Introduction

The term *lipids* represent structurally diverse compounds with different chemical and physical properties. Thus, lipids are a unique category of compounds that are soluble in solvents such as chloroform and ether, and do not generally dissolve in water. They may be broadly defined as <u>hydrophobic</u> or <u>amphiphilic</u> small molecules. This group consists of fats, oils, waxes, fatty acids, monoglycerides, diglycerides, triglycerides, fat soluble vitamins, sterols, steroids and phospholipids.

Lipids are a diverse and ubiquitous group of compounds which have many key biological functions, such as acting as structural components of cell membranes, serving as energy storage sources and participating in signaling pathways.

1. Fatty acids

1.1. Definition

Fatty acids are **hydrocarbon structures** (containing carbon and hydrogen atoms) formed by four or more carbon <u>attached to an acidic functional group</u> called **carboxyl group**. The fatty acyl structure represents the major lipid building block of complex lipids and therefore is one of the most fundamental categories of biological lipids.

Chemically, a fatty acid is a carboxylic acid with an aliphatic tail (chain). The predominant fatty acids are straight chain, can be saturated or contain carbon-carbon double bonds with an even number of carbon atoms. There is a wide spectrum of chain lengths, ranging from 4-carbon fatty acids in dairy fat to 30-carbon fatty acids in some marine lipids.







Figure 2: structure of Butyric acid (n-butanoic acid, C₄H₈O₂)

1.2. Classification of fatty acids

Fatty acids, according to their structure, can be classified on:

- Saturated fatty acid: <u>without</u> contain carbon-carbon double bonds.
- > Unsaturated fatty acid: containing 1 or more double bonds in the chain:
 - Monounsaturated fatty acid: contains 1 double bond in the chain.
 - **4** Polyunsaturated fatty acid: contains **more than 1** double bond.



In almost all naturally occurring unsaturated fatty acids, the double bonds are in the cis configuration and are typically positioned at the 3rd, 6th or 9th carbon atom from the terminal methyl group. A cis configuration means that the hydrogen atoms attached to the double bonds are on the same side. If the hydrogen atoms are on opposite sides, the configuration is called trans.



1.3. Nomenclature

Although fatty acids are long-chained carboxylic acids, they are not always named at such. Instead, fatty acids are often named using systems that provide details about the atoms present in the molecule. A carbon designation is given to indicate the number of carbon atoms in the fatty acid, number of carbon-carbon double bonds, and the location of the carbon-carbon double bond(s).

4 There are two systems that provide details on the location of carbon-carbon double bonds:

- The delta (A) system: In this system, carbon 1 is assigned to the carbon of the functional group and the chain is, numbered to assign locator numbers to the first carbon in each carbon-carbon double bond present in the molecule
- The omega (ω) system: This system, which is often used in nutrition, begins numbering the carbon chain at the opposite end of the molecule. In this system, carbon 1 is assigned to the carbon farthest from the functional group. Another difference is that the omega system only indicates the location of the first carbon of the first carbon-carbon double bond.



Figure 6: Applying omega (red) and delta (blue) numbering systems to linoleic acid.

<u>1 a</u>	tty uclus nomencluture	
		Systematic name:
≻	Saturated fatty acid:	parent hydrocarbon + <i>oic</i>
		e.g. C18: Octadecan <i>oic acid</i>
≻	Unsaturated fatty acid:	with one double bond: + <i>enoic</i>
		e.g. C18: Octadec <i>enoic</i> acid
		with two double bonds:+ <i>dienoic</i>
		e.g.C18: Octadeca <i>dienoic</i> acid
		with three double bonds: + <i>trienoic</i>
		e.g. C18: Octadeca <i>trienoic</i> acid

Fatty acids nomenclature

Table	1:	Nom	enclature	e of the	alip	hatic	hy	drocarbons
							~	

Number of Carbons	Alkane C _n H _{2n+2}				
1	Methane				
2	Ethane				
3	Propane				
4	Butane				
5	Pentane				
6	Hexane				
7	Heptane				
8	Octane				
9	Nonane				
10	Decane				
11	Hendecane ^d				
12	Dodecane				
13	Tridecane				
14	Tetradecane				
15	Pentadecane				
16	Hexadecane ^e				
17	Heptadecane				
18	Octadecane				
19	Nonadecane				
20	Eicosane				
21	Heneicosane				
22	Docosane				
23	Tricosane				
24	Tetracosane				
25	Pentacosane				
26	Hexacosane				
27	Heptacosane				
28	Octacosane				
29	Nonacosane				
30	Triacontane				

1.4. Physicochemical properties of fatty acids

- **4** Physical properties
 - Melting point: It depends on two criteria; the chain length and the degree of unsaturation. An increase in the number of carbon atoms leads to an increase in the melting point, while an increase in the number of double bonds leads to a decrease in the melting point.
 - Solubility: fatty acids are amphiphilic (or amphipathic), they have two poles; a hydrophobic chain (a carbon chain) and a hydrophilic acid function.
 - > **Density:** The density of fatty acids is low, the oil floats on water.
 - Spectral properties: Whether they are saturated or not, FAs do not absorb light in the visible range, but they do absorb in the ultraviolet. The maximum absorption depends on the number of double bonds.

Chemical Properties

- Properties related to the carboxyl group
 - Formation of alkaline salts (Saponification): In the presence of a base (KOH, NaOH), fatty acids yield salts (sodium or potassium salts) commonly known as soaps.

R-COOH + NaOH \longrightarrow R-COO-Na⁺

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-COOH + R'-OH → R-(C=O)-O-R' + H2O

FA + alcohol _____ ester

• Properties due to the possible presence of double bonds

> Hydrogenation reactions: Saturation of double bonds

-CH₂-CH=CH-CH₂... + H₂... -CH₂-CH

Oxidation of double bonds: Oxidation by KMnO₄ in an alkaline medium causes the cleavage of the fatty acid at the double bond, resulting in two carboxylic acids.

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

-There is formation of an acid and a dicarboxylic acid for each double bond

- Oxidation by the oxygen in the air or by enzymes in the cell.

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2.Lipids classification

Lipids are grouped into different classes, which stem from their structural composition. Generally, they are classified as simple lipids, conjugated lipids (or compound lipids), and finally derived lipids. Simple lipids consist of triacylglycerol and waxes. whereas conjugated lipids have additional molecules together with what the simple lipids contain. Derived lipids are lipids obtained upon hydrolysis of simple or compound lipids.



2.1. Simple lipids

2.1.1. Triacylglycerol

Lipids that contain three molecules of fatty acids and a molecule of glycerol are called triacylglycerols. Triacyglycerols are esters composed of three fatty acid units joined to *glycerol*, a trihydroxy alcohol.



4 They may contain:

- one type of fatty acid. In this case, they are considered as simple triacylglycerols. This means the three fatty acids attached to the glycerol are the same.
- > more than one type of fatty acid. In this case, they are referred to as **mixed triacylglycerols**.



- They are usually called oils when <u>liquid</u> or fats when <u>solid</u> at room temperature. This property occurs as a result of *length of fatty acid chains attached to the glycerol unit* and the degree of saturation. Those that are oils are composed of short-chain unsaturated triacylglycerols, whereas the solids are composed of long-chain unsaturated triacylglycerols.
- They are not usually associated with membranes; however, *they constitute the largest proportion of storage fats* that are present in plants and animals. The various sources of fat are based on animals like lard, butter, fish and oils from plant sources like olive or corn. Triacylglycerol can be obtained in diets as well as synthesized in the body.

4 Physicochemical Properties

- Triacylglycerols are nonpolar and hydrophobic, conferring on them the inability to dissolve in water and as such form floats on the surface of water.
- They do not have any color and are odorless.
- In hydrolysis, they are broken down into fatty acids and glycerol by the action of heat or enzymes.
- The hydrolysis of fats and oils in the presence of a base is used to make soap and is called saponification.

2.1.2. Waxes

Waxes are esters formed from long-chain fatty acids and long-chain alcohols. Most natural waxes are mixtures of such esters. Plant waxes on the surfaces of leaves, stems, flowers, and fruits protect the plant from dehydration and invasion by harmful microorganisms. Animals also produce waxes that serve as protective coatings, keeping the surfaces of feathers, skin, and hair pliable and water repellent.



2.2. Conjugated Lipids (compound lipids)

Compound lipids are the esters of fatty acids which contain an additional group in addition to an alcohol and a fatty acid. The various type of compound lipids are as follows:

2.2.1. Phospholipids

The term "phospholipids" is usually taken to mean phosphoglycerides, which have a common backbone of phosphatidic acid. They consist of **two fatty acids**, **a molecule of glycerol** and **one alcohol modified phosphate group**. Phospholipids possess <u>both hydrophilic</u> (phosphate group) and <u>hydrophobic</u> (*uncharged fatty acids*) properties.



- The structure of phospholipids is usually simplified representing the polar end as a sphere and the fatty acids as two parallel rods.
- Figure 11 shows the chemical structure of phosphatidic acid in its simplified representation. The amphipathic character of phosphatidic acid can be increased by joining to the phosphate different basic and polar molecules that increases the polarity to the extreme of the sn-3 position.
- When the substituent of the phosphate group is the amino acid serine it is formed phosphatidylserine; when it is etanolamine it is formed phosphatidylethanolamine (cephalin); when choline is substituent it is formed phosphatidylcholine (lecithin); and when the substituent is the polyalcohol inositol it is formed phosphatidylinositol, a very important molecule involved in cell signaling.



2.2.2. Glycolipids

The term glycolipid means the coexistence of carbohydrate and lipid in the same compound. Glycolipids are also known as **cerebrosides** because they are very useful for the brain. Cerebrosides are technically the simplest glycolipids. **Glycolipids** also consist of a sphingosine backbone together with a fatty acid, but lacking a phosphate moiety. It is considered as a ceramide that has been attached to a saccharidic unit through glycosidic bonds. They are usually made up of one or more sugar units. Most of the time, it is either galactose or glucose. They may also be considered as amphipathic since the sugar units make one end of the structure polar, with the nonpolar region containing hydrocarbon units.



The sphingolipids: called gangliosides are more complex, usually containing a branched chain of three to eight monosaccharides and/or substituted sugars. Because of considerable variation in their sugar components, about 130 varieties of gangliosides have been identified. Most cell-to-cell recognition and communication processes (e.g., blood group antigens) depend on differences in the sequences of sugars in these compounds. Gangliosides are most prevalent in the outer membranes of nerve cells, although they also occur in smaller quantities in the outer membranes of most other cells. Because cerebrosides and gangliosides contain sugar groups, they are also classified as glycolipids



2.3. Derived Lipids

These lipids are derived from simple or conjugated lipids by hydrolysis. This class includes fatty acids, glycerol, fatty aldehydes, ketone bodies, steroids, hydrocarbons, lipid soluble vitamins, and hormones.

2.3.1. Steroids

Perhydrocyclopentanophenanthrene is a well-known term in the study of steroids. It is the parent structure from which all steroids are formed. It consists of one five-membered ring named D and three six-membered rings named A (cyclohexane), B. and C. These rings are fused together to create this parent molecule. The structure has 17 carbon atoms. Steroid molecules may also be

considered as derivatives of a tricyclic aromatic hydrocarbon that has been fused with a cyclo-pentane. Functional groups, carbon—carbon double bonds, and hydrocarbons can be introduced to the parent ring structure, which results in the various steroid molecules. The natural steroids usually harbor a methyl group at the carbon-10 position.



Figure 13: Structures of steroid nucleus, which is present in all steroids.

Cholesterol is formed when a hydroxyl group is introduced to the parent structure mentioned above. This means an alcohol group has been introduced. It is then referred to as a sterol. The human body is able to produce cholesterol but it can also be supplied to the body through diet. There are other sterols such as ergosterol and sligmaslerol that are similar in structure to cholesterol.



2.3.2. Terpenes, terpenoids

Terpenes are *simple hydrocarbons* which consist of five carbon isoprene units which are attached to each other in different ways. These are the largest class of secondary metabolites and found in resin acids, essential oils, rubber and plant originated pigments like carotenoids and lycopene's. <u>The modified form of terpenes with different functional groups</u> is known as **terpenoids**. Depending on the carbon units' terpenoids may be classified as monoterpenes, diterpenes, triterpenes, sesterpenes and sesquiterpenes.

Biochemistry

Lipid vitamins (A, D, E, and K), carotenoids, chlorophyll, ubiquinone, and plastoquinone are some of the notable isoprenoid lipids. The pigments carotenoids and chlorophyll are also essential plant pigments that also consist of repeating isopre noid units.

Isoprene