Lipids

Ref. Biochemistry by Gupta

Lipids

What are lipids?

Lipids are heterogeneous bio-organic compounds soluble in organic solvents such as chloroform, ether, benzene, etc., but not in water. They constitute about 5% of cell structure.

General properties of lipids

1. Lipids are ideal form for storing energy in the human body compared to carbohydrates and proteins because
(a) Energy content of fat is higher.
(b) Only fat can be stored in concentrated water free form which not possible with carbohydrates and protein.
2. Lipids are relatively insoluble in water
3. They are soluble in nonpolar solvent
4. The hydrophobic nature of lipids due to the predominant of hydrocarbon chains in their structure.

Biological functions of lipids

1. **In diet:**

Lipids are important dietary constituent because:

(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) Lipid in adipose tissue serves as storage form of energy.
(b) They serve as thermal insulator in the subcutaneous tissues.
(c) Lipoprotein (a combination of fat and protein) are important because :
(i) They are inter in the structure of cell membrane and mitochondria

(ii) They serve as transport form of lipids in the blood.

Classification of lipids

There is no single, internationally accepted system for lipid classification. According to **Bloor's classification**, lipids have been classified into four major groups:

1- **Simple lipids:** ester of fatty acids with alcohols. They are including fats and oils (esters of fatty acids with glycerol, e.g., TGs) and waxes (esters of fatty acids with alcohols other than glycerol).
2- **Compound lipids:** ester of fatty acids and alcohols with some additional groups. They are including several of types such as **phospholipids** (composed of fatty acids, glycerol or sphingosine, Pi and nitrogenous bases). The phospholipids are subdivided into two types, [glycerophospholipids (composed of fatty acids, glycerol, Pi, and nitrogenous base) and sphingophospholipids (composed of fatty acids, sphingosine, Pi, and nitrogenous base)], **glycolipids** (composed of fatty acids, sphingosine and sugar residue). Glycolipids are

subdivided into two types, cerebrosides (simple glycolipids which are composed of fatty acids, sphingosine and glucose /galactose residue) and gangliosides, a complex glycolipides (composed of fatty acids, sphingosine, hexose residues and sialic acid), and **proteolipids** (composed of lipids and protein, e.g. VLDL, LDL and HDL, etc.)

3- **Derived lipids:** as in steroids which are derived from steroid nucleus. They are including sterols, bile acids and steroid hormones.

4- **Miscellaneous lipids:** such as in terpenes, the compounds are formed from condensation of isoprene units, e.g. β- carotene, the source of vitamin A.

Lipids

Simple lipids	**compound lipids**	**derived lipids**	**miscellaneous lipids**
-Fats & oils	**- Glycerophospholipids**	**- Steroids**	**- Terpenes**
-Waxes	**- Sphingophospholipids**	**--Sterols**	**-- β-carotene**
	- Proteolipids	**--bile acids**	**-- vitamin A**
	-Glycolipids	**-- steroid hormones**	**-- vitamin K**
	--Cerebrosides		
	-- Gangliosides		
	- Sulfolipids		

Lipids classification

Fatty acids

- **Fatty acids are monocarboxylic organic compounds with a saturated or unsaturated straight aliphatic hydrocarbon chain (straight alkyl chain) and contain even number of carbon atoms.**
- Fatty acids mainly occur as esters in lipids (fats, oils, phospholipids and glycolipids)

Types of fatty acids:

The fatty acids have been divided into two groups on the bases of presence of double bond: **(i) saturated fatty acids** and **(ii) unsaturated fatty acids**. Both saturated and unsaturated fatty acids occur in all natural lipids, but their proportion varies in plants and animal fats.

(i) Saturated fatty acids

The alkyl chain of saturated fatty acids contains no double bond. The general formula for saturated fatty acids is **CnH2n+1.COOH**. Examples of some common saturated fatty acids are given in table (1). The saturated fatty acids having ten carbon atoms or less are liquid in room temperature and are called **''lower fatty acids''**, e.g. **butyric acid, caproic acid, caprylic acid and capric acid**. The saturated acids having carbon atoms more than ten are solid at room temperature and are called as **''higher fatty acids''**, e.g. lauric acids, myristic acid, palmitic acid, stearic acid, arachidic acid, etc. Fatty acids with higher number of carbon atoms are found in waxes.

The systematic name of a saturated fatty acid is based on the hydrocarbon from which derived and ends with suffix –**anoic**, e.g. a saturated fatty acid with carbon atoms 4 and 6 are named as n-butanoic acid and hexanoic acid, respectively.

Table (1): some common saturated fatty acids present in natural fats and oils

Common name	systematic name	chemical structure	source
Butyric acid	**n-butanoic acid**	**CH3-(CH2)2-COOH**	**butter, milk**
Caproic acid	**n-hexanoic acid**	**CH3-(CH2)4-COOH**	**butter, milk, coconut**
Lauric acid	**n-dodecanoic acid**	**CH3-(CH2)10-COOH**	**butter, coconut**
Myristic acid	**n-tetradecanoic acid**	**CH3-(CH2)12-COOH**	**butter, coconut**
Palmitic acid	**n-hexadecanoic acid**	**CH3-(CH2)14-COOH**	**animal and plant fats**
Stearic acid	**n-octadecanoic acid**	**CH3-(CH2)16-COOH**	**animal and plant fats**
Arachidic acid	**n-eicosanoic acid**	**CH3-(CH2)18-COOH**	**peanut oil**

(ii) Unsaturated fatty acids

The alkyl chain of unsaturated fatty acids contains one or more double bond (c=c) or ethylenic groups. Most natural occurring unsaturated fatty acids have ***cis* double bonds**.

The systematic name of unsaturated fatty acids is based on the hydrocarbon from which it is derived and ends with suffix –**enoic,** e.g. palmitoleic acid with carbon atoms 16 is named as cis-9- Hexadec**enoic**.

The unsaturated fatty acids have been divided into two major groups on the basis of the number of double bonds**: (a) mono-unsaturated fatty acids. (b) Polyunsaturated fatty acids.**

(a) Monounsaturated fatty acids (mono**enoic fatty acids):**

These fatty acids contain one double bond and have general formula **CnH2n-1.COOH**. In most monounsaturated fatty acids, the double bond is present between C-9 and C-10. **Palmitoleic acid** and **oleic acid** are examples of monounsaturated fatty acids.

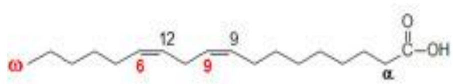
Palmitoleic acid 16:1 Δ9

Oleic acid 18:1 Δ9

(b) Polyunsaturated fatty acids (polyenoic fatty acids):

Polyunsaturated fatty acids contain two or more double bonds. Linoleic acid, linolenic acid and arachidonic acid are examples for polyunsaturated fatty acids. The polyunsaturated fatty acids can be classified on the base of the number of the double bonds to the following types:

Dienoic fatty acid: linoleic acid, a dienoic fatty acid, **contains two double bonds.** Linoleic acid is an essential fatty acid and it is present in many vegetable oils such as corn oil, cotton seed oil, soybean oil, etc.

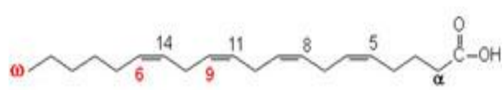


Linoleic acid 18:2 Δ9,12 (essential fatty acid)

Trienoic fatty acids: linolenic acid, a trienoic fatty acid, **contains three double bonds.** Linolenic acid is also an essential fatty acid and is found with Linoleic acid in vegetable oils**,** present in large amount in linseed.

Linolenic acid 18:3 Δ9, 12, 15 (essential fatty acid)

Tetraenoic fatty acids: Arachidonic acid, a tetraenoic fatty acid, **contains four double bonds**. Arachidonic acid is also an essential fatty acid and is found in peanut oil and animals fats.



Arachidonic acid 20:4 cΔ5, 8, 11, 14 (essential fatty acid)

Table (2): important examples of unsaturated fatty acids.

Common name	**systematic name**
Palmitoleic acid	*cis*-9-hexadec**enoic** acid
Oleic acid	*cis*-9-octadec**enoic** acid
Linoleic acid	all-cis-9, 12-octadeca**dienoic** acid
Linolenic acid	all-cis-9, 12, 15-octadeca**trienoic** acid
Arachidonic acid	all-cis-5, 8, 11, 14-eicosa**tetraenoic** acid

Nomenclature of unsaturated fatty acids:-

- The systematic name of an unsaturated fatty is based on the hydrocarbon from which it is derived and ends with a suffix –**enoic**.
- The carbon numbering in a fatty acid chain starts from **carboxyl carbon (C1)**.

- In a fatty acid chain, carbon atom to which the –COOH group is attached (i.e. **C2**) is called α-carbon, **C3** is β- carbon and **C4** is γ-carbon. The carbon atom of the terminal methyl group **($-CH_3$)** called **ω-carbon** or **n**-carbon regardless of the chain length.
- **The position of double bond** is indicated by superscript numbers following Δ (delta), e.g. Δ 9 indicates a double bond between C-9 and C-10, starting from the COOH end of fatty acid.
- **The position of double bond** can also be counted from terminal CH_3 group, i.e. from ω- carbon or n-carbon of fatty acid chain, e.g. ω-6 indicates a double bond on C-6 counting from ω-carbon of a fatty acid molecule. The oleic acid, linoleic acid, linolenic acid and arachidonic acid belong to three series of ω-fatty acids namely ω-3(or n-3), ω-6(or n-6), ω-9(or n-9) fatty acids.
- Abbreviations are used to show the total numbers of carbon atoms, total numbers of double bonds and the position of the double bonds in unsaturated fatty acids, e.g. the abbreviation of palmitoleic 16:1 Δ 9 depicts the total number of carbon atoms followed by the number of double bonds and the position of the double bonds, starting from the –COOH end.

Essential fatty acids:

Two polyunsaturated fatty acids namely **linoleic acid and linolenic acid cannot be synthesized** in our body, therefore, they are **essentially required in diet**. These fatty acids are called **essential fatty acids (EFA).**

In our body, **arachidonic acid** can be synthesized from the **essential fatty acid, linoleic acid**, which supplied in diet. The arachidonic acid also becomes **essential** if there is an **insufficient supply of its precursor**, **linoleic acid**.

The term **'essential fatty acids'** was produced by Burr and Burr in 1930. The vegetable oils such as peanut oil, sunflower oil, soybean oil, olive oil, etc., are rich in essential fatty acids. Essential fatty acids are very important for **normal growth; function and optimal growth of body,** other importance of EFAs are given below.

Biomedical significance of essential fatty acids

- EFAs are required for membrane structure and functions. These fatty acids are important constituents of phospholipids in cell membranes and help to maintain the membrane fluidity.
- EFAs are required to synthesis of **prostaglandins, thromboxans, prostacyclins and leukotrines**, which are collectively known as **eicosanoids**.
- **ω-6 (or n-6) fatty acids**, linoleic acid and arachidonic acid, **lower the blood cholesterol level**, whereas **ω-3 (or n-3)** fatty acid, linolenic acid, **lowers the blood triglyceride level**. Therefore, both **ω-3 and ω-6** fatty acids are suggested to lower the risk of **atherosclerosis**.
- **ω-3** fatty acid may decrease the risk of **heart disease and MI by inhibiting platelet aggregation.**

- Consumption of oils rich in EFAs prolongs the blood clotting time
- Deficiency of essential fatty acids (EFAs) is characterized by scaly skin (or toad skin), eczema (in children), loss of hair and poor wound healing.

Rancidity: because of unsaturated double bond(s), the unsaturated fatty acids are relatively more reactive than saturated fatty acids and undergo spontaneous (non-enzymatic) oxidation in presence of air (oxygen) to form various products such as peroxides, aldehydes, ketones, ketohydroxide, etc. which have rancid odour. This process is called **rancidification.**

The saturated fatty acids are relatively resistant to rancidification; therefore, the fats and oils containing unsaturated fatty acids are more susceptible to **rancidity**.

The rancidity of fats and oils results in development of rancid odor and unpleasant taste and occur when the fats and oils are stored for long time, exposed to air, moisture, light and warm temperature. Rancidity does not occur *in vivo*.

[Fats and oils (TGs rich in Unsaturated Fatty acids)] $\xrightarrow[\text{warm temp}]{\text{lipase}}$ **glycerol, FA.** $\xrightarrow[\text{light}]{\text{Air (O2)}}$ ***[Formation of lipid Peroxide, aldehyde, etc. gave rancid odor and unpleasant taste to fats and oils]***

Process of rancidification of oils and fats

- ***In vivo*** lipid peroxidation within the cell produces **peroxides** and **free radicals**, which may cause **damage** to **cellular proteins, nucleic acid and biomembranes leading to tissue damage.**
- **The role of free radicals** has been suggested in many **inflammatory** and **chronic diseases** such as **atherosclerosis**, **coronary heart disease, cataract formation, certain cancers, etc.**
- Diet rich in **antioxidants**, **vitamin C, vitamin E, β- carotene and selenium** has been suggested to **reduce the risk of inflammatory and chronic diseases.**
- The rancid **fats and oils are not safe to consumption.**
- Since the vegetable oils contain certain natural **antioxidants** such as carotenes, vitamin C, vitamin E, etc. they are **less susceptible to rancidity as compared to animal fats.**

Iodine number:

The iodine number (I No.) is a measure of a degree of unsaturated of the fat or oil and **is defined as the number of grams of iodine absorbed by 100 grams of fat or oil**.

In practice, the **iodine number** is used to know the **relative unsaturation of fats and oils. If a fat (oil) has lower iodine number, the fat (oil) has less quantity of**

unsaturated fatty acids whereas, if a fat (oil) has higher iodine number, the fat (oil) has greater quantity of unsaturated fatty acids.

Saponification number:

Saponification number is define as the number of milligrams (mg) of KOH required to saponify (to hydrolyze) one gram of fat or oil. Saponification number is a measure of **relative proportion of short chain and long chain fatty acids in a known quantity of fat or oil**, if a fat (oil) has **lower** saponification number, the fat (oil) has relatively **lesser** proportion of **short chain** fatty acids than **long chain** fatty acids whereas, if a fat (oil) has **higher** saponification number, the fat (oil) has relatively **greater** proportion of **short chain** fatty acid than **long chain**.