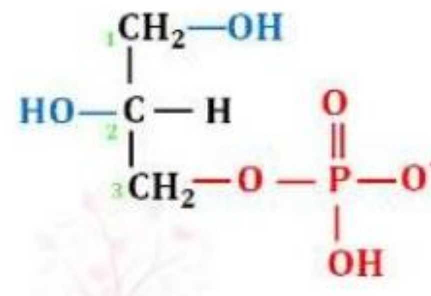
  A. Glycero-phospholipids

  B. Sphingo-phospholipids



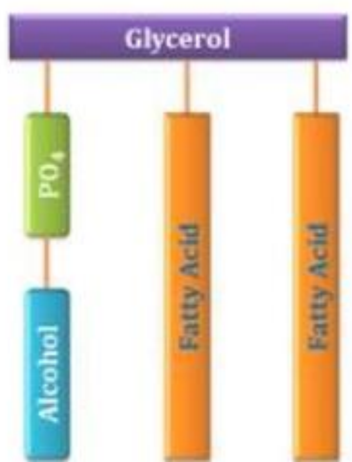
MEMBRANE LIPIDS

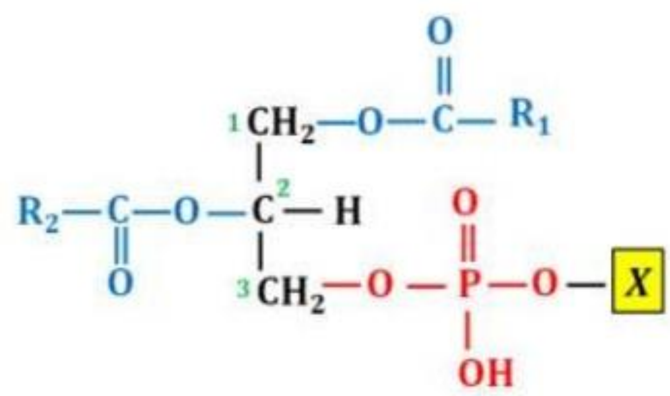
(1). Phospholipids: (A) Glycero-phospholipids:



Glycerol-3-Phosphate

- Also called as **phosphoglycerides**
- Major lipid component of biological membrane
- Consists of glycerol-3-phosphate, whose **C1** & **C2 esterified** by **fatty acids**
- The **C3** is linked to a polar group - **'X'**
- In simplest glycero-phospholipid, the **'-X'** is **- H**, is called **phosphatidic acid**

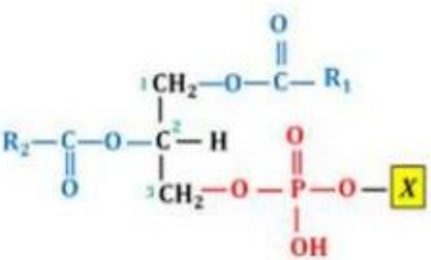




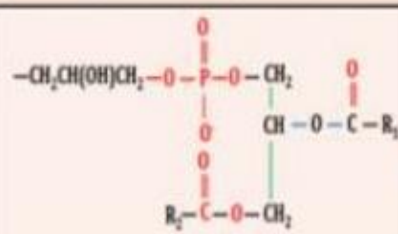
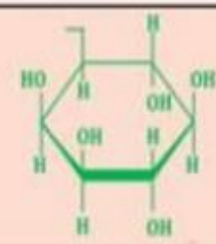
Glycerophospholipid

MEMBRANE LIPIDS

Phospho-glycerolipids are of different types based on 'X' group (table)



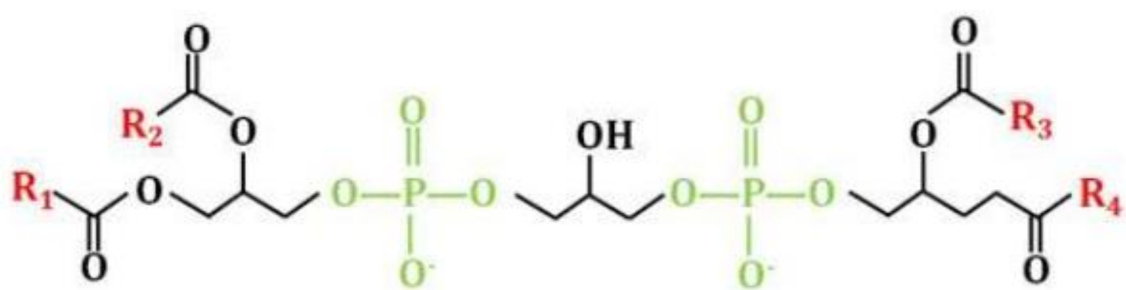
Glycerophospholipid

Name of X - OH	Formula of - X	Phospholipid Name
Water	$-H$	*Phosphatidic acid*
Ethanolamine	$-CH_2CH_2NH_3^+$	*Phosphatidylethanolamine*
Choline	$-CH_2CH_2N(CH_3)_3^+$	*Phosphatidylcholine (Lecithin)*
Serine	$-CH_2CH(NH_3^+)COO^-$	*Phosphatidylserine*
Glycerol	$-CH_2CH(OH)CH_2OH$	*Phosphatidylglycerol*
Phosphatidylglycerol		*Diphosphatidylglycerol (Cardiolipin)*
Myo-inositol		*Phosphatidylinositol*

MEMBRANE LIPIDS

(1). Phospholipids: (A) Glycero-phospholipids:

- **Cardiolipin**: an important component of the inner mitochondrial membrane
- It constitutes **20%** of the total lipids of inner mitochondrial membrane
- The only other place where **cardiolipin** can be found is in the **membranes of most bacteria**
- Thus it is an evidence for **endosymbiont** theory



Cardiolipin

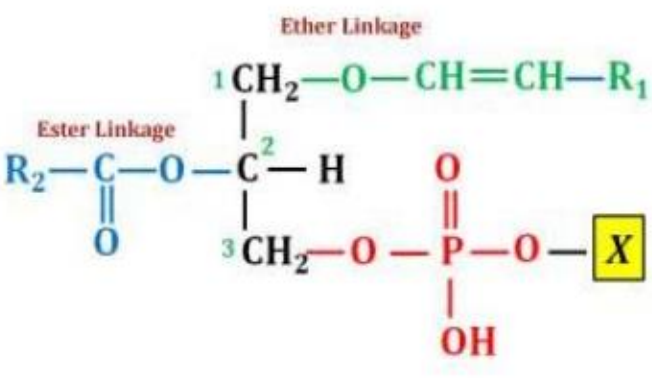
(Diphosphatidylglycerol)

MEMBRANE LIPIDS

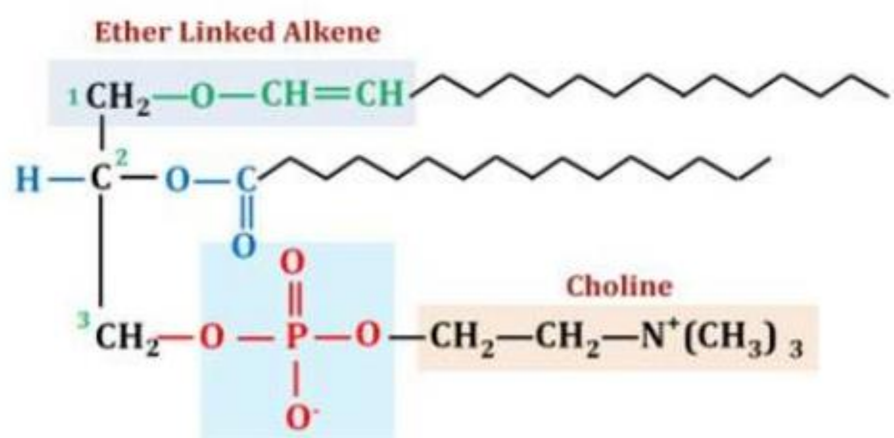
(1). Phospholipids: (A) Glycerophospholipids:

Plasmalogen:

- They are glycero-phospholipids in which the **C1** of glycerol moiety is linked via an **α, β-unsaturated ether linkage** rather than an ester linkage
- Ethanolamine, choline & serine are the most common plasmalogen heads
- Function of plasmalogens are not well understood



Plasmalogen Backbone

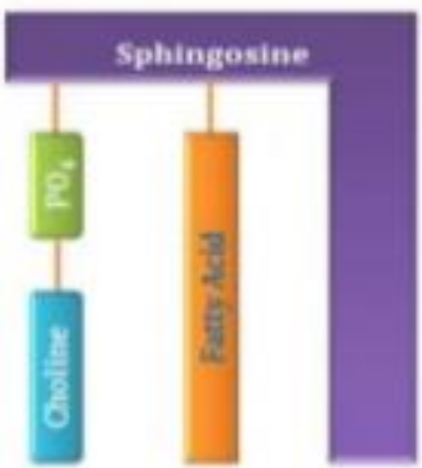


Plasmalogen

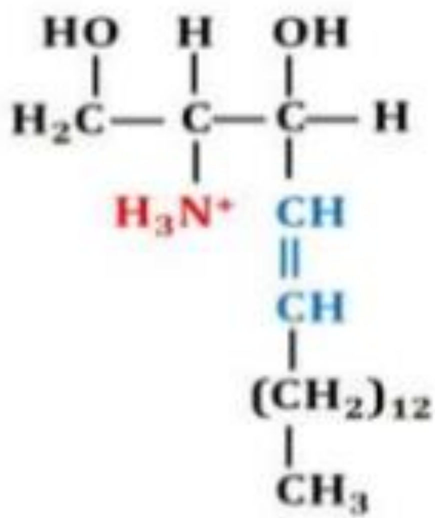
MEMBRANE LIPIDS

(1). Phospholipids: (B). Sphingo-phospholipids:

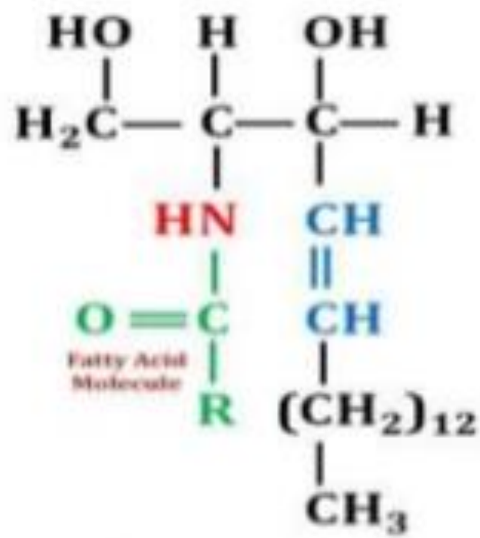
- Major class of membrane lipids
- Named after **Sphinx** because of their function in the cells was mysterious
- Most of the spingolipids are derivatives of **C18** amino alcohol **Sphingosine**
- **N-acyl fatty acid** derivative of sphingosine are known as **ceraminde**



Sphingo-phospholipid



Sphingosine



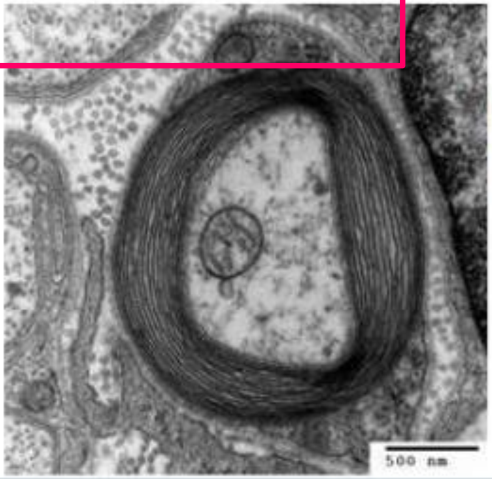
Ceramide

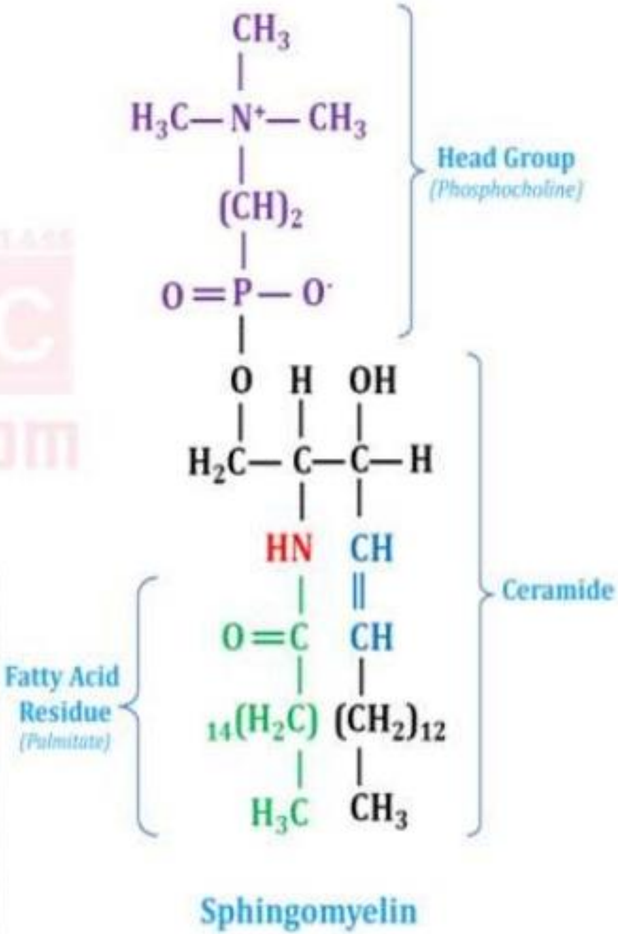
MEMBRANE LIPIDS

(1). Phospholipids: (B). Sphingo-phospholipids: **Sphingomyelins**

- Most common sphingolipid
- Make up 10 – 20% of plasma membrane lipids
- They are **ceramides** with **phosphocoline** or **phosphoehtanolamine** head
- **Myelin sheath** of nerve cell axons are rich in sphingomyelins

Electron Micrograph of Myelinated Nerves: *See the spirally wrapped membrane around each nerve axon. Myelin sheath may be 10 -15 layers thick and the high lipid content makes it an electrical insulator*

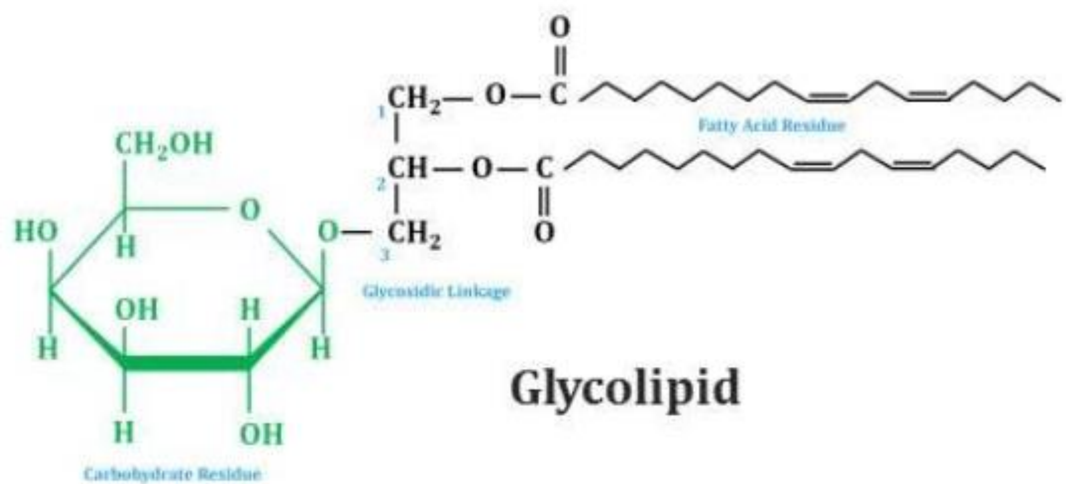




MEMBRANE LIPIDS

(2). Glycolipids:

- Lipids conjugated with carbohydrates
- Three main role:
    - Part of biological membrane system
    - Provide energy
    - Markers for cellular recognition

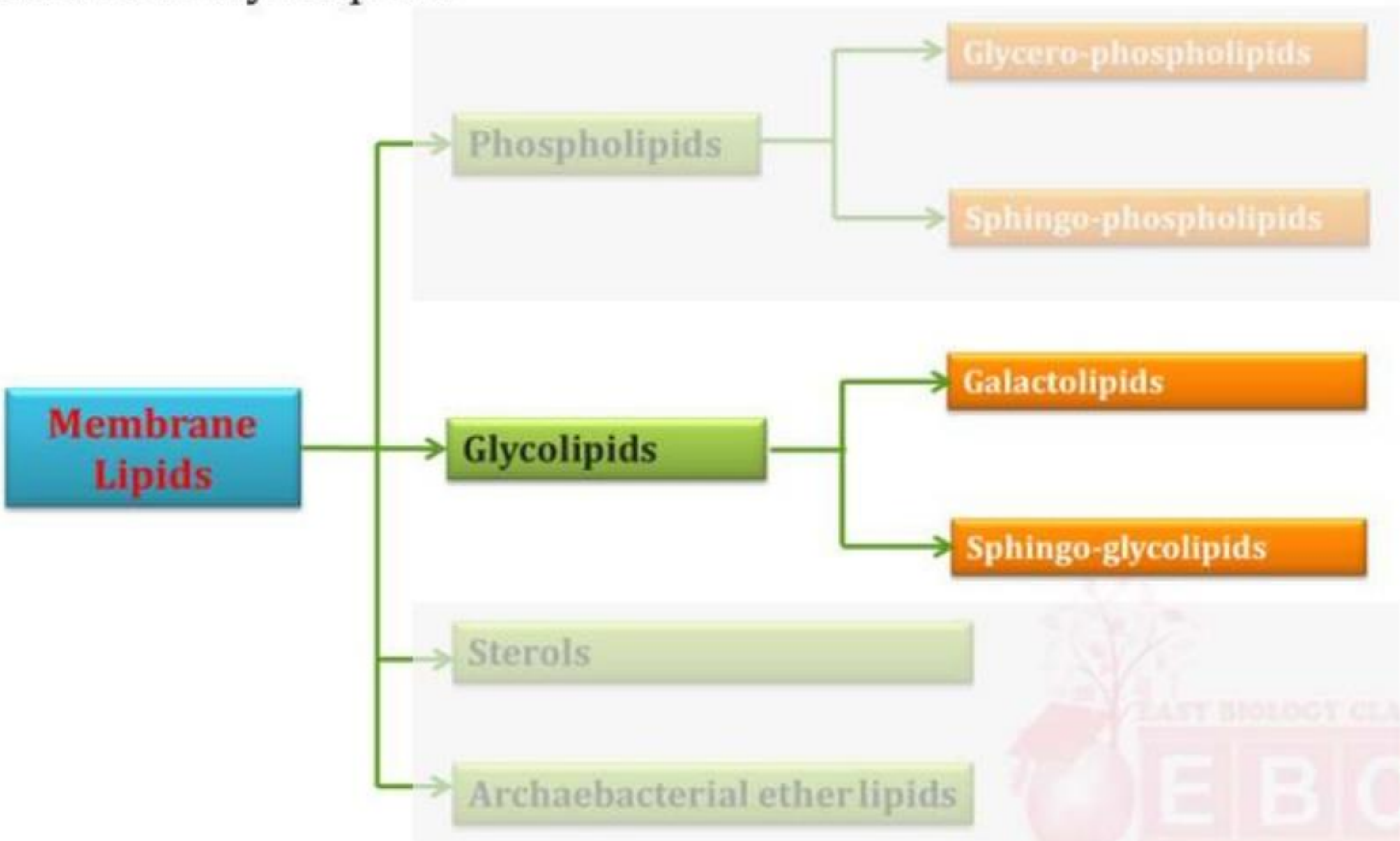


Glycolipid

MEMBRANE LIPIDS

(2). Glycolipids:

- Classification of Glycolipids:



MEMBRANE LIPIDS

(2). Glycolipids:

Different class of glycolipids are:

- **(A). Glyceroglycolipids:** *Glycerole backbone with carbohydrates*

    a) Galactolipids

    b) Sulfolipids

- **(B). Sphingo-glycolipids:** *Sphingosine backbone with carbohydrates*

    a) Cerebrosides

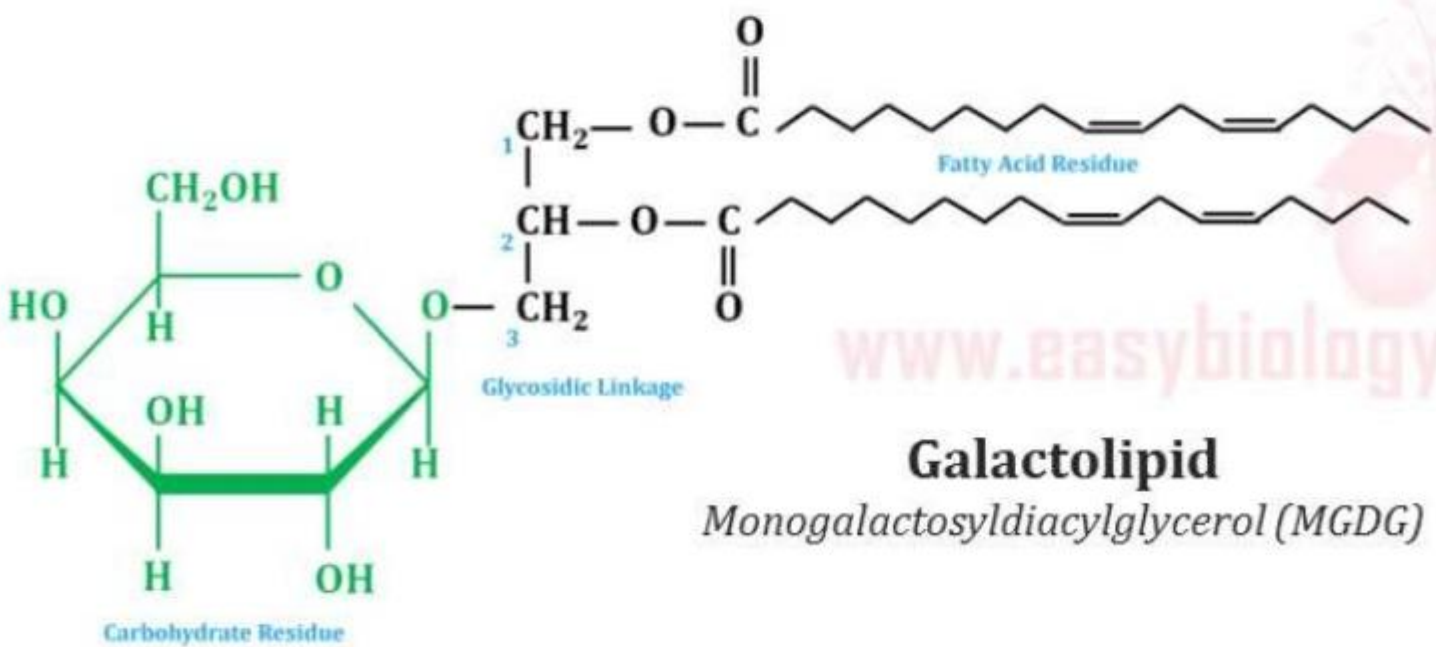
    b) Globosides

    c) Gangliosides

MEMBRANE LIPIDS

(2). Glycolipids: (A). Glycero-glycolipids: → Galactolipids

- One or two **galactose** residues present
- Galactose connected by a **glycosidic** linkage **to C3** of a Glycerol
- **C1** and **C2** of glycerol are esterified with **fatty acids**



Galactolipid

Monogalactosyldiacylglycerol (MGDG)

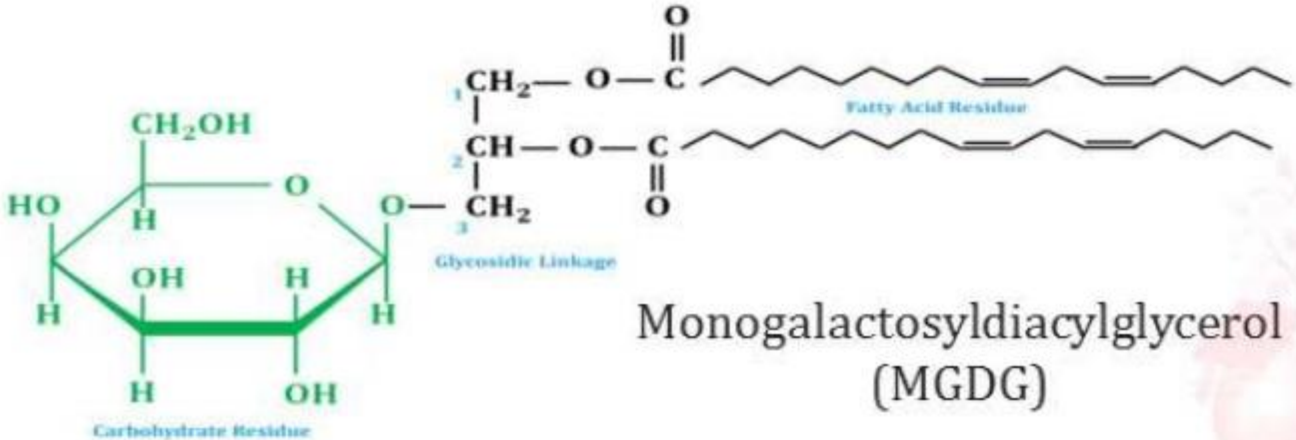
MEMBRANE LIPIDS

(2). Glycolipids: (A). Glycero-glycolipids: → Galactolipids

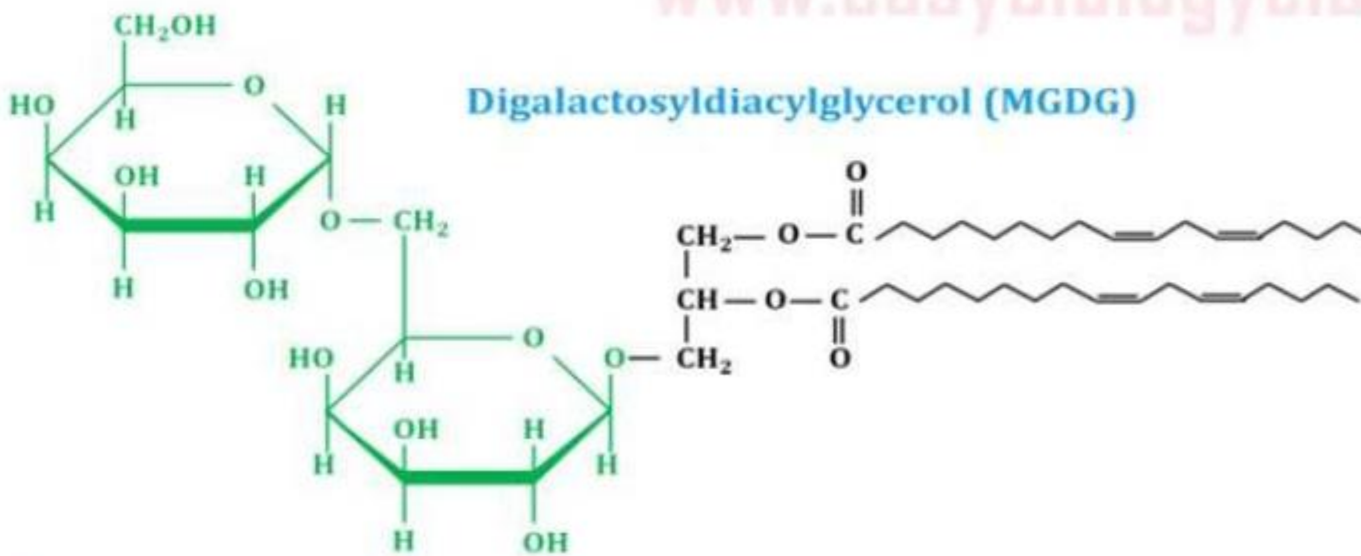
- Galactolipids are predominant in plant cells
- They are abundant in thylacoid membrane of chloroplasts
- They constitute ~ 70% to 80% of membrane lipids of vascular plants
- Probably they are the most abundant membrane lipids in the biosphere

MEMBRANE LIPIDS

- ***Galactolipids of chloroplasts:***



Monogalactosyldiacylglycerol (MGDG)

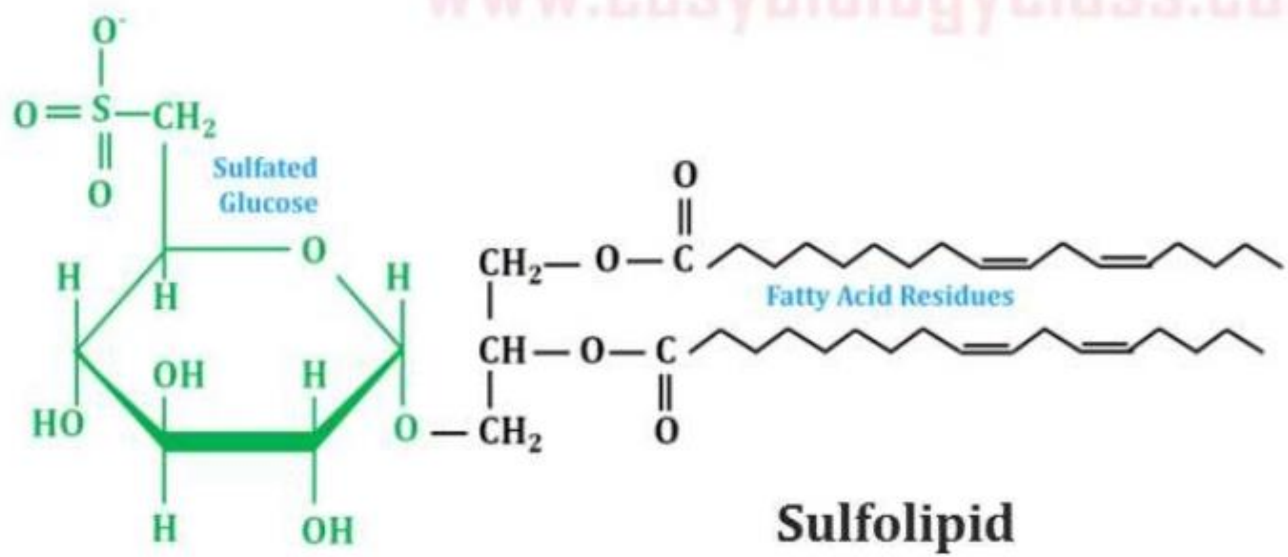


Digalactosyldiacylglycerol (MGDG)

MEMBRANE LIPIDS

(2). Glycolipids: (A). Glycero-glycolipids: → Sulfolipids:

- A class of glycero-glycolipid with **sulfur** containing functional groups
- **Sulfonated glucose** is joined to the **C3** of diacylglycerol in **glycosidic** linkage
- Plant membranes also contain sulpholipids
- Sulfonate head hold **negative charge** (like phosphate group in phospholipids)

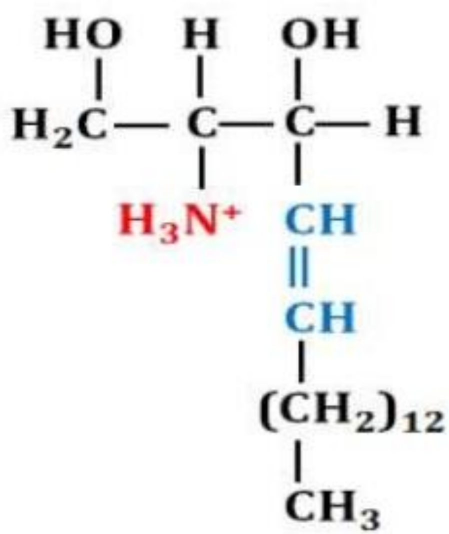


Sulfolipid

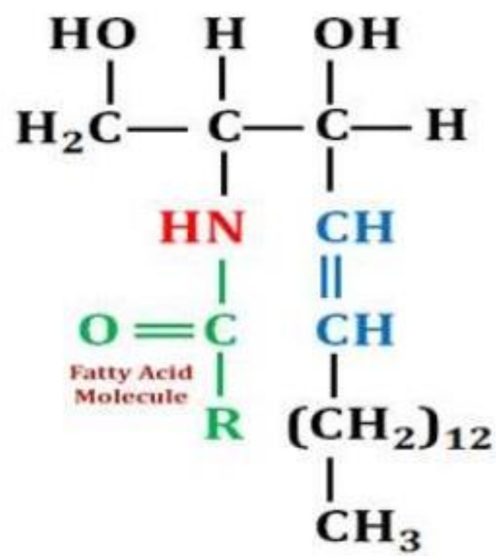
MEMBRANE LIPIDS

(2). Glycolipids: (B). Sphingo-glycolipids:

- A category of glycolipid
- Contains an amino alcohol **sphingosine** instead of glycerol
- **N-acyl** fatty acid derivative of sphingosine are known as ceramide
- Sphingo-glycolipids includes:
  - ***a) Cerebrosides***
  - ***b) Gangliosides***
  - ***c) Globosides***



Sphingosine

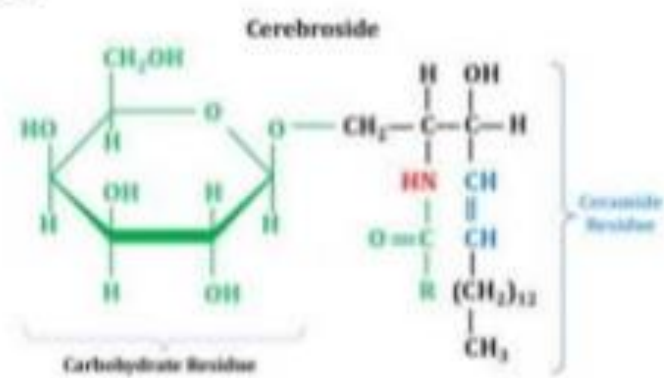


Ceramide

MEMBRANE LIPIDS

(2). Glycolipids: (B). Sphingo-glycolipids: a). Cerebrosides:

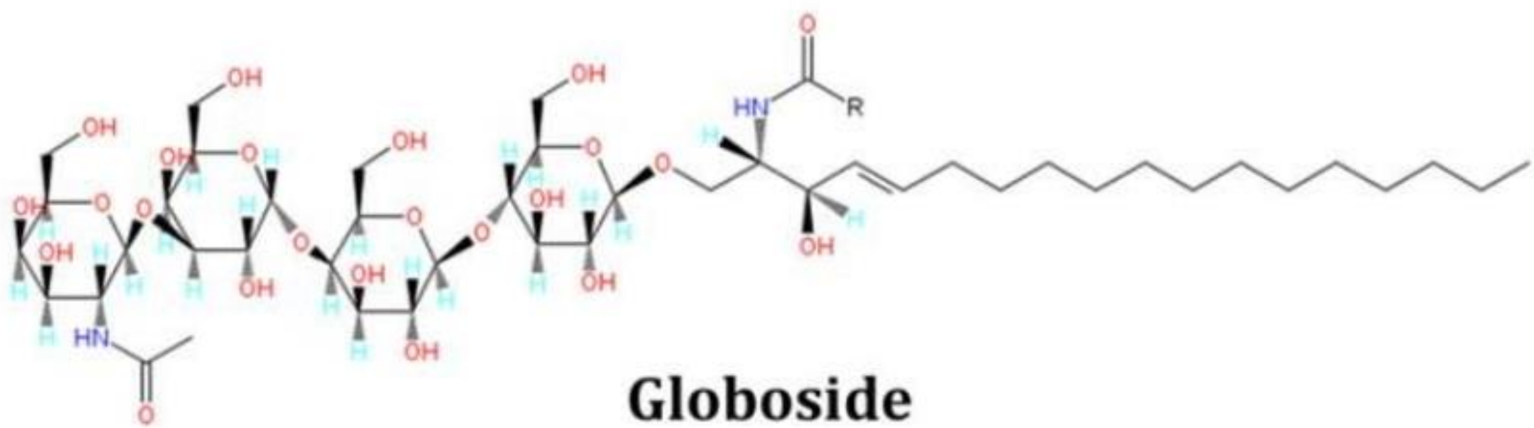
- It is a ceramide with **single sugar** residue at the **C1**-hydroxyl moiety
- Sugar residue can be either **glucose** or **galactose**
- Thus two categories: **Glucocerebrosides**, **Galactocerebrosides**
- Cerebrosides lack phosphate groups and thus they are **nonionic** (no charge)
- Abundant in animal muscle and nerve cell membranes
- Galactocerebrosides are typically found in nerves
- Glucocerebrosides are found in other tissues



MEMBRANE LIPIDS

(2). Glycolipids: (B). Sphingo-glycolipids: b). Globosides:

- A sphingo-glycolipid with **more than one sugars** as side chain of **ceramide**
- Sugars are usually a combination of N-Acetylgalactosamine, D-glucose or D-galactose

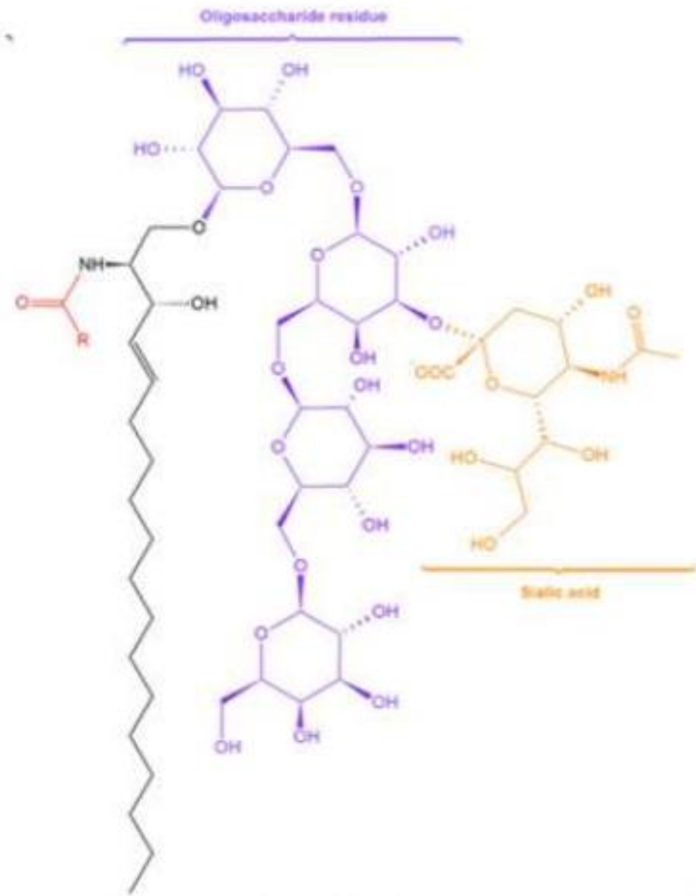


Globoside

MEMBRANE LIPIDS

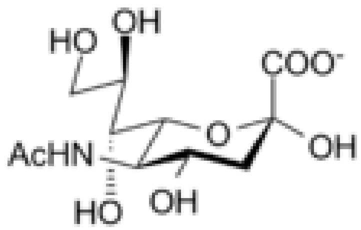
(2). Glycolipids: (B). Sphingo-glycolipids: c). Gangleosides:

- A glyco-sphingolipid (ceramide & oligosaccharide) with one or more **sialic *acids*** linked on the sugar chain
- Most complex sphingo-glycolipid
- 6% of **brain** lipids are gangleosides
- First isolated from **ganglion** of brain cells
- Abundant in **lipid-rafts** of plasma membrane

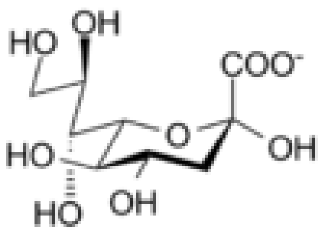


A Ganglioside

Sialic acid is a generic term for the *N*- or *O*-substituted derivatives of neuraminic acid, a monosaccharide with a nine-carbon backbone. It is also the name for the most common member of this group, N-acetylneuraminic acid (Neu5Ac or NANA).

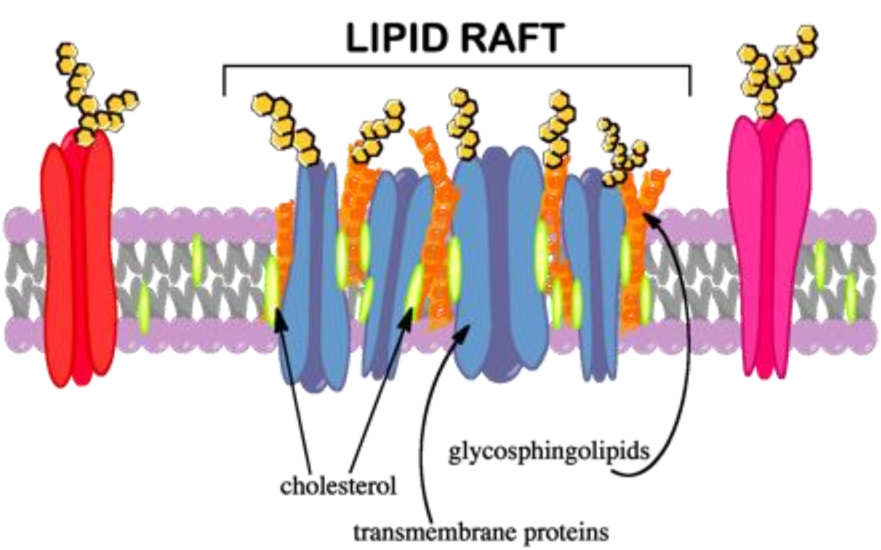


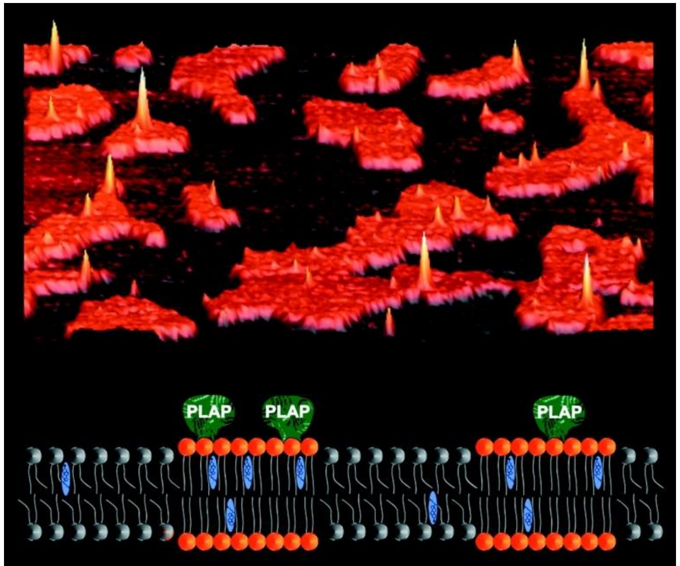
N-Acetylneuraminic acid
Neu5Ac



2-Keto-3-deoxynonic acid
Kdn

Lipid rafts are subdomains of the plasma membrane that contain high concentrations of cholesterol and glycosphingolipids. They exist as distinct liquid-ordered regions of the membrane that are resistant to extraction with nonionic detergents.





MEMBRANE LIPIDS

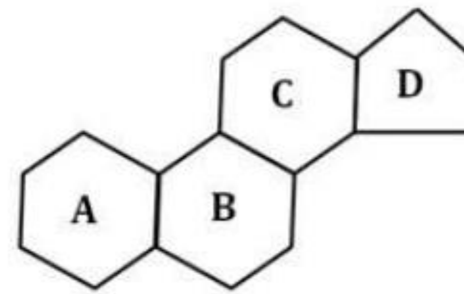
(2). Glycolipids: (B). Sphingo-glycolipids: c). Gangleosides:

Physiological/Medical significance of Gangleosides:

- Considerable physiological and medical significance
- Act as specific receptors for glycoprotein hormones
- Act as receptors for some bacterial protein toxins such as **cholera toxin**
- Act as specific determinants of cell–cell recognition (important in growth and differentiation of tissues and in carcinogenesis)
- **Tay-Sachs disease** is a hereditary disorder of ganglioside breakdown leading to fatal neurological deterioration in the early childhood

MEMBRANE LIPIDS

(3). Sterols:



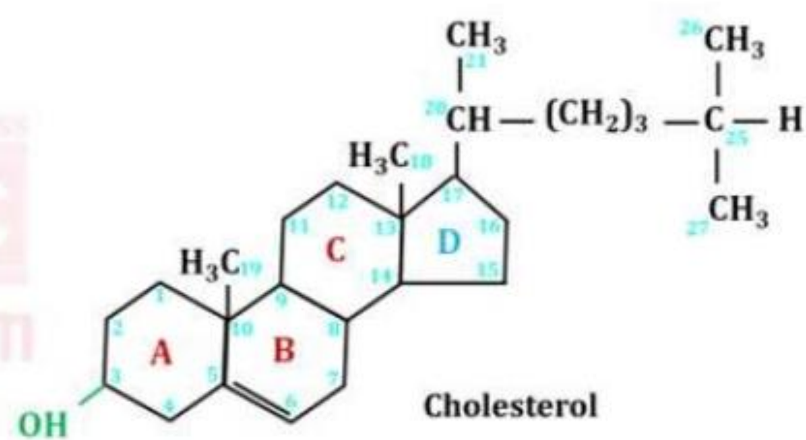
Cyclopentanoperhydrophenanthrene

- **Third** major class of membrane lipids
- Usually present in the membranes of eukaryotic cells
- Sterol consists of **four** fused carbon rings (**A, B, C, D**) and an alkyl **side chain**
- Alkyl chain is called ***'hydrocarbon side chain'***
- Ring **A**, **B** and **C** are with **six carbons** and Ring **D** is with **five carbons**
- This fused ring is called the **Steroid Nucleus**
- Steroid nucleus is derived from **cyclopentanoperhydrophenanthrene**
- Fused ring structure do **not** allow C – C free rotation

MEMBRANE LIPIDS

(3). Sterols:

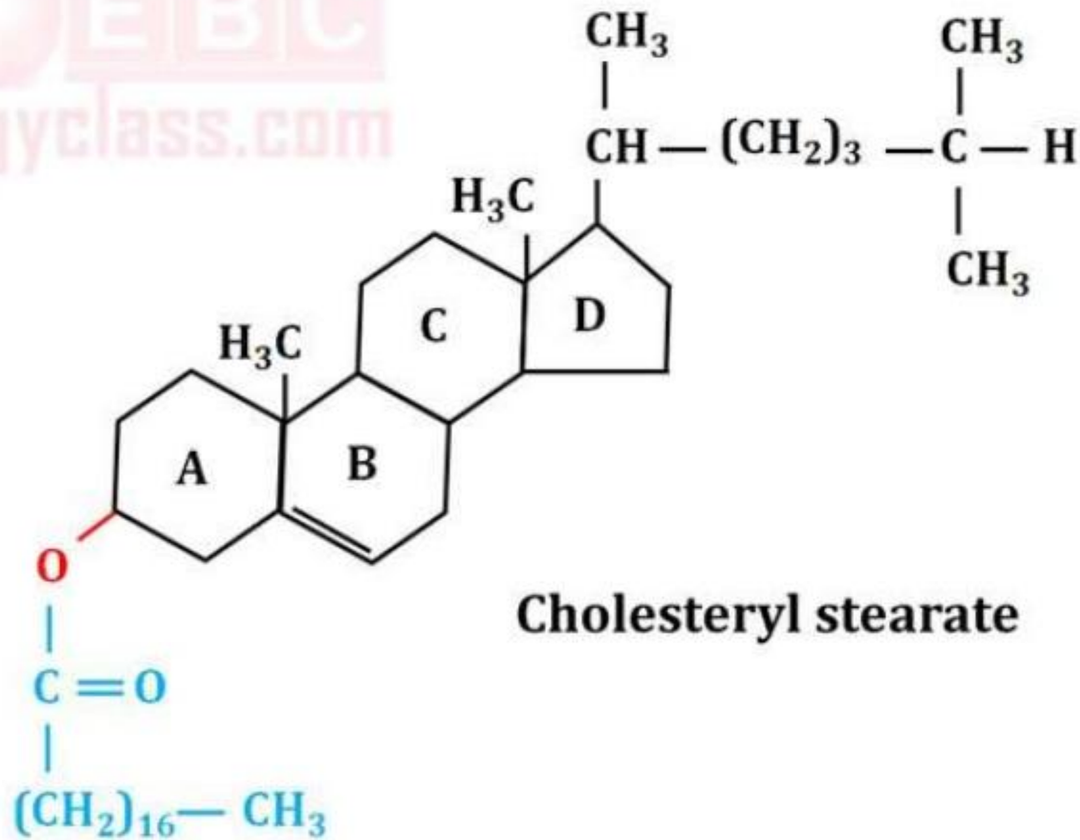
- Cholesterol is a major sterol of animal membranes
- Constitute about **30-40%** all membrane lipids in animals
- Cholesterol is **amphipathic** with **polar hydroxyl (-OH) 'head'** and **non-polar hydrocarbon 'tail'**
- The **–OH** and the **hydrocarbon chain** are attached to the **C3** and **C17** of steroid nucleus respectively



MEMBRANE LIPIDS

(3). Sterols:

- Cholesterol can **esterify** with long chain fatty acids to form **cholesteryl esters** such as **cholesteryl stearate**

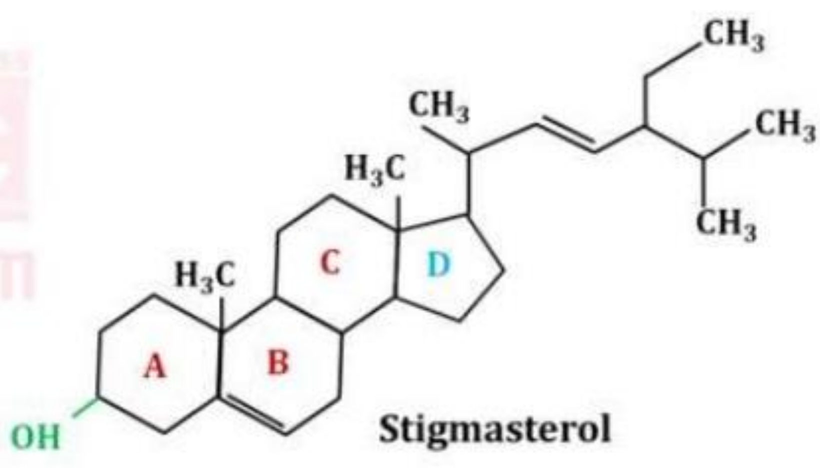


Cholesteryl stearate

MEMBRANE LIPIDS

(3). Sterols:

- In mammals, cholesterol is the metabolic **precursor** of **steroid hormones**
- Cholesterol very **rarely** found in **plants** (other sterols occurs in plants)
- **Stigmasterol**: important membrane sterol in plants (**phytosterol**)
- **Campesterol** and **sitosterol** are other plant sterols
- **Ergosterol**: sterol found in fungal membrane system



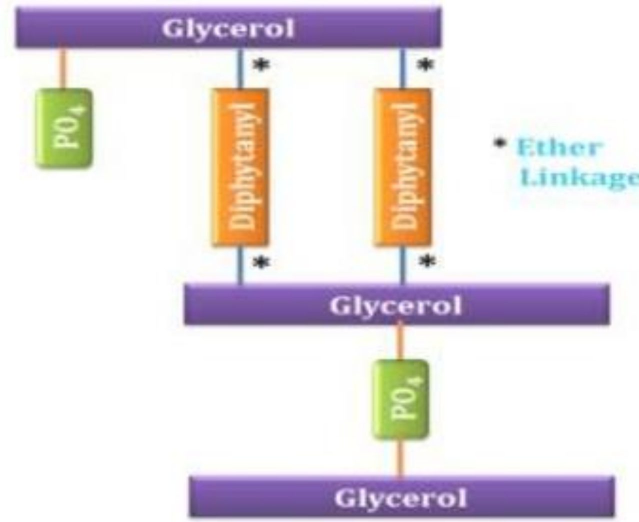
Stigmasterol

MEMBRANE LIPIDS

(3). Sterols:

- Bacteria **cannot** synthesize any sterol
- Thus bacterial membrane generally lacks sterol
- Some bacteria can incorporate exogenous sterol in to their membrane
- **Lanosterol:** sterol precursor of animals and fungi
- **Cycloartenol:** sterol precursor of plants
- Both Lanosterol and Cycloartenol are derived from the **cyclization** of **triterpenoid - squalene**

MEMBRANE LIPIDS



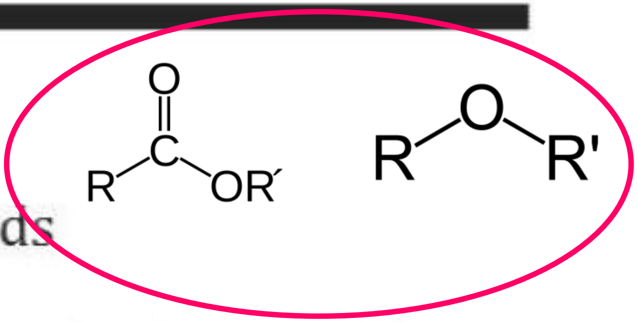
Archaebacterial Ether Lipid

(4). Archaebacterial ether lipids:

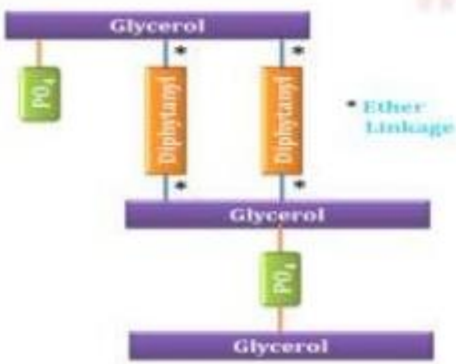
- **Fourth** major class of membrane lipids
- They are membrane lipids of **archaebacteria**
- **Absent** in prokaryotes and eukaryotes
- Majority of archaebacteria lives in extreme conditions (high temperature)
- Archaebacterial ether lipids contain long (**32C**) branched hydrocarbon chains linked at **both end to glycerol**
- Linkages are through **ether bonds (R – O – R')**

MEMBRANE LIPIDS

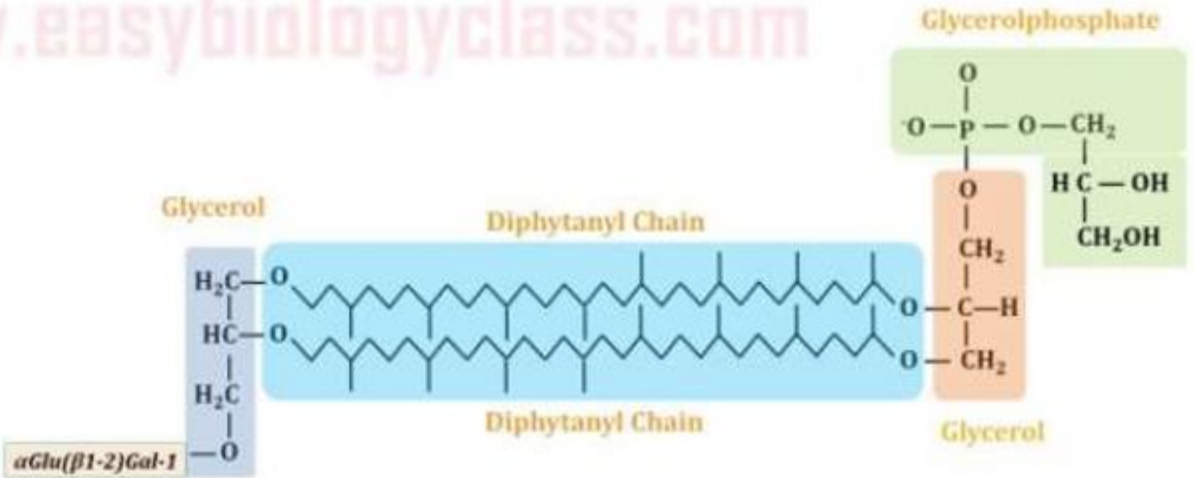
(3). Archaebacterial ether lipids:



- Ether bonds are more **stable** than ester bonds
- They are **twice** the length of phospholipids and sphingolipids
- They span the width of the surface membrane
- At each end of the molecule **two glycerol** moieties are present
- This glycerol is linked to either **phosphate** or **sugar** residues



Archaebacterial Ether Lipid



Archaebacterial Ether Lipid

AMPHIPATHIC LIPIDS SELF-ORIENT AT OIL:WATER INTERFACES

- They Form **Membranes**, **Micelles**, **Liposomes**, **&** **Emulsions**

- In general, lipids are insoluble in water since they contain a predominance of non-polar (hydrocarbon) groups. However, fatty acids, phospholipids, sphingolipids, bile salts, and, to a lesser extent, cholesterol **contain polar groups**. Therefore, part of the molecule is hydrophobic, or water-insoluble; and part is hydrophilic or water-soluble. Such molecules are described as **amphipathic.** They become oriented at **oil : water** interfaces with the polar group in the water phase and the nonpolar group in the oil phase.

- A bilayer of such amphipathic lipids has been regarded as a basic structure in **biologic membranes**

- When a critical concentration of these lipids is present in an aqueous medium, they form **micelles.**

- Aggregations of bile salts into micelles and liposomes and the formation of mixed micelles with the products of fat digestion are important in facilitating absorption of lipids

- **Liposomes** may be formed by sonicating an amphipathic lipid in an aqueous medium. They consist of spheres of lipid bilayers that enclose part of the aqueous medium. They are of potential clinical use—particularly when combined with tissue specific antibodies—as carriers of drugs in the circulation, targeted to specific organs, eg, in cancer therapy.

- In addition, they are being used for gene transfer into vascular cells and as carriers for topical and transdermal delivery of drugs and cosmetics.

- **Emulsions** are much larger particles, formed usually by nonpolar lipids in an aqueous medium. These are stabilized by emulsifying agents such as amphipathic lipids (eg, lecithin), which form a surface layer separating the main bulk of the nonpolar material from the aqueous phase