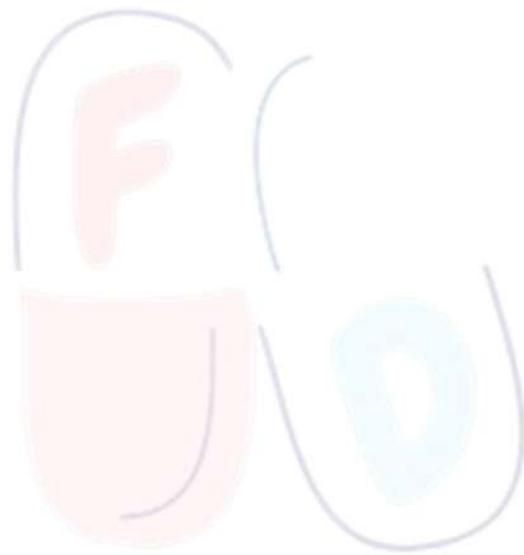


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PHARMACEUTICAL ORGANIC CHEMISTRY - II

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.

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Fats and Oils

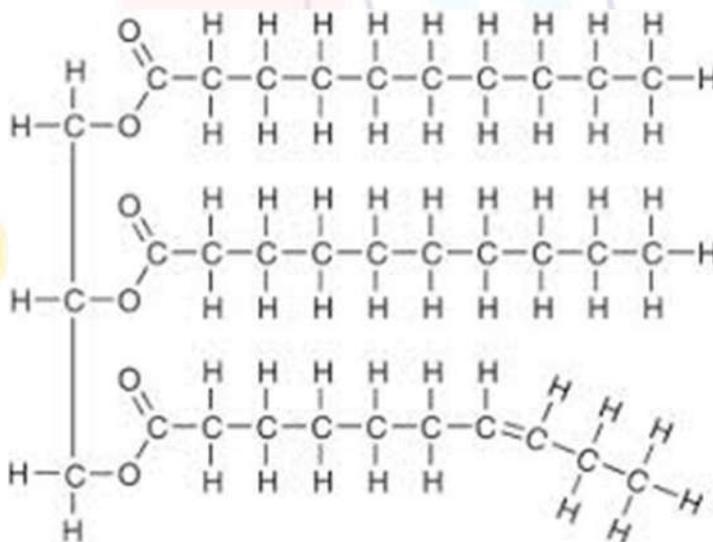
→ Fats and oils are simple lipids formed by the esterification of glycerol (a trihydric alcohol) with fatty acids.

→ 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:



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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.

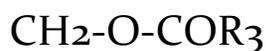
Example:



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Where R₁, R₂, R₃ = different fatty acids like oleic, palmitic, stearic, etc.

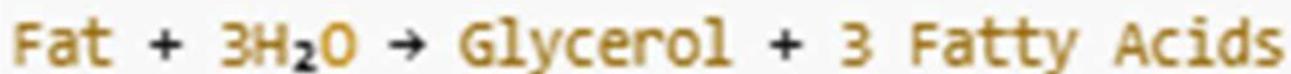
Reactions of Fats and Oils

→ 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.

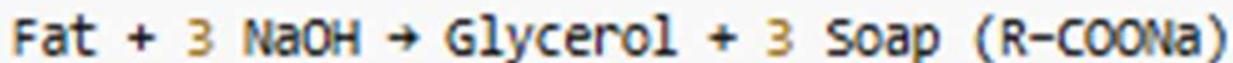
Reaction:



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:



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

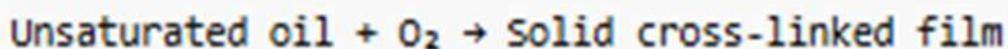
- Rancidity is the spoilage of fats and oils due to exposure to light, air (oxygen), heat, or moisture, leading to bad odor and sour taste.
- Rancid oils are inedible and unhealthy.

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.



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:

$$\text{Saponification Value} = (B - S) \times N \times 56.1 / W$$

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)

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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:

$$\text{Acetyl Value} = 56.1 \times (B - A) \times N / W$$

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)

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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:

$$\text{RM Value} = \text{Volume of } 0.1 \text{ N KOH used} / 5$$

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