

## Lipids and Classification:

### **Lipids:**

Biological lipids are a chemically diverse group of organic compounds which are insoluble or only poorly soluble in water. They are readily soluble in non-polar solvents such as ether, chloroform or benzene. The hydrophobic nature of lipids is due to the predominance of hydrocarbon chains (-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-) in their structures unlike the proteins, nucleic acids and polysaccharides; lipids are not polymers.

### **Functions:**

Biological lipids have diverse functions. The four general functions of biological lipids have been identified.

- They serve as a storage form of metabolic fuel.
- They serve as a transport form of metabolic fuel.
- They provide the structural components of membranes.
- They have protective functions in bacteria, plants, insects, and vertebrates, serving as a part of the outer coating between the body of the organism and the environment.

Apart from the general functions biological lipids serve as pigments (carotene), hormones (Vitamin D derivatives, sex hormones), signalling molecules (eicosanoids, phosphatidylinositol), co-factors (vitamin K), detergents (bile salt) and many other specialized functions.

### **Classification of lipids:**

The lipids may be classified into three major groups-

#### **1. Storage lipids:**

- a) Ester linkage ————— fats and oils (palm oil)
- b) Ether linkage
  - Glycerol derive lipids (glyceryl ethers)
  - Long chain alcohol derived lipids (waxes)

#### **2. Membrane lipids:**

- a) Phospholipids
  - Glycerol back bone
    - Ester linkage (lecithin)
    - Ether linkage (plasmalogens)

- > Sphingosine back bone (Sphingomyelin)
- b) Glycolipids —————> Sphingosine back bone (cerebrosides)
- c) Steroidal —————> Cholesterol

### 3. Other lipids:

- a) Enzyme cofactor —————> Vitamin E, K, quinines
- b) Pigments —————> Carotenoids
- c) Hormones —————> Testosterone, prostaglandin
- d) Signal molecule —————> Phosphatidyl inositol
- e) Vitamin —————> A, D

### Fatty acid:

Fatty acids are the simplest form of lipids and serve as constituents in a large number of complex forms of lipids. Fatty acids are long chain hydrocarbons (4 to 36 carbons long) with one carboxyl group. Fatty acids in biological system usually contains an even number of carbon atoms. The 16 and 18 carbon fatty acids are most common. The alkyl chain may be saturated or unsaturated. Unsaturated fatty acids may contain one or more double bonds. Fatty acids are amphiphatic by nature that is they have both non polar and polar ends.

All naturally occurring unsaturated fatty acids are in cis conformation.

1. Palmitic acid (16 carbon saturated) 16:0
2. Oleic acid ( 18 carbon with one double bond between carbon 9 and 10) 18:1;9 or 18:1( $\Delta^9$ )
3. Linoleic acid (18 carbon with two double bonds between 9 and 10, 12 and 13) 18:2;9,12 or 18:2( $\Delta^{9,12}$ ).
4. Arachidonic acid 20:4( $\Delta^{5,8,11,14}$ )
5. Eleostearic acid 18:3( $\Delta^{9,11,13}$ )

### Storage lipids:

The major class of lipids are the storage lipids. These are common known as fats and oils. They are universally used as stored form of energy. These store the maximum amount of energy (9 kcal/g) as compared to carbohydrates and proteins which have only 4 kcal/g.

### Saturated and unsaturated fatty acids:

Saturated fatty acids have no double bonds in the chain. Their general formula is  $\text{CH}_3-(\text{CH}_2)_n-\text{COOH}$  where  $n$  specifies the number of methylene groups between the methyl and carboxyl carbons.

Unsaturated fatty acids have one or more double bonds and called monounsaturated or polyunsaturated respectively.

### **Essential fatty acids:**

Mammals lack the enzymes to introduce double bonds at carbon atoms beyond C-9 in the fatty acids chain. Hence, mammals cannot synthesize linoleate and linolenate. These are two essential fatty acids. The term essential means that they must be obtained from the diet because they are required by an organism and cannot be endogenously synthesized.

### **Melting point of fatty acids:**

The melting points of fatty acids depend on chain length and degree of unsaturation. The longer the chain length, the higher the melting point and greater the number of double bonds, the lower the melting point. The presence of double bonds makes unsaturated chain more rigid. As a result, unsaturated chains cannot pack themselves in crystals efficiently and densely as saturated chain, so they have lower melting point as compared to saturated fatty acids. Similarly, the unsaturated fatty acids with *cis* conformation have lower melting points than the unsaturated fatty acids with *trans* configuration. (*Why unsaturated fatty acids have low melting points?*)

Fats are composed of saturated fatty acids and are solid at room temperature, while oils are composed of unsaturated fatty acids and are in liquid form at room temperature.

### **Triacylglycerol :**

Triacylglycerol (also called triglycerides) are trimer of fatty acids and glycerol. They are composed of three fatty acids and a glycerol molecule. Triacylglycerols are of two types- simple and mixed type. Those containing a single kind of fatty acids are called simple triacylglycerols and with two or more different kinds of fatty acids are called mixed triacylglycerols.

Triglycerols are non polar, hydrophobic in nature and a major form of stored lipids. Because triglycerols have no charge (i.e the carboxyl group of each fatty acid is joined to glycerol through a covalent bond), they are sometimes referred to as neutral lipids.

Triglycerol molecules contain fatty acids of varying length which may be unsaturated or saturated. Triacylglycerols can be distinguished as fat and oil on the basis of physical state at room temperature.

Fats-----Saturated

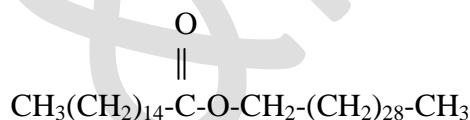
Oils-----Unsaturated

Hydrolysis of triacylglycerols with alkalis such as NaOH or KOH is called **saponification**. Saponification yields salts of free fatty acids (termed soap) and glycerol.

### **Waxes:**

Natural waxes are typically ester of fatty acids and long chain alcohol. They are formed by esterification of long chain fatty acids (saturated and unsaturated) and high molecular weight monohydroxy alcohols (carbon 14 to carbon 36).

Waxes are biosynthesized by many plants or animals. The best known animal wax is bee wax. Triacontanoylpalminate (an ester of palmitic acid with the alcohol triacontanol) is the major component of bee wax.



*General structure of a wax*

### **Degradation of glycerol:**

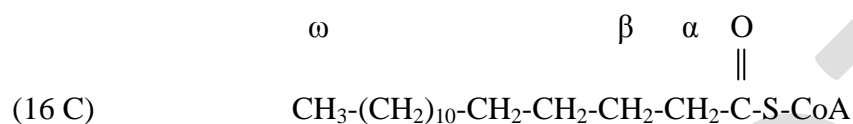
The major fraction of energy of a triacylglycerol comes from the three fatty acids molecules. This makes up to 95% of the total energy. Only 5% of the total energy comes from glycerol moiety. After liase hydrolysis triacylglycerol is broken into glycerol and three molecules of fatty acids. The glycerol is phosphorylated by glycerol kinase to produce glycerol-3-phosphate. This is then oxidised dihydroxy aceton phosphate dehydrogenase. This isomerises to glyceraldehydes-3-phosphate. The reaction is catalysed by triose phosphate isomerise. Glycealdehyde-3-phosphate then enters to the glycolytic pathway.

### **$\beta$ -oxidation:**

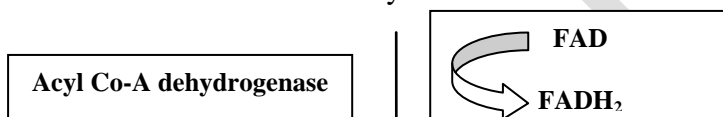
In this type of oxidation, it is the  $\beta$  carbon which is oxidized to keto and then acyl group and therefore, it is popularly known as  $\beta$ -oxidation. It is the most common pathway of degradation of fats.

1. The acyl Co-A dehydrogenase removes two hydrogen atoms, one each from  $\alpha$  and  $\beta$  carbon introducing a double bond between them. This produces trans  $\Delta^2$  enoyl Co-A. The hydrogen is accepted by FAD which changes to FADH<sub>2</sub>.
2. The second step is hydration step. A molecule of water is added as H and OH at  $\alpha$  and  $\beta$  carbon respectively removing the double bond. The product is L- $\beta$  hydroxyacyl Co-A. This reaction is catalyzed by enoyl Co-A hydratase.
3. The third step is further oxidation where  $\beta$ -hydroxy acyl Co-A dehydrogenase removes two hydrogen atoms from  $\beta$  carbon introducing a keto group. This makes a  $\beta$ -keto acyl Co-A. The hydrogen accepting molecule is NAD<sup>+</sup> which changes to NADH + H<sup>+</sup>.
4. The fourth step is catalysed by acyl Co-A acetyl transferase (thiolase). The enzyme splits  $\beta$ -keto acyl between  $\alpha$  and  $\beta$  carbon. The  $\beta$  carbon is linked to a new molecule of Co-A-SH forming acyl Co-A (this acyl group is shorter by two carbons) and releasing acetyl Co-A. This reaction also called thiolysis.

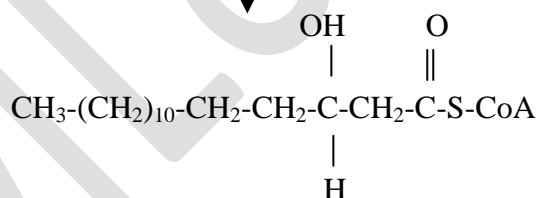
**Example:** Palmitoyl CoA a 16 carbon fatty acid complex.



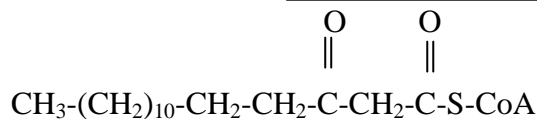
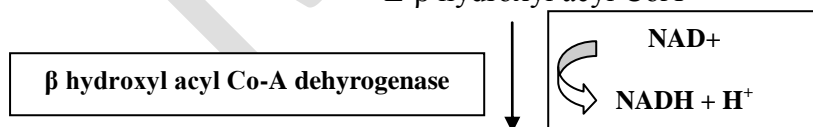
Palmitoyl Co-A



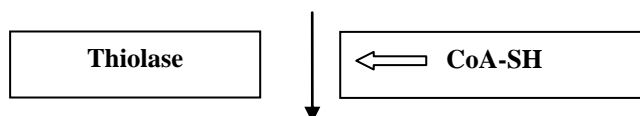
Trans  $\Delta^2$  enoyl CoA

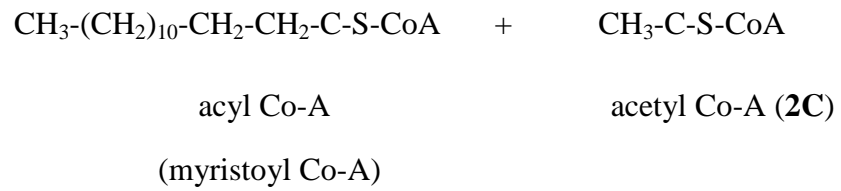


L- $\beta$  hydroxyl acyl CoA



$\beta$  ketoacyl Co-A





Thus the final result when the whole chain has been oxidized will be \_\_\_\_\_

