Lipids

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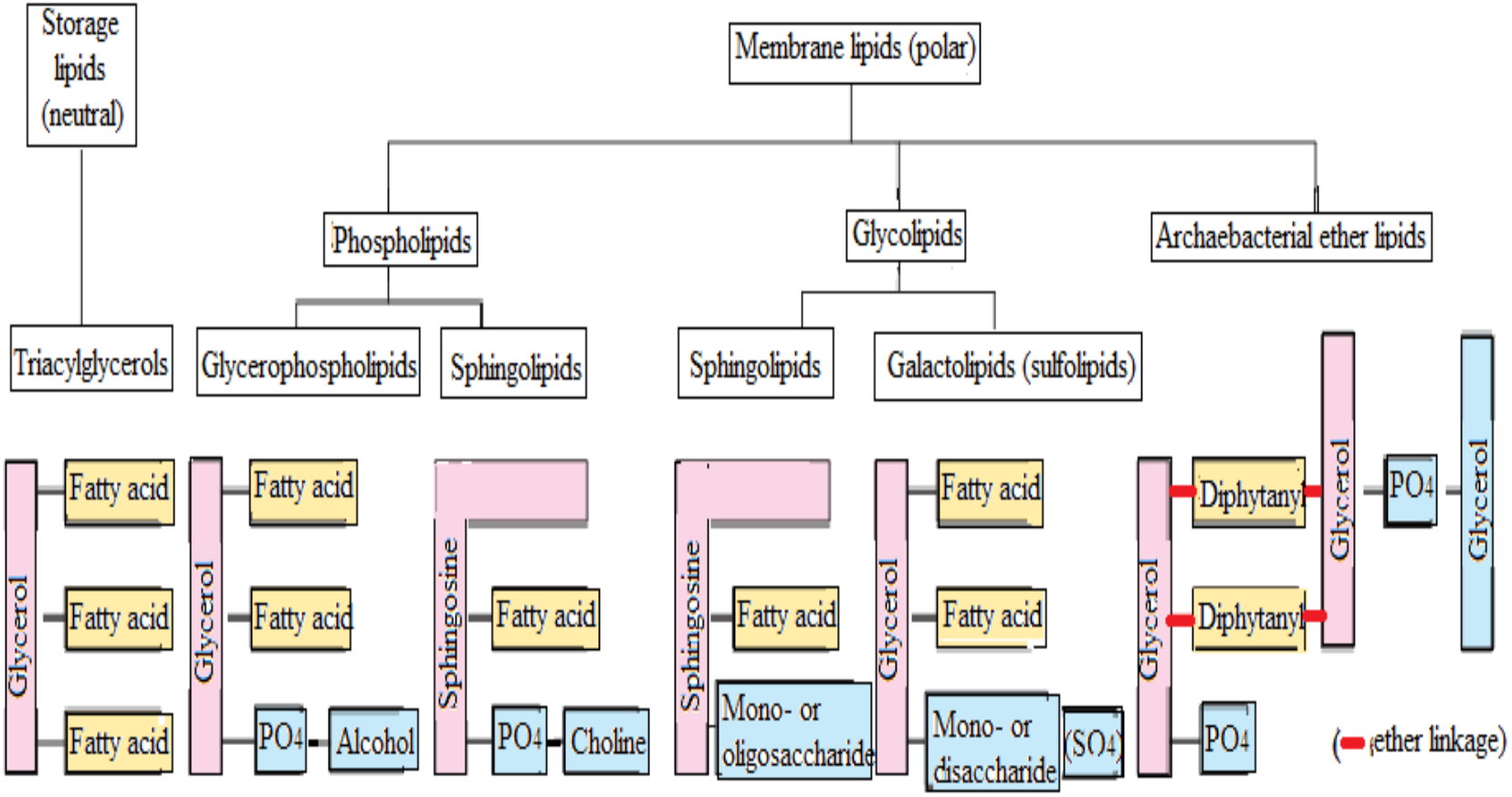
3.Lipids classification

Lipids constitute a group of organic compounds with diverse chemical structures, characterized by their solubility in non-polar organic solvents (e.g., hexane, benzene, chloroform).

Lipids play an important biological role, which can be summarized as follows:

- ❖Energy storage: fats and oils (1 g of lipid → 9 kcal).
- ❖Structural role in biological membranes (phospholipids, sterols).
- ❖Vitamins (A, D, E, K).
- ❖Electron carriers.
- ❖Light-absorbing pigments.
- ❖Steroid hormones.
- ❖Intracellular messengers.

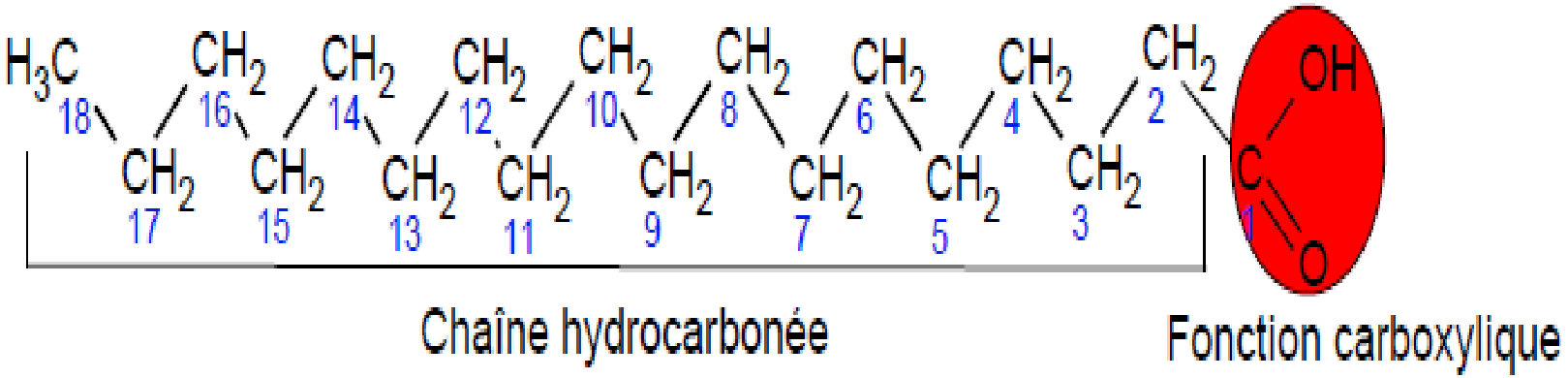
There are several classifications of lipids; here, we present the one that takes into account the role of lipids as both neutral storage molecules and polar structural molecules



3.1.Fatty acids

A fatty acid is a molecule composed of a hydrocarbon chain (4 to 36 carbons, even or odd in number) and a terminal carboxylic acid group

The hydrocarbon chain may be saturated (no double bonds), monounsaturated (a single double bond), or polyunsaturated (two or more double bonds); branches and hydroxyl groups may also be found in the chains of certain fatty acids.



❑In general, the fatty acids most commonly found in nature share the following characteristics:

➢An even number of carbon atoms, ranging from 12 to 24.

➢A linear hydrocarbon chain that may be saturated or unsaturated; in the latter case, the double bonds are non-conjugated and almost always in the *cis* configuration.

❑The majority of fatty acids occur in a combined (non-free) state.

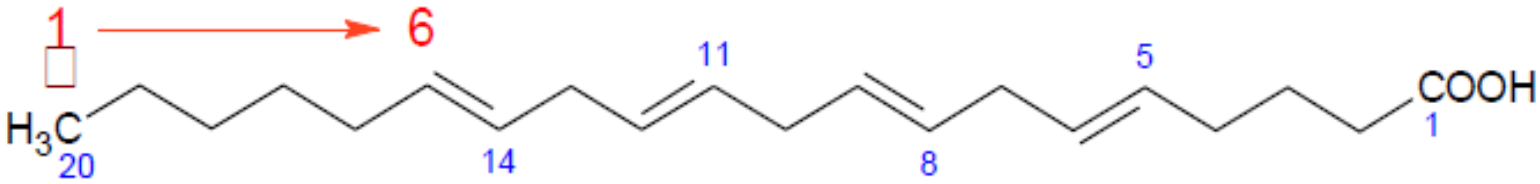
3.1.1.Fatty acid nomenclature

A fatty acid has both a common name and a systematic name; to identify it, we must consider the following points:

- The length of the hydrocarbon chain-that is, the number of constituent carbon atoms; these carbons are numbered using arabic numerals starting from the carboxylic group.

- The number of double bonds, their positions (the number of the carbon preceding the double bond), and their configurations (cis or trans).

Example 1: Arachidonic acid



- 1st notation: C20:4 (Δ5, 8, 11, 14): a fatty acid with a 20-carbon chain and 4 double bonds at positions 5, 8, 11, and 14.

- 2nd notation: 20:4n-6: a fatty acid with a 20-carbon chain and 4 double bonds (4n); the "6" indicates the position of the carbon involved in the last double bond, counting from the terminal methyl group (carbon 20). In this case, the fatty acid is classified as an omega-6 fatty acid, denoted as ω-6.

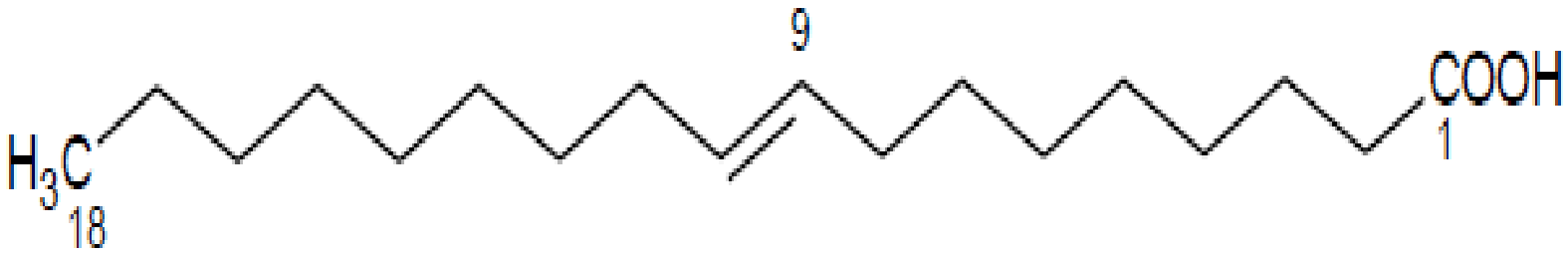
- Systematic name: cis,cis,cis,cis-5,8,11,14-Eicosatetraenoic acid.

Role

In humans, arachidonic acid is a derivative of linoleic acid, which is an essential fatty acid.

Arachidonic acid is the precursor to eicosanoids, hormones involved in reproduction, inflammation, and blood pressure regulation.

Example 2: Oleic acid



1st notation: C18:1(Δ9)
2nd notation: 18:1n-9.
Systematic name: cis-9-octadecenoic acid

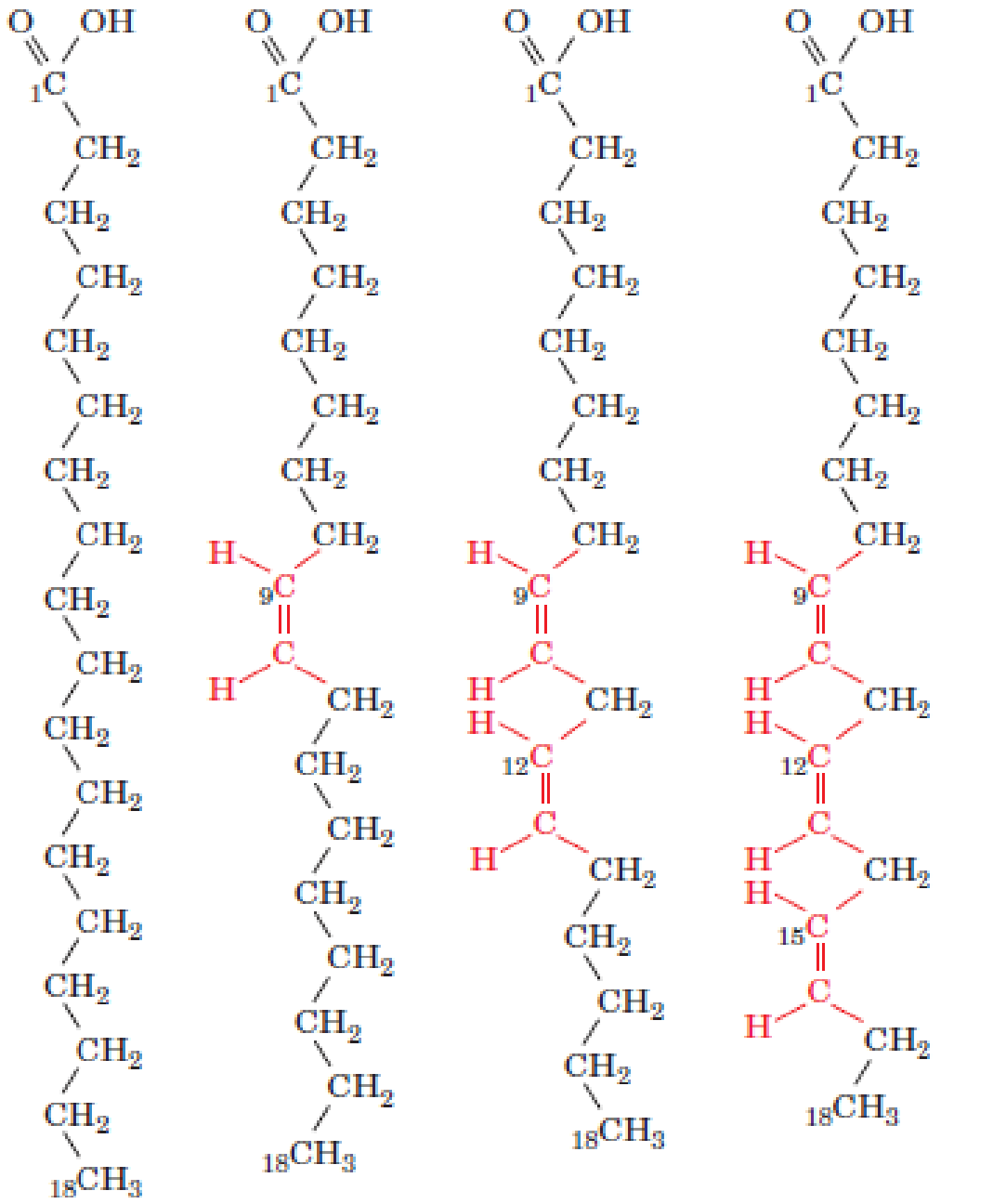
Role

It is the predominant fatty acid in olive oil, accounting for 84% of all fatty acids present in the oil

For humans, there are two so-called essential fatty acids- which the body cannot synthesize and must therefore obtain from the diet-namely linoleic acid [C18:2(Δ9,12); Omega-6] and α-linolenic acid [C18:3(Δ9,12,15); Omega-3].

Common name	Stucture	Rating	Melting point (°C)
Lauric acid	CH3(–CH2)10–COOH	C12:0	44
Myristic acid	CH3(–CH2)12–COOH	C14:0	54
Palmitic acid	CH3(–CH2)14–COOH	C16:0	63
Stearic acid	CH3(–CH2)16–COOH	C18:0	69
Arachidic acid	CH3(–CH2)18–COOH	C20:0	77
Behenic acid	CH3(–CH2)20–COOH	C22:0	81
Lignoceric acid	CH3(–CH2)22–COOH	C24:0	84

Common name	Stucture	Rating	Double bonds Δ	Melting point (°C)
Palmitoleic acid	CH3(–CH2)5–CH=CH(-CH2)7–COOH	16:1	cis-Δ9	1
Oleic acid	CH3(–CH2)7–CH=CH(–CH2)7–COOH	18:1	cis-Δ9	13
Linoleic acid	CH3(–CH2)3(–CH2–CH=CH)2(–CH2)7–COOH	18:2	all-cis-Δ9,12	-5
α-Linolenic acid	CH3(–CH2–CH=CH)3(–CH2)7–COOH	18:3	all-cis-Δ9,12,15	-11
Arachidonic acid	CH3(–CH2)3(–CH2–CH=CH)4(–CH2)3–COOH	20:4	all-cis-Δ5,8,11,14	-49
Eicosapentanoic acid	CH3(–CH2–CH=CH)5(–CH2)3–COOH	20:5	all-cis-Δ5,8,11,14,17	-54


Stearic acid
Oleic acid
Linoleic acid
α-Linolenic acid

Symbol[a]	Common Name	Systematic Name	Structure	mp (°C)
Saturated fatty acids				
12:0	Lauric acid	Dodecanoic acid	$CH_3(CH_2)_{10}COOH$	44.2
14:0	Myristic acid	Tetradecanoic acid	$CH_3(CH_2)_{12}COOH$	52
16:0	Palmitic acid	Hexadecanoic acid	$CH_3(CH_2)_{14}COOH$	63.1
18:0	Stearic acid	Octadecanoic acid	$CH_3(CH_2)_{16}COOH$	69.6
20:0	Arachidic acid	Eicosanoic acid	$CH_3(CH_2)_{18}COOH$	75.4
22:0	Behenic acid	Docosanoic acid	$CH_3(CH_2)_{20}COOH$	81
24:0	Lignoceric acid	Tetracosanoic acid	$CH_3(CH_2)_{22}COOH$	84.2
Unsaturated fatty acids (all double bonds are cis)				
16:1*n*–7	Palmitoleic acid	9-Hexadecenoic acid	$CH_3(CH_2)_5CH{=}CH(CH_2)_7COOH$	−0.5
18:1*n*–9	Oleic acid	9-Octadecenoic acid	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	13.4
18:2*n*–6	Linoleic acid	9,12-Octadecadienoic acid	$CH_3(CH_2)_4(CH{=}CHCH_2)_2(CH_2)_6COOH$	−9
18:3*n*–3	α-Linolenic acid	9,12,15-Octadecatrienoic acid	$CH_3CH_2(CH{=}CHCH_2)_3(CH_2)_6COOH$	−17
18:3*n*–6	γ-Linolenic acid	6,9,12-Octadecatrienoic acid	$CH_3(CH_2)_4(CH{=}CHCH_2)_3(CH_2)_3COOH$	
20:4*n*–4	Arachidonic acid	5,8,11,14-Eicosatetraenoic acid	$CH_3(CH_2)_4(CH{=}CHCH_2)_4(CH_2)_2COOH$	−49.5
20:5*n*–3	EPA	5,8,11,14,17-Eicosapentaenoic acid	$CH_3CH_2(CH{=}CHCH_2)_5(CH_2)_2COOH$	−54
22:6*n*–3	DHA	4,7,10,13,16,19-Docosahexenoic acid	$CH_3CH_2(CH{=}CHCH)_6CH_2COOH$	
24:1*n*–9	Nervonic acid	15-Tetracosenoic acid	$CH_3(CH_2)_7CH{=}CH(CH_2)_{13}COOH$	39

[a]Number of carbon atoms: number of double bonds. For unsaturated fatty acids, n is the number of carbon atoms, $n - x$ is the double-bonded carbon atom, and x is the number of that carbon atom counting from the methyl terminal (ω) end of the chain.

3.1.2.Solubility of fatty acids

Fatty acids have very low solubility in water, and this solubility decreases as the number of carbon atoms increases. However, fatty acids are soluble in organic solvents.

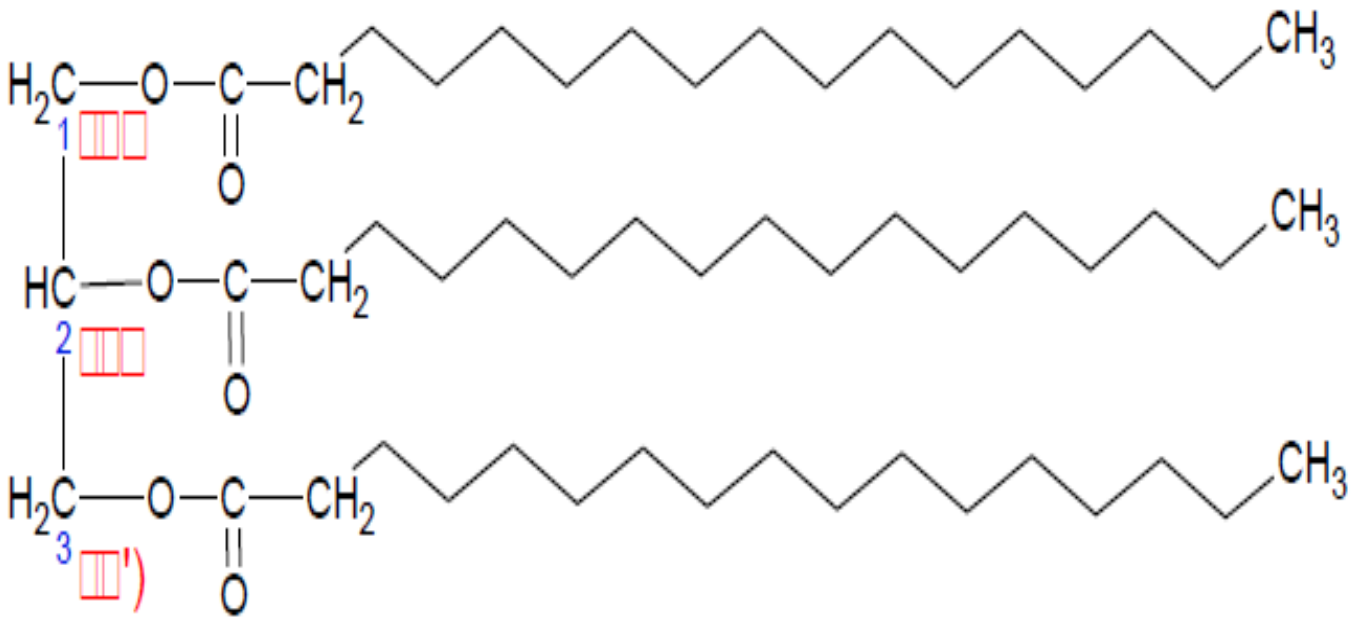
3.1.3.Melting point of fatty acids

The melting point of fatty acids depends heavily on two structural factors: the length of the hydrocarbon chain and the number of double bonds:

- Linear saturated fatty acids ranging from C12:0 to C24:0 have higher melting points than unsaturated fatty acids of the same length.
- For saturated fatty acids, the melting point increases with the length of the hydrocarbon chain.
- For unsaturated fatty acids, the melting point decreases as the number of double bonds increases.

3.2.Triglycerides

- Triglycerides (also known as triacylglycerols) are esters of glycerol and three fatty acids
- They are energy-storage lipids (oils and fats),
- Their hydrophobic nature allows them to aggregate into lipid droplets within the cell cytoplasm.



❑If a triglyceride carries three identical fatty acids, it is called a homogeneous triglyceride.
Examples: Tristearin is a homogeneous triglyceride carrying three stearic acids (C16:0

❑If a triglyceride bears two or three different fatty acids, it is called a mixed (or heterogeneous) triglyceride; its nomenclature requires consideration of the nature of the fatty acids and their attachment positions on the glycerol backbone (1, 2, 3 or α, β, α').

❑Monoglycerides (monoacylglycerols) and diglycerides (diacylglycerols) are esters of glycerol with one and two fatty acids

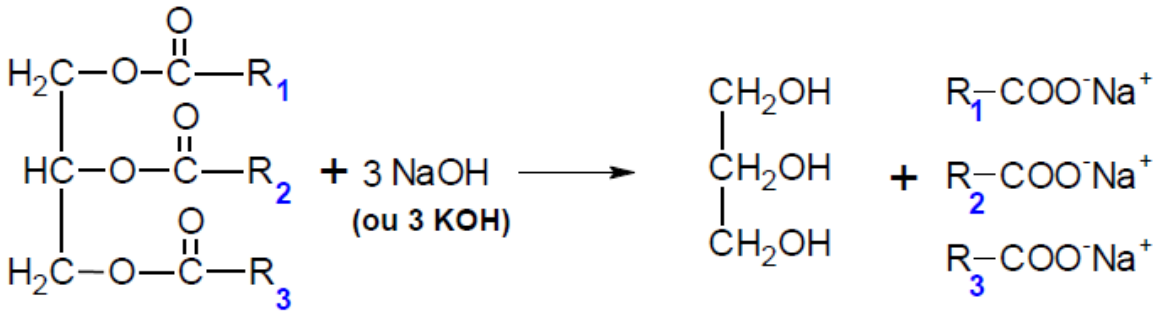
3.2.1.Triglycerides can be solid or liquid

At room temperature (25°C), triglycerides can exist as a solid (animal fats) or a liquid (vegetable oils)

This depends on the melting points of their constituent fatty acids, which in turn depend on the length of the hydrocarbon chain, the presence or absence of double bonds, and their configurations.

3.2.2.Saponification of triglycerides (basic hydrolysis)

Triacylglycerols treated with bases (KOH, NaOH) under heat form salts called soaps



❑The saponification index is the amount of potassium hydroxide, expressed in milligrams, required to saponify one gram of fatty substance (fatty acid or glyceride).

❑The saponification index is an indirect measure of the molar mass of a fatty substance.

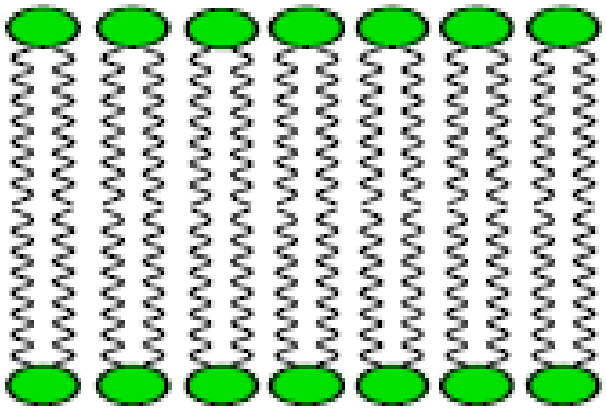
3.2.3.Addition of iodine to double bonds

- Iodine index: Unsaturated fatty acids can bind iodine molecules; this is an iodine addition reaction at the double bonds.
- Thus, the iodine value can be defined as the quantity of iodine (in grams) that can bind to 100 g of a fatty substance.
- The iodine value is a measure of the degree of unsaturation; one double bond binds one iodine molecule (I_2).

- The iodine value and the saponification value are necessary to determine the structure of a glyceride.

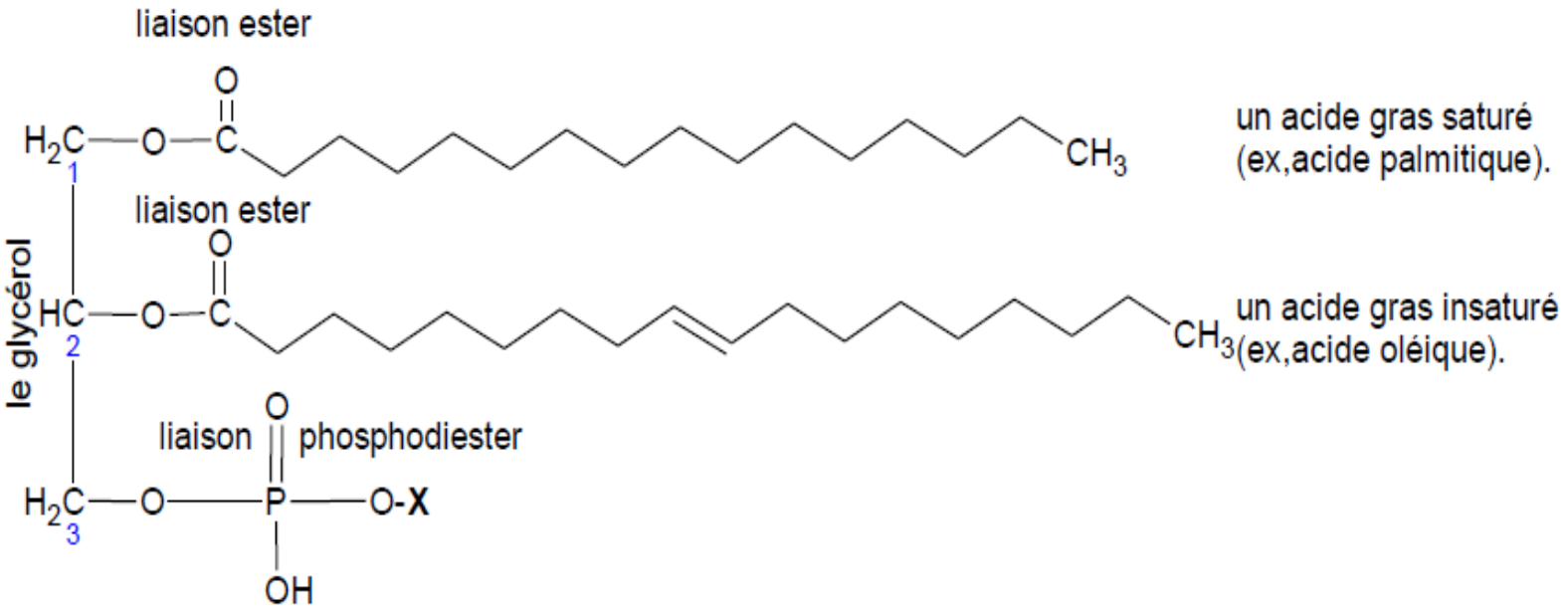
3.3.Membrane lipids

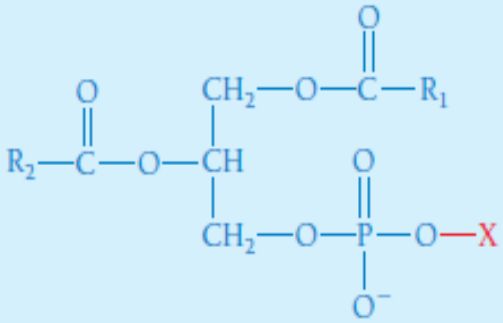
Biological membranes are composed of a lipid bilayer, which acts as a barrier (selective transport). These lipids are described as amphipathic because they possess a hydrophilic (polar) head and a hydrophobic (non-polar) tail

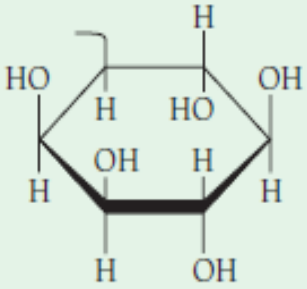
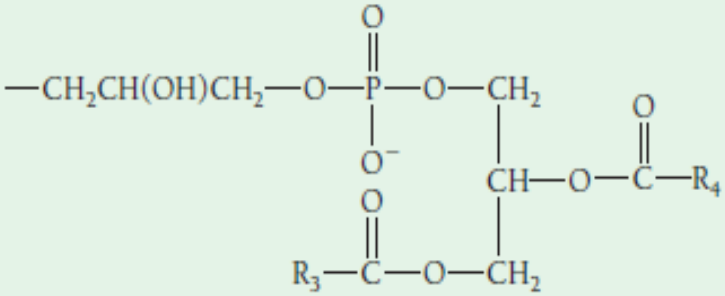


3.3.1.Glycerophospholipids (phosphoglycerides)

- This is a family of lipids composed of glycerol (a tri-alcohol) linked to two fatty acids and a phosphate group.
- The phosphate group can, in turn, be linked to another polar group (choline, serine, ethanolamine, etc.)

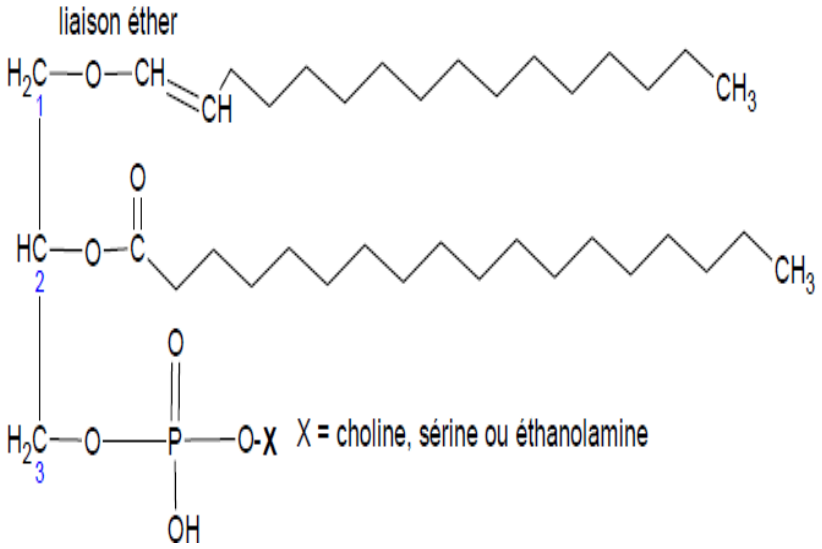


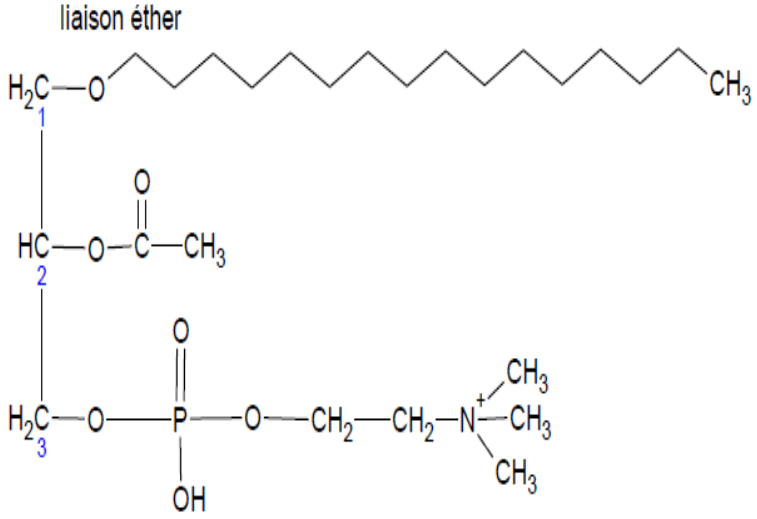


Name of X—OH	Formula of —X	Name of Phospholipid
Water	—H	Phosphatidic acid
Ethanolamine	$-CH_2CH_2NH_3^+$	Phosphatidylethanolamine
Choline	$-CH_2CH_2N(CH_3)_3^+$	Phosphatidylcholine (lecithin)
Serine	$-CH_2CH(NH_3^+)COO^-$	Phosphatidylserine
myo-Inositol		Phosphatidylinositol
Glycerol	$-CH_2CH(OH)CH_2OH$	Phosphatidylglycerol
Phosphatidylglycerol		Diphosphatidylglycerol (cardiolipin)

3.3.1.1.Ether glycerophospholipids

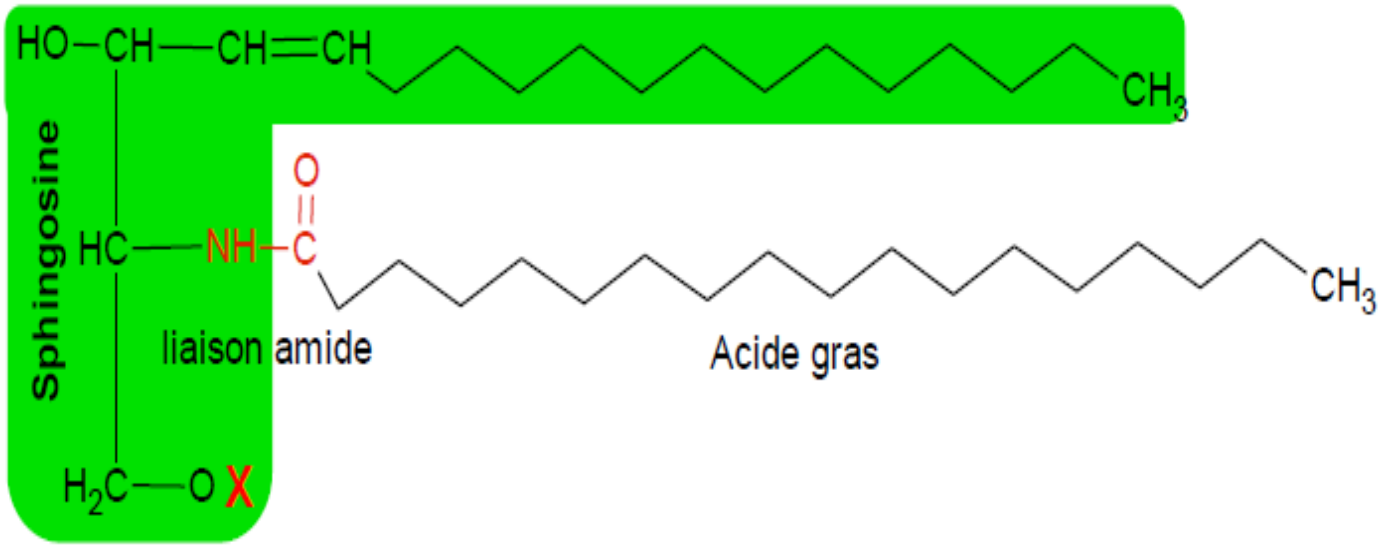
These are glycerophospholipids in which the ester bond at the C1 position is replaced by an ether bond. Two types are known: plasmalogens-which make up half of the phospholipids in the heart and are also found in halophilic bacteria -and PAF (platelet-activating factor), a chemical messenger.





3.3.2.Sphingolipids

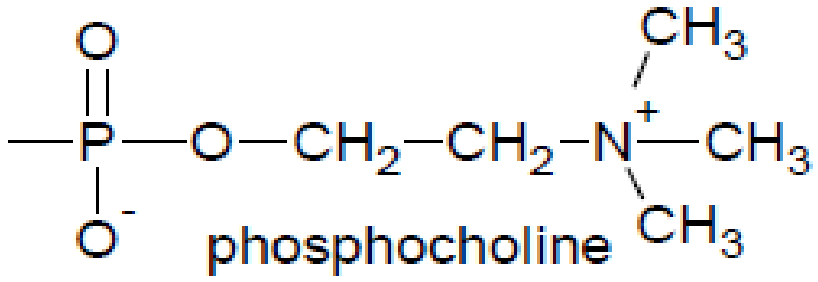
Sphingolipids are a class of membrane lipids containing sphingosine, an 18-carbon amino alcohol linked to a fatty acid to form a ceramide



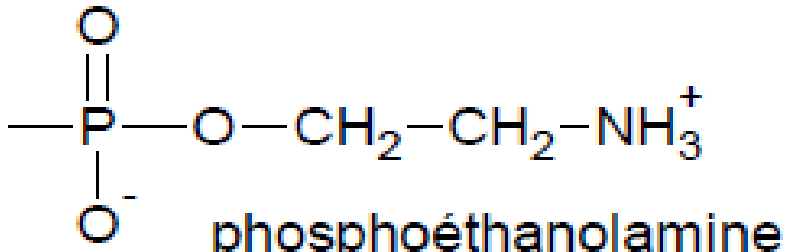
3.3.2.1.Sphingomyelins

- These are molecules formed by the esterification of the C1 hydroxyl group of a ceramide with phosphocholine or phosphoethanolamine.
- Sphingomyelins play an important role in the nervous system.

X =



phosphocholine



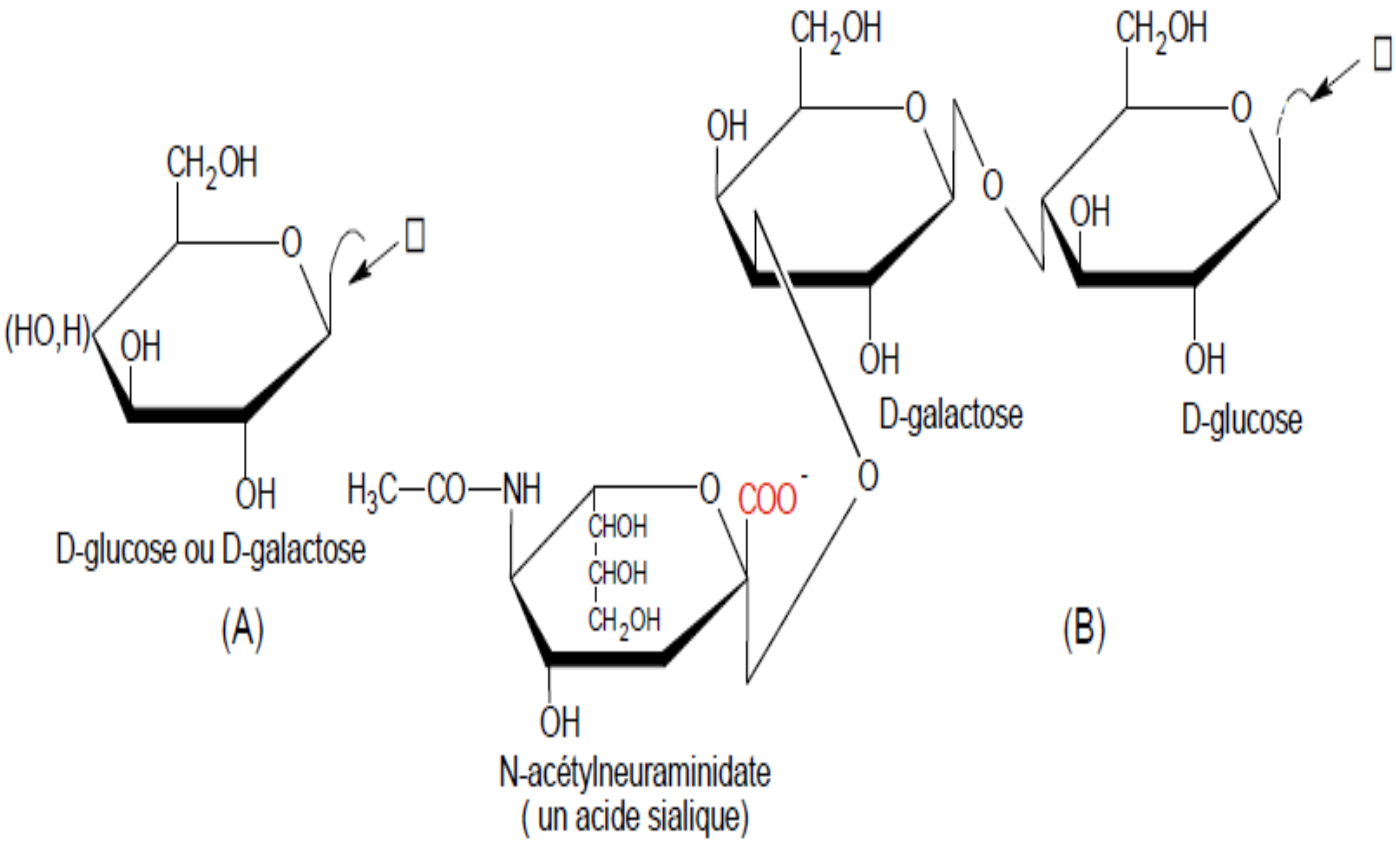
phosphoéthanolamine

3.3.2.2.Glycosphingolipids

These are molecules formed by the addition of one or more sugars linked to the hydroxyl group at the C1 position of a ceramide; the resulting glycosidic bond is of the β type.

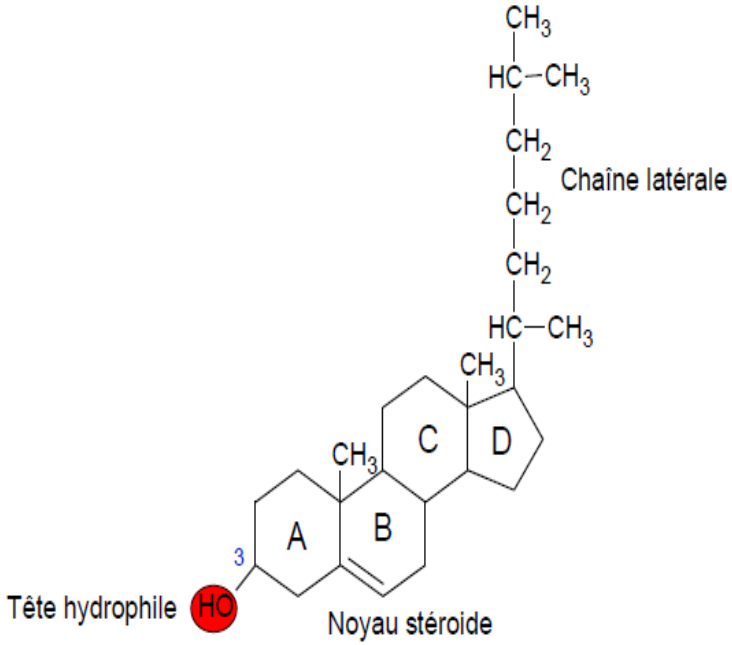
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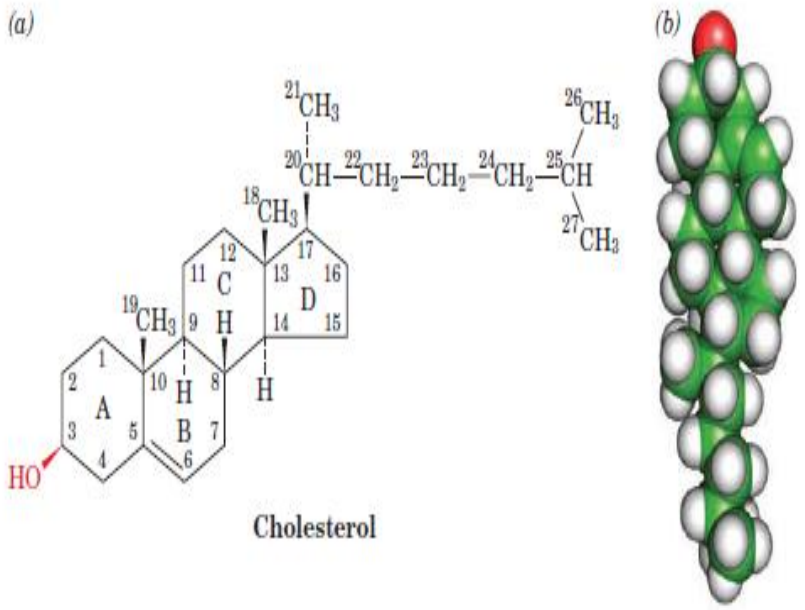
- Cerebrosides: a ceramide + a monosaccharide (D-glucose or D-galactose)
- Sulfatides: a ceramide + D-galactose esterified with a sulfate group at the 3-position.
- Gangliosides: a ceramide + three or more monosaccharides, one of which is a sialic acid (e.g., N-acetylneuraminic acid).


CH2OH
O
(HO,H)
OH
OH
D-glucose ou D-galactose
(A)
H3C—CO—NH
CHOH
CHOH
CH2OH
O
COO-
OH
N-acétylneuraminidate
(un acide sialique)
CH2OH
O
OH
OH
D-galactose
O
CH2OH
O
OH
OH
D-glucose
(B)

3.3.Sterols

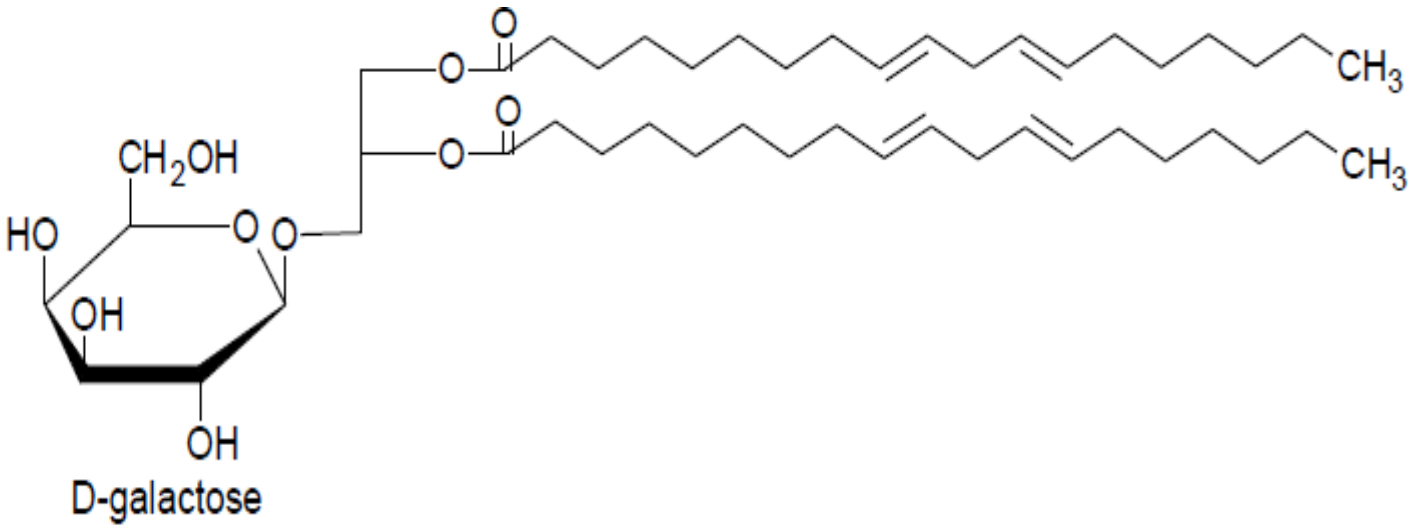
- Sterols are membrane lipids composed of a steroid nucleus (four fused rings: A, B, C, and D).
- Cholesterol is the major sterol in animal tissues; it is the precursor to steroid hormone, such as androgens, estrogens, and glucocorticoids, as well as to bile acids.





3.4.Galactolipids

These are plant cell membrane lipids; their structure consists of one or two galactose residues linked via a glycosidic bond to the C-3 position of a 1,2-diacylglycerol.



3.5.Archaebacterial lipids

Archaebacteria possess membrane lipids characterized by long (32-carbon), branched hydrocarbon chains linked at each end to glycerol by ether bonds.

