THIRD CHAPTER: Structure and physicochemical properties of lipids

Lipids are a broad class of molecules that all share the characteristic that they have at least a portion of them that is hydrophobic (do not interact appreciably with water). They are a diverse collection of biomolecules that are composed mostly of carbon and hydrogen, i.e., hydrocarbons.

One type of lipid, the triglycerides, is sequestered as fat in adipose cells, which serve as the energy-storage depot for organisms and also provide thermal insulation. Some lipids such as steroid hormones serve as chemical messengers between cells, tissues, and organs, and others communicate signals between biochemical systems within a single cell. The membranes of cells and organelles are microscopically thin structures formed from two layers of phospholipid molecules. Membranes function to separate individual cells from their environments and to compartmentalize the cell interior into structures that carry out special functions. So important is this compartmentalizing function that membranes, and the lipids that form them, must have been essential to the origin of life itself.

I. Classification of lipids according to structure

Based on their chemical structure, we distinguish:

a. Fatty acids

b. Simple lipids:

- Glycerides
- Sterides
- Cerides

c. Complex lipids:

- Phospholipids
- Sphingolipids
- Plasmalogens

d. Isoprene lipids:

- Isoprene carbides
- Sterols and steroids
- Quinones and fat-soluble vitamins.

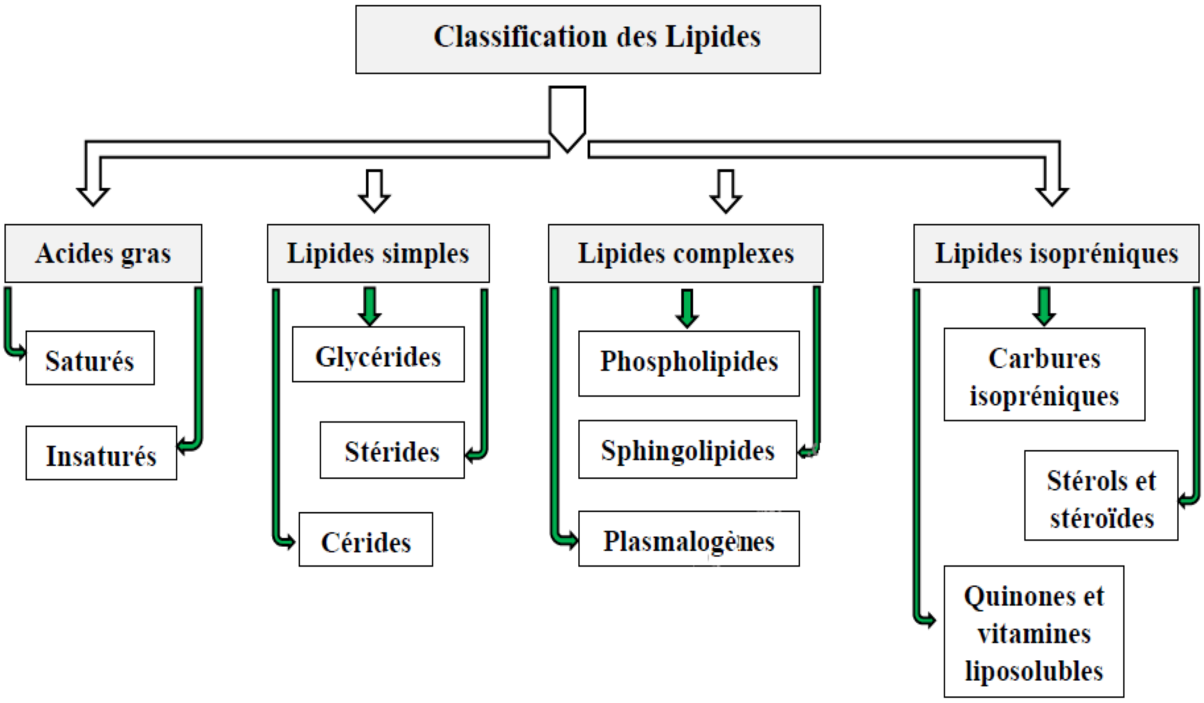

Fig 1. Classification of lipids according to structure.

II. Structure and properties of fatty Acids

Arguably, the most important lipids in our cells are the fatty acids, because they are components of all of the other lipids, except some of the steroids and fat-soluble vitamins. Fatty acids rarely occur as free molecules in nature but are usually found as components of many complex lipid molecules such as fats (energy-storage compounds) and phospholipids (the primary lipid components of cellular membranes).

Consisting of a carboxyl group (COOH) linked to a long aliphatic tail. This common form for biological lipids—one that contains well-separated hydrophobic and hydrophilic parts—is called amphipathic. Although the chains are usually between 12 and 24 carbons long, several shorter-chain fatty acids are biochemically important.

Fatty acids are described as either saturated (linear chains of CH_2 groups linked by carbon-carbon single bonds with one terminal carboxylic acid group, no double bonds) or unsaturated (one or more carbon-carbon double bonds). Fatty acids with more than one double bond are described as polyunsaturated, the multiple double bonds are almost always separated by a CH_2 group ($—CH_2—CH{=}CH—CH_2—CH{=}CH—CH_2—$). Increasing the amount of unsaturated fatty acids (and the amount of unsaturation in a given fatty acid) in a fat decreases its melting temperature.

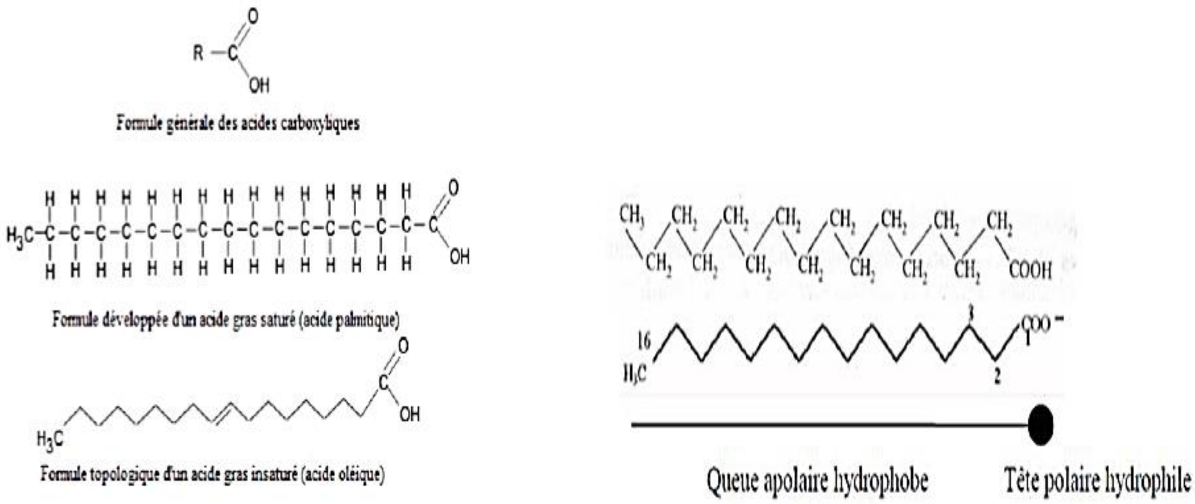

Fig 2. Structure of fatty acids.

The most common fatty acids in our body include palmitate, stearate, oleate, linolenate, linoleate, and arachidonate. Fatty acids are numbered by two completely different schemes. The delta numbering scheme has the carboxyl group as #1, whereas the omega number scheme starts at the other end of the fatty acid with the methyl group as #1. Fatty acids are described as essential if they must be in the diet (can't be synthesized by the organism). Animals, including humans, cannot synthesize fatty acids with double bonds beyond position delta 9, so linoleic and linolenic acids are considered essential in these organisms.

	Number of Carbon Atoms	Unsaturation	Formula
Palmitoleic	16	$16{:}1\text{—}\Delta^{9}$	$CH_3\,(CH_2)_5CH{=}CH(CH_2)_7CO_2H$
Oleic	18	$18{:}1\text{—}\Delta^{9}$	$CH_3\,(CH_2)_7CH{=}CH(CH_2)_7CO_2H$
Linoleic	18	$18{:}2\text{—}\Delta^{9,12}$	$CH_3\,(CH_2)_4CH{=}CH(CH_2)CH{=}CH(CH_2)_7CO_2H$
Linolenic	18	$18{:}3\text{—}\Delta^{9,12,15}$	$CH_3\,(CH_2CH{=}CH)_3(CH_2)_7CO_2H$
Arachidonic	20	$20{:}4\text{—}\Delta^{5,8,11,14}$	$CH_3\,(CH_2)_4CH{=}CH(CH_2)_4(CH_2)_2CO_2H$

Fig 3. Important unsaturated fatty acids.

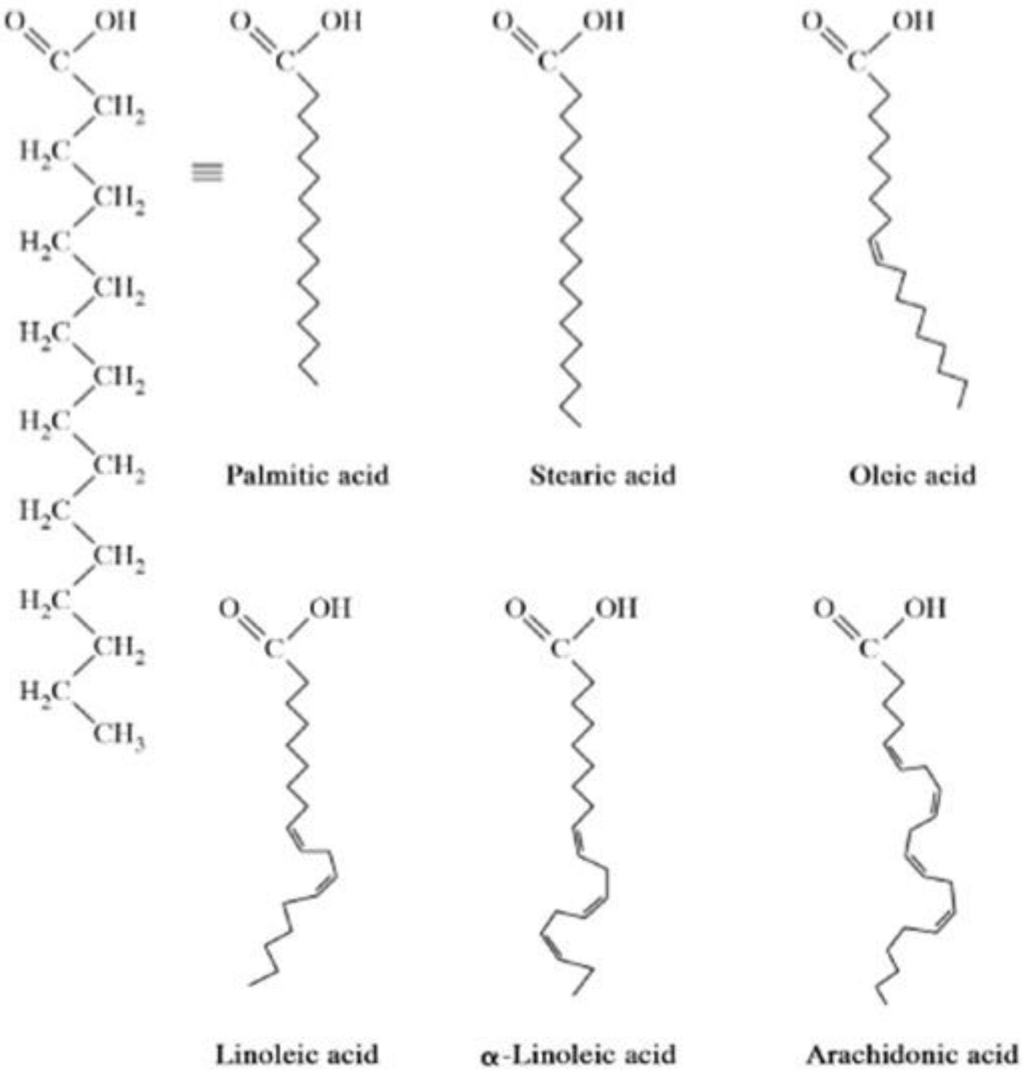

Fig 4. Fatty acids **[1]**.

III. Properties of fatty acids

Physical properties

- **Solubility:** Fatty acids are amphiphilic (or amphipathic), they have 2 poles; a hydrophobic chain (a carbon chain) and a hydrophilic acid function. The hydrophobic character of the hydrocarbon chain of most biological fatty acids exceeds the hydrophilic nature of the carboxylic acid group, making the water solubility of these molecules very low. Water solubility decreases exponentially with the addition of each carbon atom to the hydrocarbon chain.
- **Density:** The density of fatty acids is low, the oil floats on water.

- **Melting point:** The melting temperatures of saturated fatty acids of biological interest are above 27 °C and rise with increasing length of the hydrocarbon chain. Monounsaturated and polyunsaturated molecules melt at substantially lower temperatures than do their saturated analogs, with the lowest melting temperatures occurring when the carbon-carbon double bonds are located near the centre of the hydrocarbon chain, as they are in most biological molecules. As a result, these molecules form viscous liquids at room temperature.
- Spectral properties: Whether saturated or not, fatty acids do not absorb light in the visible, but they absorb in the ultraviolet. The absorption maximum depends on the number of double bonds.

Chemical properties

The most chemically reactive portion of fatty acids is the acidic carboxyl group (COOH). It reacts with alcohols (R′OH) to form products known as esters (RCOOR′) and releases water in the process.

- **Properties linked to the carboxyl function**

- Formation of alkaline salts (Saponification): In the presence of Base (KOH, NaOH), fatty acids give salts (sodium or potassium salts) commonly called soaps.

$$R\text{-}COOH + NaOH \longrightarrow R\text{-}COO^{-}Na^{+}$$

Fatty acid + Base (NaOH ou KOH) ⟶ Formation of soaps

- **Esterification of alcohols:** The carboxylic acid function can esterify an alcohol function to give a fatty acid ester, in order to form more complex lipids.

$$R\text{-}COOH + R'\text{-}OH \longrightarrow R\text{-}(C{=}O)\text{-}O\text{-}R' + H_2O$$

AG + alcohol ⟶ ester

- **Properties due to the presence of double bonds**

- Hydrogenation reactions: Saturation of double bonds

$$\ldots\ \text{-}CH_2\text{-}CH{=}CH\text{-}CH_2\ \ldots + H_2 \longrightarrow \ldots\ \text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}\ldots$$

- Oxidation of double bonds: Oxidation by $KMnO_4$ in an alkaline medium causes the cleavage of the fatty acid at the double bond, which gives two carboxylic acids.

$$R\text{-}CH{=}CH\text{-}R'\text{-}COOH + KMnO_4 \longrightarrow R\text{-}COOH + HOOC\text{-}R'\text{-}COOH$$

An acid and a diacid are formed for each double bond.

IV. Simple lipids

They are esters of fatty acids and alcohol. They are made up of C, H and O, and include:

- Glycerides: alcohol is glycerol;
- Cerides: alcohols are long chain (fatty);
- Steroids: alcohol is a sterol (polycyclic).

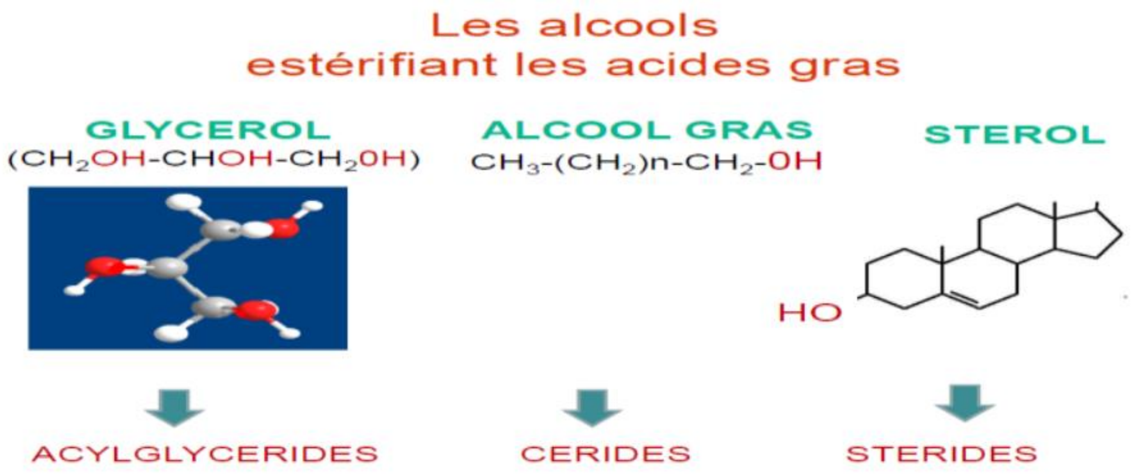

Fig 5. Alcohols esterifying fatty acids.