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PHARMACEUTICAL ORGANIC CHEMISTRY - II

UNIT 3

TOPIC :

- **Fats and Oils**

  a. Fatty acids- reactions.

  b. Hydrolysis, Hydrogenation, Saponification and Rancidity of oils, Drying
  oils.

  c. Analytical constants- Acid value, Saponification value, Ester value,
  Iodine value, Acetyl value, Reichert Meissl (RM) value- significance and
  principle involved in their determination.

Fats and Oils

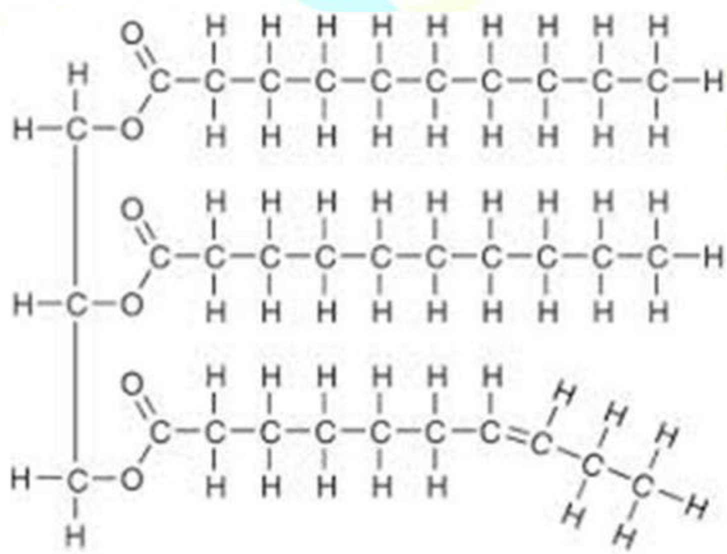
→ Fats and oils are simple lipids formed by the esterification of glycerol (a trihydric alcohol) with fatty acids.

→ They are also known as triglycerides or triacylglycerols.

General Properties:

- They are esters of glycerol + fatty acids.
- Commonly called triacylglycerols (TAG).
- Insoluble in water but soluble in organic solvents like ether, chloroform.
- Exist as fats (solid) or oils (liquid) at room temperature depending on the saturation of fatty acids.

Structure of Triglycerides::



Fatty Acids:

- Long-chain hydrocarbons with a carboxylic acid (-COOH) group.
- Two types:
    - Saturated fatty acids: No double bonds.
      Examples: Lauric acid, Palmitic acid.

- Unsaturated fatty acids: One or more double bonds.
  Example: Oleic acid.

Types of Fats and Oils

1. Simple Fats/Oils

- All three fatty acid chains are the same.
- Formed by glycerol + 3 molecules of the same fatty acid.

Example Structure:

CH_2-O-COR

|

CH -O-COR

|

CH_2-O-COR

Where R = same fatty acid group (e.g., butyric acid)

2. Mixed Fats/Oils

- The three fatty acid chains are different.
- Formed by glycerol + 3 different fatty acids.

Example:

CH_2-O-COR_1

|

CH -O-COR_2

|

CH_2-O-COR_3

Where R_1, R_2, R_3 = different fatty acids like oleic, palmitic, stearic, etc.

Reactions of Fats and Oils

→ Fats and oils undergo several important chemical reactions that are biologically and industrially significant. These include:

1. Hydrolysis

- Hydrolysis is the breakdown of triglycerides (fats and oils) into glycerol and fatty acids by the addition of water.
- In the human body, hydrolysis is catalyzed by the enzyme lipase found in the digestive tract.

Reaction:

$$\text{Fat} + 3H_2O \rightarrow \text{Glycerol} + 3\ \text{Fatty Acids}$$

2. Saponification (Soap Formation)

- Saponification is a base-catalyzed hydrolysis of fats or oils to form glycerol and soap (sodium salts of fatty acids).
- Common bases used: NaOH or KOH

Reaction:

$$\text{Fat} + 3\ NaOH \rightarrow \text{Glycerol} + 3\ \text{Soap}\ (R\text{-}COONa)$$

3. Hydrogenation

- Hydrogenation is the process of converting unsaturated fatty acids into saturated fatty acids by the addition of hydrogen (H_2) in the presence of metal catalyst (Ni).
- Used in converting vegetable oils into solid fats like vanaspati ghee.

4. Hydrogenolysis

- This is the cleavage of triglycerides into glycerol and long-chain primary alcohols using hydrogen in presence of metal catalyst such as copper chromite at high temperatures.

5. Rancidification

- Rancidity is the spoilage of fats and oils due to exposure to light, air (oxygen), heat, or moisture, leading to bad odor and sour taste.
- Rancid oils are inedible and unhealthy.

Types of Rancidity:

- Oxidative Rancidity: Due to oxidation of double bonds in unsaturated fatty acids, forming volatile carboxylic acids.
- Hydrolytic Rancidity: Due to hydrolysis of triglycerides forming free fatty acids and glycerol, causing unpleasant flavor.

6. Drying (Oxidative Polymerization)

- When oils (especially highly unsaturated oils like linseed oil) are exposed to air, they undergo oxidation and polymerization to form a thin solid film.
- Such oils are called drying oils and are used in paints and varnishes.

$$\text{Unsaturated oil} + O_2 \rightarrow \text{Solid cross-linked film}$$

Analytical Constants of Fats and Oils

Various analytical constants are used to assess the quality and composition of fats and oils. These include:

- Acid Value
- Saponification Value
- Ester Value
- Iodine Value
- Acetyl Value
- Reichert-Meissl (RM) Value

1. Acid Value

- The number of milligrams of KOH required to completely neutralize the free fatty acids (FFA) present in 1 gram of fat or oil.

Significance:

- Indicates the amount of free fatty acids in a sample.
- High acid value suggests hydrolysis due to poor storage (presence of moisture or air).
- Edible and pharmaceutical oils should have low or no acid value.

Principle:

Fat/oil is titrated against KOH/NaOH using phenolphthalein as an indicator.

Formula:

$$\text{Acid Value} = (V \times N \times 56.1) / W$$

Where:

- V = Volume of KOH (in mL)
- N = Normality of KOH

- W = Weight of sample (in grams)

2. Saponification Value

- The number of milligrams of KOH required to saponify 1 gram of fat/oil.

Significance:

- Indicates average molecular weight of the fatty acids.
- Higher SV = shorter fatty acid chains.
- Lower SV = longer chains.

Principle:

Oil is refluxed with excess alcoholic KOH. The remaining KOH is titrated with HCl using phenolphthalein.

Formula:

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Saponification Value = (B - S) × N × 56.1 / W
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Where:

- B = Volume of HCl in blank titration
- S = Volume of HCl in sample titration
- N = Normality of HCl
- W = Weight of sample (in grams)

3. Ester Value

- ➢ The number of milligrams of KOH needed to saponify the esters in 1 gram of fat or oil.

Formula:

Ester Value = Saponification Value - Acid Value

Significance:

- Measures the ester content.
- High ester value may indicate flavoring or fragrance oils.

4. Iodine Value

- ➢ The number of grams of iodine absorbed by 100 grams of fat or oil.

Significance:

- Indicates the degree of unsaturation.
- Higher iodine value = more unsaturated (more double bonds).
- Useful to assess drying oils and susceptibility to rancidity.

Principle:

Fat/oil is treated with iodine monochloride. The excess iodine is reacted with KI to release I_2, which is titrated with sodium thiosulphate.

Formula:

$$\text{Iodine Value} = (B - S) \times N \times 12.69 / W$$

Where:

- B = Volume of thiosulfate used in blank
- S = Volume used in sample
- N = Normality of thiosulfate
- W = Weight of sample (g)

5. Acetyl Value

- The number of mg of KOH required to neutralize acetic acid liberated from 1 gram of fat/oil after acetylation.

Significance:

- Indicates the number of hydroxyl (-OH) groups in the sample.
- Higher acetyl value = higher free hydroxyl content.

Formula:

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Acetyl Value = 56.1 × (B - A) × N / W
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Where:

- B = Volume of KOH used for acetylated sample
- A = Volume used for original fat/oil
- N = Normality of KOH
- W = Weight of sample (g)

6. Reichert–Meissl (Rm) Value

- The number of mL of 0.1 N KOH required to neutralize volatile, water-soluble fatty acids distilled from 5 g of fat/oil.

Significance:

- Useful for detecting butter adulteration.
- Butter has an RM value of 24–33.
- Most vegetable oils have RM value close to zero.

Principle:

The fat is saponified and acidified to release volatile fatty acids, which are distilled and titrated.

Formula:

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RM Value = Volume of 0.1 N KOH used / 5
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