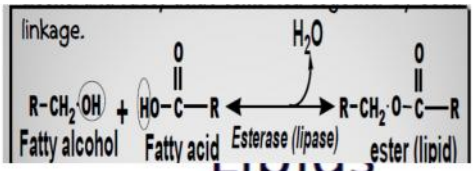
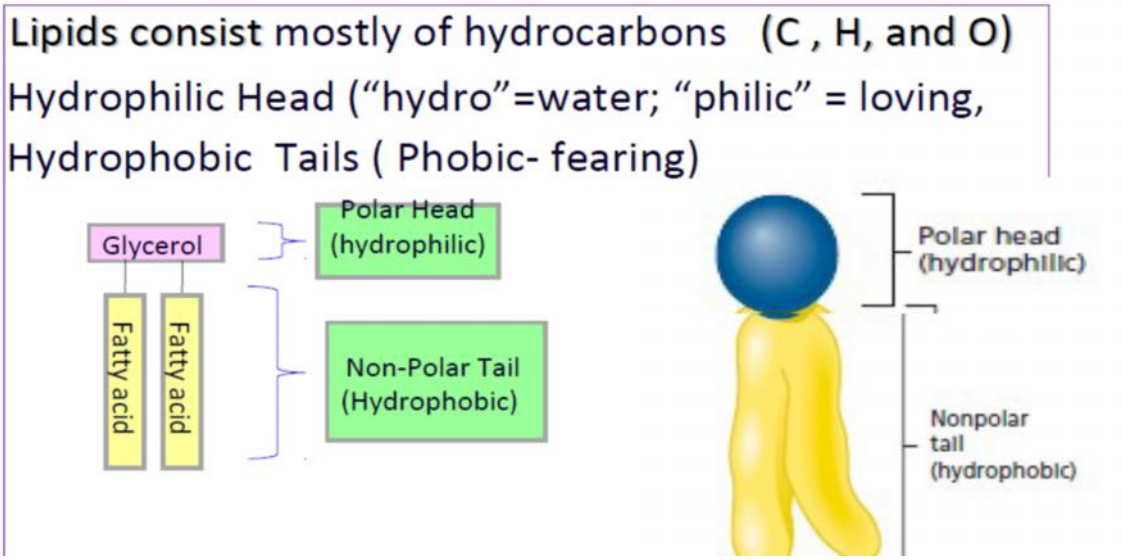
LIPIDS

Definition

Lipids are organic compounds formed mainly from alcohol and fatty acids combined together by ester linkage. Lipids are naturally occurring molecules from plants or animals that are soluble in nonpolar organic solvents





Lipids are insoluble in water, but soluble in fat or organic solvents (ether, chloroform, acetone, benzene). Lipids include oils, waxes, fats and related compounds. They are widely distributed in nature both in plants and in animals

Biological Importance of Lipids

They are more palatable and storable to unlimited amount compared to carbohydrates. They have a high-energy value (25% of body needs) and they provide more energy per gram than carbohydrates and proteins but carbohydrates are the preferable source of energy. (9, 4.4 Kcal/g). Supply the essential fatty acids that cannot be synthesized by the body. Supply the body with fat-soluble vitamins (A, D, E and K). They are important constituents of the nervous system. Tissue fat is an essential constituent of cell membrane and nervous system. It is mainly phospholipids in nature that are not affected by starvation.

Stored lipids "depot fat" is stored in all human cells acts as:

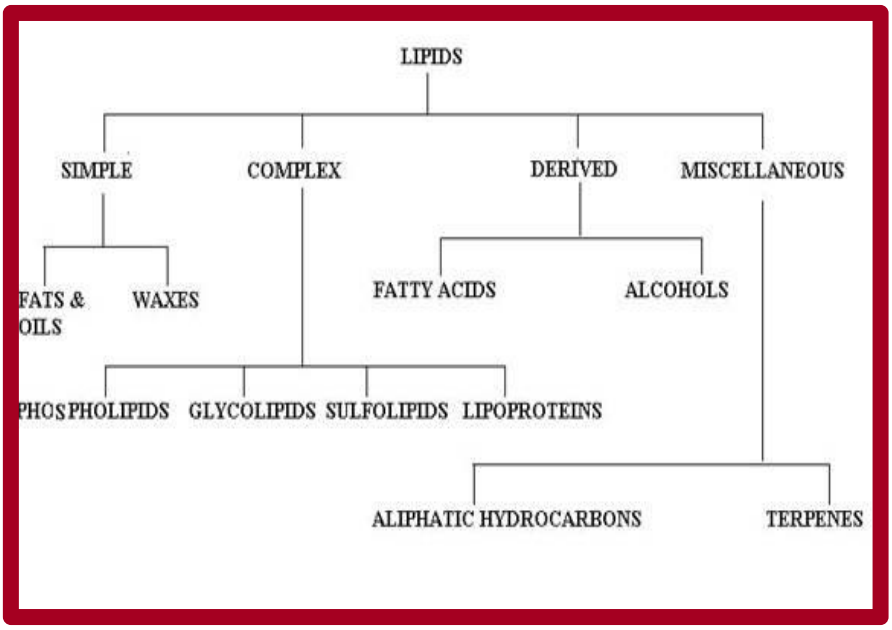
- A store of energy.
- A pad for the internal organs to protect them from outside shocks.
- A subcutaneous thermal insulator against loss of body heat.

Lipoproteins: which are complex of lipids and proteins, are important cellular constituents that present both in the cellular and subcellular membranes.

Cholesterol: enters in membrane structure and is used for synthesis of adrenal cortical hormones, vitamin D3 and bile acids.

Lipids: provide bases for dealing with diseases such as obesity, atherosclerosis, lipid-storage diseases, essential fatty acid deficiency, respiratory distress syndrome

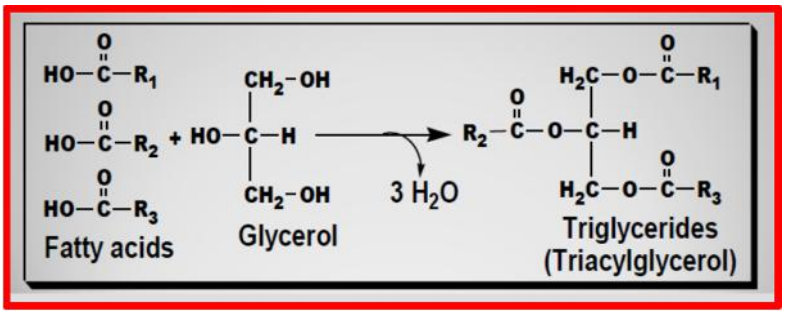
CLASSIFICATION OF LIPIDS



Simple Lipids

A) Neutral fats or oils (Triglycerides)

Esters of fatty acids with glycerol and monohydric alcohols. Depending upon the constituent alcohols they are further subdivided into fats or oils and waxes. Fats, also termed as triacylglycerol are esters of fatty acids with glycerol e.g. Plants- vegetable oils; Animals-ghee and butter. Waxes are esters of fatty acids and alcohols other than glycerol e.g., Plant wax-carnauba wax;



Types of triglycerides

a) Simple triglycerides:

If the three fatty acids connected to glycerol are of the same type, the triglyceride is called simple triglyceride

b) Mixed Triglycerides

If the three fatty acids connected to glycerol are of different type, the triglyceride is called mixed triglyceride

Natural fats are mixture of mixed triglycerides with a small amount of simple triglycerides. The commonest fatty acids in animal fats are palmitic, stearic and oleic acids. The main difference between fats and oils is for oils being liquid at room temperature, whereas, fats are solids. This is mainly due to presence of larger percentage of unsaturated fatty acids in oils than fats that has mostly saturated fatty acids

B-Waxes

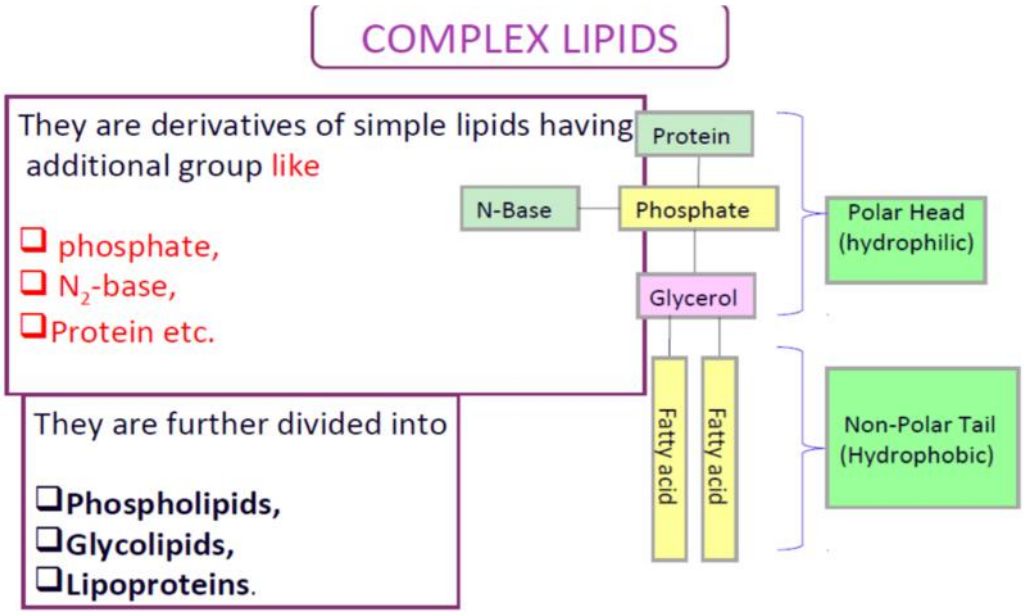
Waxes are solid simple lipids containing a monohydric alcohol (with a higher molecular weight than glycerol) esterified to long-chain fatty acids. Examples of these alcohols are palmitoyl alcohol, cholesterol, vitamin A or D. Waxes are insoluble in water, but soluble in fat solvents and are negative for Acrolein test. Waxes are not easily hydrolyzed as the fats and are indigestible by lipases and are very resistant to rancidity. Thus they are of no nutritional value

Physical properties of fat and oils

Freshly prepared fats and oils are colourless, odourless and tasteless. Any color, or taste is due to association with other foreign substances, e.g., The yellow color of body fat or milk fat is due to carotene pigments (cow milk). Fats have specific gravity less than 1(one) and, therefore, they float on water. Fats are insoluble in water, but soluble in organic solvents as ether and benzene. Melting points of fats are usually low, but higher than the solidification point,

Difference between fat and oil

Oils	fats
1.The glycerides which exist in liquid form at room temperature are known as oils.	1.The triglycerides which exist in solid form at room temperature are known as fats.
2.≥The degree of unsaturation of fatty acid residue in oil is higher.	2.The degree of unsaturation of fatty acid residue in fat is lower.
3.Oils are the triglycerides of unsaturated fatty acids.	3.Fats are the triglycerides of saturated fatty acids.



They are lipids that contain additional substances, e.g., sulfur, phosphorus, amino group, carbohydrate, or proteins beside fatty acid and alcohol.

Compound or conjugated lipids are classified into the following types according to the nature of the additional group

a) Phospholipids
b) Glycolipids.
c) Lipoproteins
d) Sulfolipids and amino lipids

A-Phospholipids

Phospholipids or phosphatides are compound lipids, which contain phosphoric acid group in their structure

Every animal and plant cell contains phospholipids. The membranes bounding cells and subcellular organelles are composed mainly of phospholipids. Important role in signal transduction across the cell membrane. They are source of polyunsaturated fatty acids for synthesis of eicosanoids.

Sources: They are found in all cells (plant and animal), milk and egg yolk in the form of lecithins.

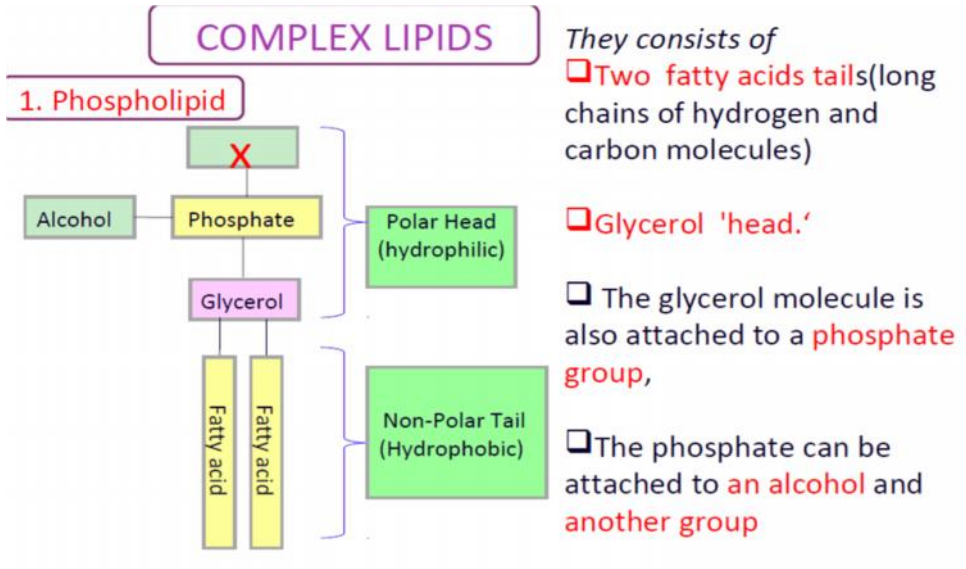
Structure: phospholipids are composed of:

Fatty acids (a saturated and an unsaturated fatty acid).

Nitrogenous base (choline, serine, threonine, or ethanolamine).

Phosphoric acid.

Fatty alcohols (glycerol, inositol or sphingosine



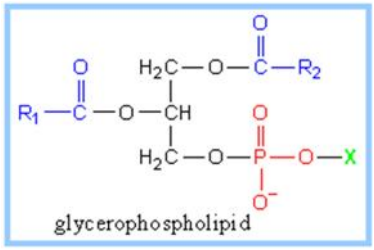
Classification of Phospholipids

Are classified into 2 groups according to the type of the alcohol present into two types

A-Glycerophospholipids: They are regarded as derivatives of phosphatidic acids that are the simplest type of phospholipids

Phosphatidic acids: those lipids which on hydrolysis give rise to one molecule of glycerol and phosphoric acid and two molecules of fatty acids

1. Lecithins
2. Cephalins.
3. Plasmalogens.
4. Inositides.
5. Cardiolipin



Lecithins

Lecithins are glycerophospholipids that contain choline as a base beside phosphatidic acid. They exist in 2 forms a- and b- lecithins. The common fatty acids in lecithins are stearic, palmitic, oleic, linoleic, linolenic, or arachidonic acids.

Cephalins

Cephalins resemble lecithins in structure except that choline is replaced by ethanolamine, serine or threonine amino acids. Certain cephalins are constituents of the complex mixture of phospholipids, cholesterol and fat that constitute the lipid component of the lipoprotein.

Inositides

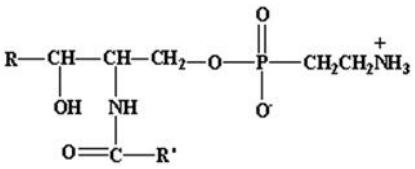
They are similar to lecithins or cephalins but they have the cyclic sugar alcohol, inositol as the base. They are formed of glycerol, one saturated fatty acid, one unsaturated fatty acid, phosphoric acid and inositol

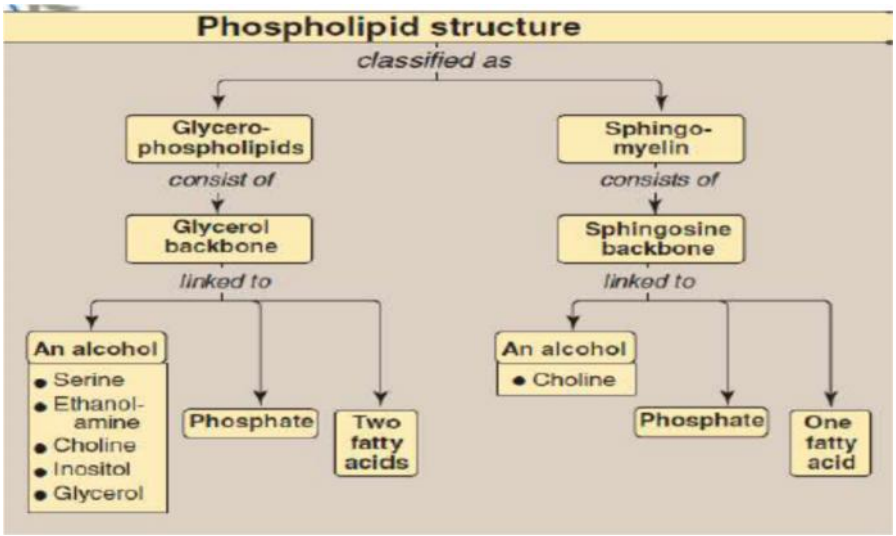
B-Sphingo phospholipids

Sphingophospholipids are found in the seeds of several plant species.

Sphingomyelins

Sphingomyelins are found in large amounts in brain and nerves and in smaller amounts in lung, spleen, kidney, liver and blood. Sphingomyelins differ from lecithins and cephalins in that they contain sphingosine as the alcohol instead of glycerol, they contain two nitrogenous bases: sphingosine itself and choline





B-Glycolipids

Glycolipids are structurally characterised by the presence of one or more monosaccharide residues and the absence of a phosphate. They are lipids that contain carbohydrate residues with sphingosine as the alcohol and a very long-chain fatty acid (24 carbon series). The monosaccharides commonly attached are D-glucose, D-galactose or N-acetyl D-galactosamine

C-Lipoproteins

.

Protein molecules associated with triacylglycerol, cholesterol or phospholipids are called lipoproteins The protein part of lipoprotein is known as apoprotein. Lipoproteins occur in milk, egg-yolk and also as components of cell membranes

Structural lipoproteins

These are widely distributed in tissues being present in cellular and subcellular membranes

Transport lipoproteins:

These are the forms present in blood plasma. They are composed of a protein called apolipoprotein and different types of lipids. (Cholesterol, cholesterol esters, phospholipids and triglycerides.

sulpholipids

Sulfolipids are a class of lipids which possess a sulfur-containing functional group. The predominant fatty acid present in sulpholipid is linolenic acid. The sulpholipid is mostly present in chloroplasts, predominantly in the membranes of thylakoid. Plant sulfolipid is found in the photosynthetic membranes of plastids and provides negative charge in the thylakoid membrane where it is thought to stabilize photosynthetic complexes

Derived lipids

They occur as such or are released from the other two major groups because of hydrolysis that is are the building blocks for simple and complex lipids

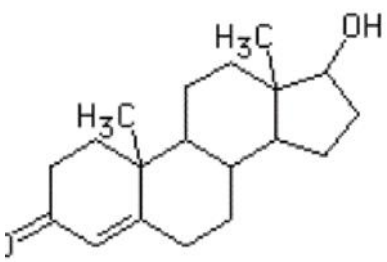
They include fatty acid and alcohol , Fatty soluble vitamin A,D, E and K, hydrocarbon and sterols.

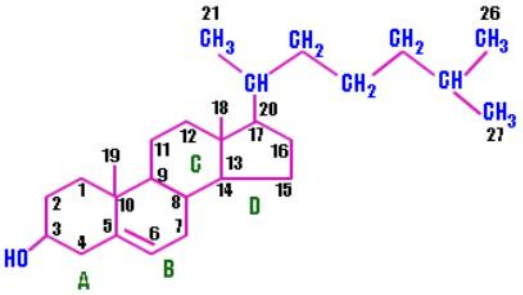
Steroids

Steroids constitute an important class of biological compounds

The steroids do not contain fatty acids but are included in lipids as they have fat like properties

Composition: Contain a characteristic arrangement of 3 Cyclohexane ring, 1 Cyclopentane ring, a total of 17-carbon atoms in four fused Carbon ring.





Classification

Sterol

- Also known as steroid alcohols
- occur naturally in plants, animals, and fungi, with the most familiar type of animal sterol being cholesterol
- TYPES:
- Phytosterols – plant sterol (campesterol, sitosterol, and stigmasterol)
- blocks cholesterol absorption sites in the human intestine, thus helping to reduce cholesterol in humans
- Zoosterol – animal sterol (cholesterol)
- Ergosterol – sterol present in the cell membrane of fungi

Examples of steroids:

I) Cholesterol:

- An important component of animal cell membrane.
- Precursor molecule of all hormones such as aldosterone, sex hormone and Vitamin D
- Aldosterone helps to regulate Na+ ions in the blood
- Sex hormones e.g. testosterones, progesterone, oestrogens help to maintain male and female characteristics

Terpenoides

- Are large and diverse class of naturally occurring organic compounds
- Terpenoides are lipid derivatives, lipid soluble & water insoluble
- Do not contain fatty acids like steroids.
- Composed of units known as isoprenoid units or isoprene units
- Isoprene unit: five carbon hydrocarbon with a branched chain structures.
- Isoprene units join together by condensation process resulting different type of compounds e.g. Carotenoides, terpenes and rubber etc

Carotenoides

- Carotenoides are yellow,orange,red or brown pigments in plants
- They are of two types
- i) Carotene: ii) xanthophylls
- i) Carotene:
- Orange, red in Colour, beta carotene is a type of carotene. Present in carrot & rice.
- The breakdown of beta carotene in human body yields two molecules of Vitamin A.
- ii) Xanthophyll: Accessory pigments
- yellow in colour found in leaves of plants.

Plant Fatty Acids

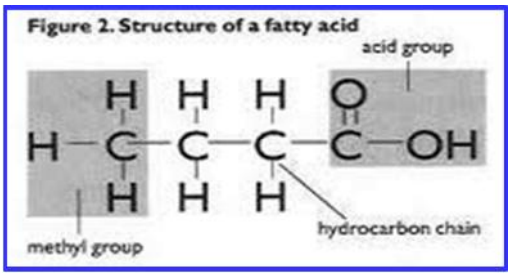
They are basic building blocks of lipids (simplest lipids). Fatty acids are carboxylic acids with a long hydrocarbon chain attached

Definition:

Aliphatic mono-carboxylic acids that are mostly obtained from the hydrolysis of natural fats and oils.

The general formula R-(CH2)n-COOH and mostly have straight chain (a few exceptions have branched and heterocyclic chains). "n" is mostly an even number of carbon atoms (2-34)

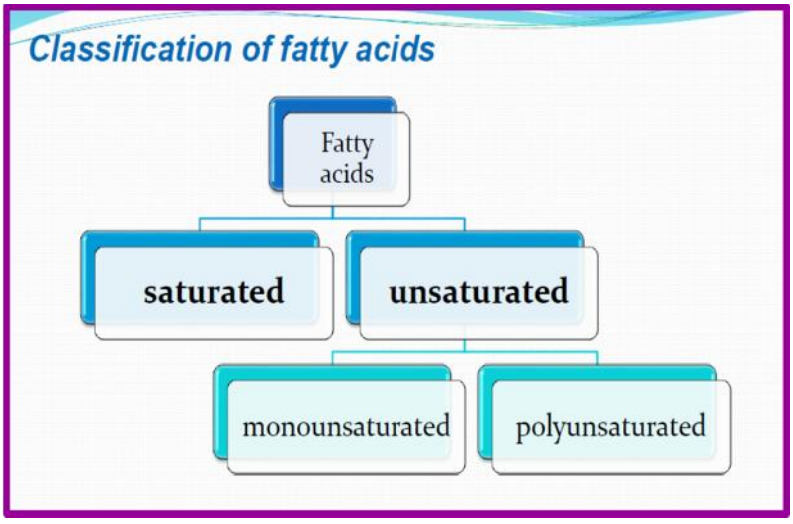
Structure of fatty acids



A fatty acid consists of a hydrophobic hydrocarbon chain with a terminal carboxyl group

All of the lipid molecules in cell membranes are amphipathic (or amphiphilic) because they have both polar (Hydrophilic) and non –polar (hydrophobic) portions in their structure

`



1-Saturated Fatty Acids

a. No double bonds with 2-24 or more carbons.
b. Solid at RT except if they are short chained.
c. May be even or odd numbered.
d. Molecular formula, CnH2n+1COOH

Saturated Fatty acids could be:

A-Short chain Saturated F.A. (2-10 carbon).

a - Short chain Saturated volatile F.A.(2-6 C).

b - Short chain Saturated non-volatile F.A.(7-10 C).

A- Saturated- short chain Volatile short -chain Fatty acids:

Liquid in nature and contain 1-6 C water-soluble volatile at room temperature

e.g., acetic, butyric, & caproic acids.

Acetic F.A. (2 C) CH_3-COOH.

Butyric F.A. (4 C) CH_3-$(CH_2)_2$-COOH.

Caproic F.A. (6C) CH_3-(CH_2)4-COOH

Non -volatile short - chain fatty acids:

Solids at room temperature, contain 7-10 carbons. Water-soluble, non-volatile at RT include caprylic and capric F.A.

Caprylic (8 C) CH_3-$(CH_2)_6$-COOH.

Capric (10 C) CH_3-$(CH_2)_8$-COOH

B - Saturated - Long -chain fatty acids:

<10 carbon atoms.

In hydrogenated oils, animal fats, butter and coconut and palm oils.

Non-volatile, Water-insoluble

E.g. palmitic, stearic, & lignoceric F.A.

- Palmitic (16 C) CH_3-$(CH_2)_{14}$-COOH
- Stearic (18 C) CH_3-$(CH_2)_{16}$-COOH
- Lignoceric (24C) CH_3-$(CH_2)_{22}$-COOH

2 **–Unsaturated Fatty Acids**

- Contain double bond

A. monounsaturated: they contain one double bond.

(CnH2n-1 COOH)

B. polyunsaturated; they contain more the one double bond

(CnH2n-# COOH).

A-Mono unsaturated fatty acids:

1-Palmitoleic acid:

It is found in all fats. It is C16:1Δ9, i.e., has 16 carbons and one double bond located at carbon number 9 and involving carbon 10.

CH_3-(CH_2)5CH = CH-(CH_2)7 –COOH

2-Oleic acid

Is the most common fatty acid in natural fats?

It is C18:1Δ9, i.e., has 18 carbons and one double bond located at carbon number 9 and involving carbon 10.

$CH_{3-(}CH_2)_7$- CH=CH – $(CH_2)_7$-COOH

B -**Poly unsaturated fatty acids**

Definition:

They are essential fatty acids that cannot be synthesized in the human body and must be taken in adequate amounts in the diet. They are required for normal growth and metabolism

Source: vegetable oils such as corn oil, linseed oil, peanut oil, olive oil, cottonseed oil, soybean oil and many other plant oils, cod liver oil and animal fats.

Deficiency: Their deficiency in the diet leads to nutrition deficiency disease.

Symptoms: poor growth and health with susceptibility to infections, dermatitis, decreased capacity to reproduce, impaired transport of lipids, fatty liver, and lowered resistance to stress.

1-Linoleic:

C18: 2D 9, 12.

It is the most important since other essential fatty acids can be synthesized from it in the body.

CH_3-$(CH_2)_4$-CH = CH-CH_2-CH= CH- $(CH_2)_7$-COOH

2-Linolenic acid:

C 18:3D 9, 12, 15,

In corn, linseed, peanut, olive, cottonseed and soybean oils.

CH_3-CH_2-CH=CH-CH_2-CH=CH-CH_2- CH=CH-$(CH_2)_7$- COOH

3-Arachidonic acid:

C20: 4D 5, 8, 11, 14.

It is an important component of phospholipids in animal and in peanut oil from which prostaglandins are synthesized.

CH_3-$(CH_2)_4$-CH=CH-CH_2-CH=CH-CH_2- CH=CH-CH_2-CH=CH-$(CH_2)_3$-COOH

Common Fatty Acids

Chemical Names and Descriptions of some Common Fatty Acids

Common Name	Carbon Atoms	Double Bonds	Scientific Name	Sources
Butyric acid	4	0	butanoic acid	butterfat
Caproic Acid	6	0	hexanoic acid	butterfat
Caprylic Acid	8	0	octanoic acid	coconut oil
Capric Acid	10	0	decanoic acid	coconut oil
Lauric Acid	12	0	dodecanoic acid	coconut oil
Myristic Acid	14	0	tetradecanoic acid	palm kernel oil
Palmitic Acid	16	0	hexadecanoic acid	palm oil
Palmitoleic Acid	16	1	9-hexadecenoic acid	animal fats
Stearic Acid	18	0	octadecanoic acid	animal fats
Oleic Acid	18	1	9-octadecenoic acid	olive oil

Chemical Names and Descriptions of some Common Fatty Acids

Common Name	Carbon Atoms	Double Bonds	Scientific Name	Sources
Ricinoleic acid	18	1	12-hydroxy-9-octadecenoic acid	castor oil
Vaccenic Acid	18	1	11-octadecenoic acid	butterfat
Linoleic Acid	18	2	9,12-octadecadienoic acid	grape seed oil
Alpha-Linolenic Acid (ALA)	18	3	9,12,15-octadecatrienoic acid	flaxseed (linseed) oil
Gamma-Linolenic Acid (GLA)	18	3	6,9,12-octadecatrienoic acid	borage oil
Arachidic Acid	20	0	eicosanoic acid	peanut oil, fish oil
Gadoleic Acid	20	1	9-eicosenoic acid	fish oil
Arachidonic Acid (AA)	20	4	5,8,11,14-eicosatetraenoic acid	liver fats
EPA	20	5	5,8,11,14,17-eicosapentaenoic acid	fish oil
Behenic acid	22	0	docosanoic acid	rapeseed oil
Erucic acid	22	1	13-docosenoic acid	rapeseed oil
DHA	22	6	4,7,10,13,16,19-docosahexaenoic acid	fish oil
Lignoceric acid	24	0	tetracosanoic acid	small amounts in most fats

Unusual fatty acids

The unusual fatty acids are found only in few individual species or genus or a whole family.

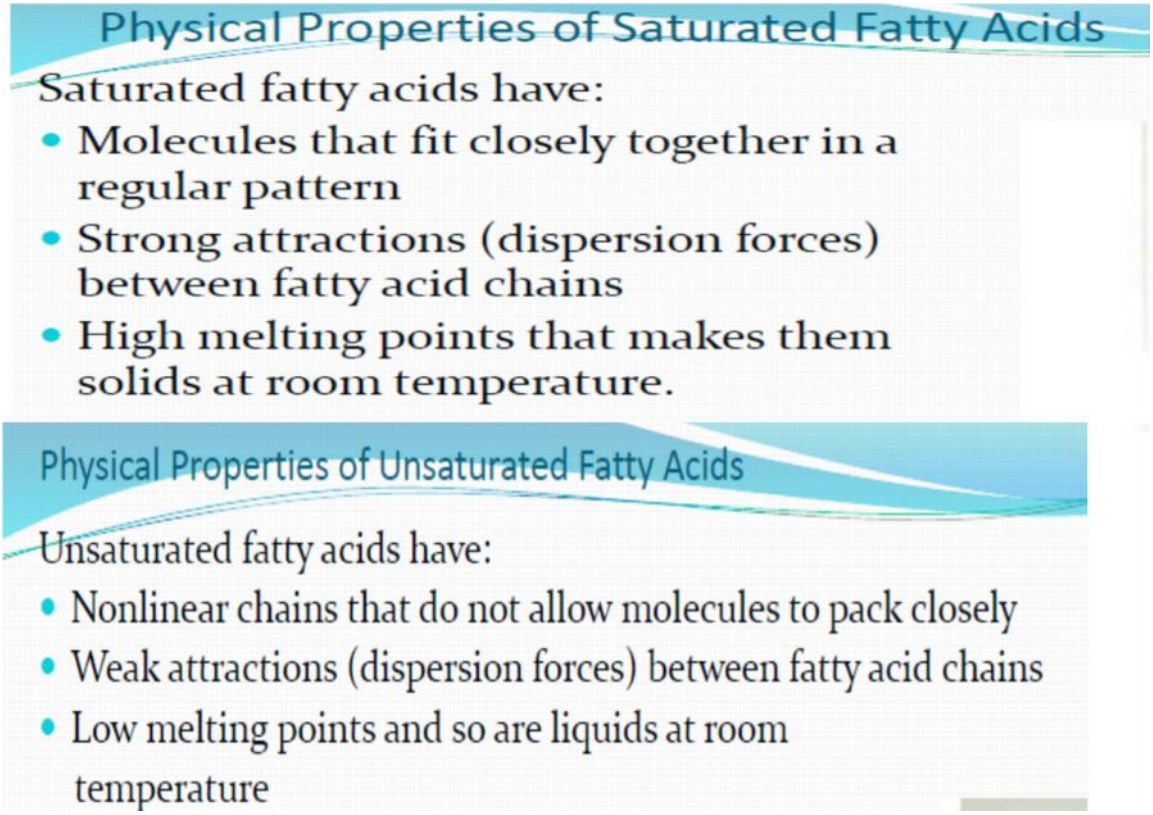
Castor bean (Ricinus communis) seed oil isrich in ricinoleic acid (90%) which is 12-hydroxy oleic acid $CH_3(CH_2)_5$-CH(OH)-CH_2-CH=CH-$(CH_2)_7$-COOH.

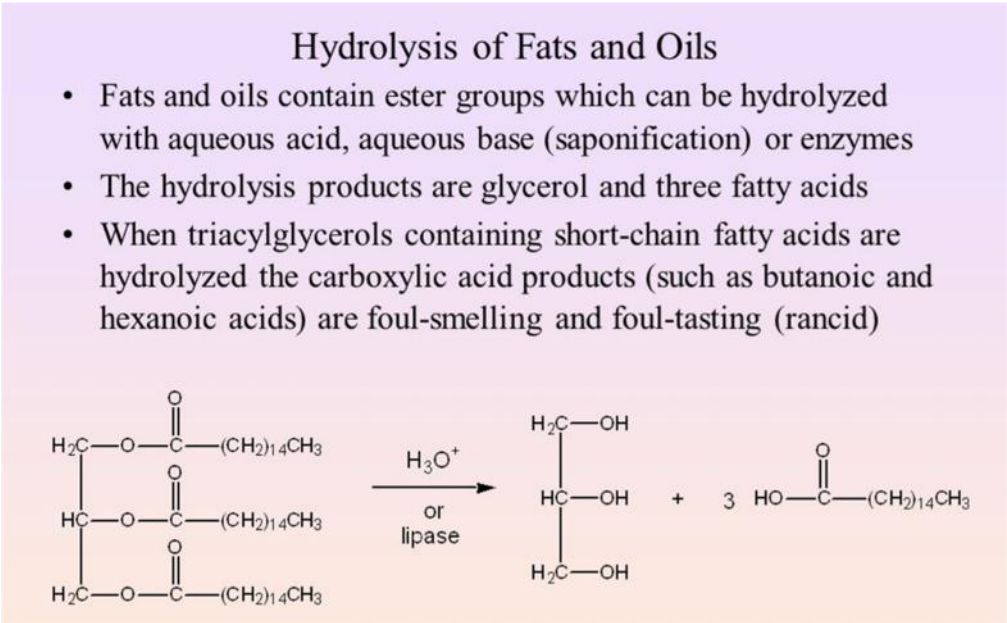
Rape seed (Brassica napus) is rich in Erucic acid

(cis-13- docosenoic acid)

$CH_3(CH_2)_7$-CH=CH-$(CH_2)_{11}$-COOH).

Hydnocarpic and chaulmoogricacids are found in chaulmoogra oil which is used in the treatment of leprosy

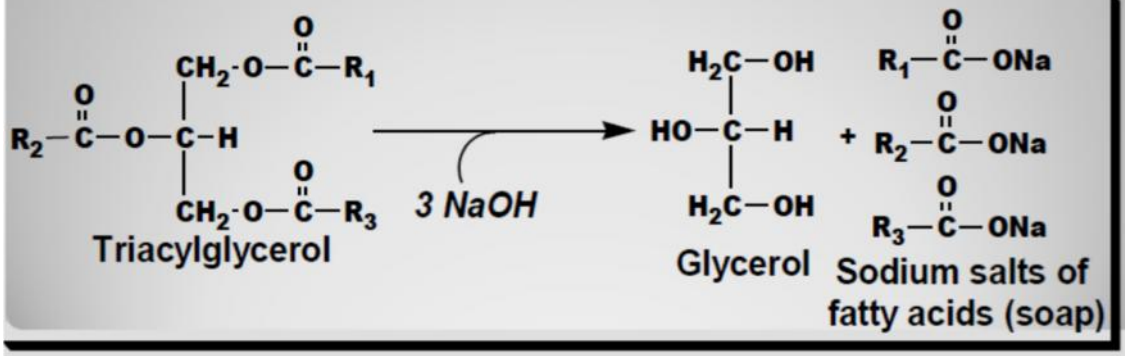




2 -Saponification.

>Alkaline hydrolysis produces glycerol and salts of fatty acids (soaps).

- Soaps cause emulsification of oily material this help easy washing of the fatty materials

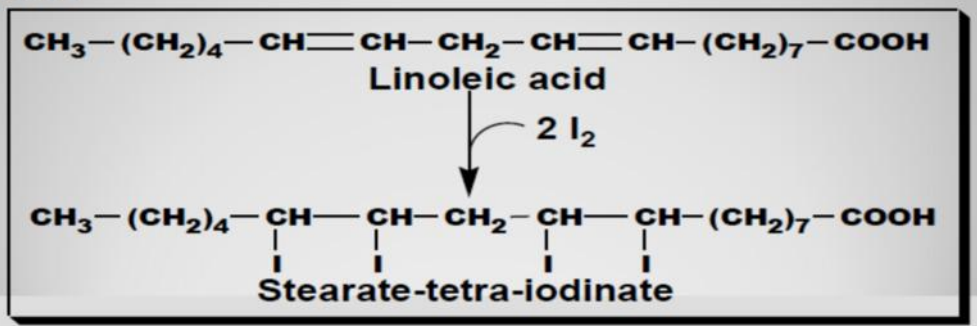


The alkali salt of fatty acid resulting from saponification is soap.

- The soaps we use for washing consists of Na or K salts of fatty acids like palmitic, stearic and oleic acid.
- The potassium soaps are soft and soluble whereas the sodium soaps are hard and less soluble in water

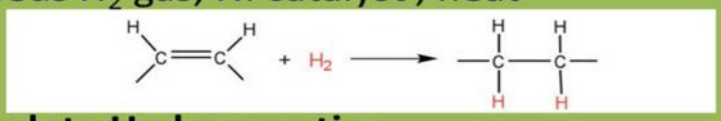
3 -Halogenation

- Neutral fats containing unsaturated fatty acids have the ability of adding halogens (e.g., hydrogen or hydrogenation and iodine or iodination) at the double bonds.
- very important property to determine the degree of unsaturation of the fat or oil that determines its biological value



1. Hydrogenation of Oils

- Industrial process to convert liquid oils into **solid fats**
- Chemical Rx that converts double (cis) bonds into single bonds
- needs H_2 gas, Ni catalyst , heat



Complete Hydrogenation

- All double bonds become single bonds

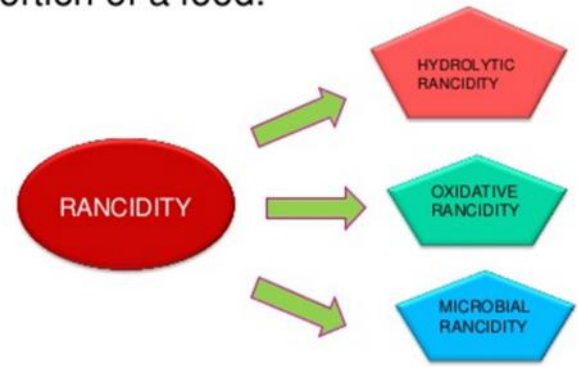
Incomplete/Partial Hydrogenation

- Some (cis) double bonds remain
- Some (cis) double bonds convert to **trans** bonds: forming **Trans Fats**

The degree of unsaturation of the fatty acids present in triacylglycerol determines whether a fat is liquid or solid at room temperature. The presence of more unsaturated fatty acids lower the melting point. The presence of highly unsaturated fatty acids makes the oil more susceptible to oxidative deterioration. The objective of hydrogenation is to reduce the degree of unsaturation and to increase the melting point of the oil. The oil can be selectively hydrogenated by careful choice of catalyst and temperature. Hydrogenation of unsaturated fats in the presence of a catalyst is known as hardening.

What is Rancidity?

Rancidity is a term generally used to denote a condition of unpleasant odours and flavours in foods resulting from deterioration in the fat or oil portion of a food.



Saturated fats resist rancidity more than unsaturated fats that have unsaturated double bonds.

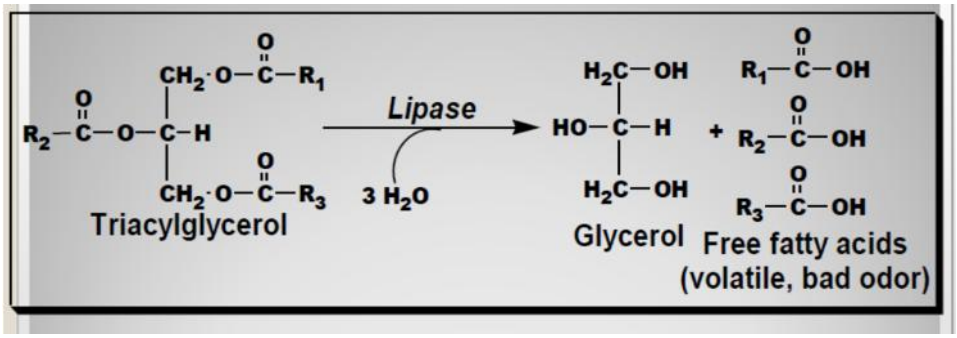
Definition

Physico-chemical change development of unpleasant odor or taste or abnormal color particularly on aging exposure to atmospheric oxygen, light, moisture, bacterial or fungal contamination and/or heat.

1-Hydrolytic rancidity:

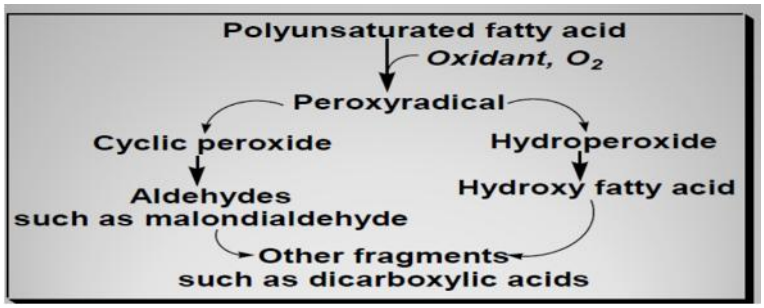
From slight hydrolysis of the fat by lipase. Bacterial contamination leading to the liberation of free fatty acids and glycerol at high temp and moisture .Volatile short-chain fatty acids have unpleasant odor. Caused by the breaking down of a lipid into its component fatty acids and glycerol. C-O-CO-R + H2O → C-O-H + HO-CO-R

The water present in the food and the high temperature will increase the rate of hydrolysis to fatty acids



2-Oxidative Rancidity

Oxidation of fat or oil by exposure to oxygen, light and/or heat producing peroxide derivatives e.g., peroxides, aldehydes, ketones and dicarboxylic acids that are toxic and have bad odor. due to oxidative addition of oxygen at the unsaturated double bond of unsaturated fatty acid of oils.



3-Ketonic Rancidity:

- It is due to the contamination with certain fungi such as Asperigillus Niger on fats such as coconut oil.
- Ketones, fatty aldehydes, short chain fatty acids and fatty alcohols are formed.
- Moisture accelerates ketonic rancidity.

- **Prevention of rancidity is achieved by:**

1. Avoidance of the causes (**exposure to light, oxygen, moisture, high temperature and bacteria or fungal contamination**). By keeping fats or oils in well-closed containers in cold, dark and dry place (i.e., **good storage conditions).**
2. Removal of catalysts such as lead and copper that catalyze rancidity.
3. Addition of **anti-oxidants** to prevent peroxidation in fat (i.e., rancidity). They include phenols, naphthols, tannins and hydroquinones. **The most common natural antioxidant is vitamin E that is important *in vitro* and *in vivo*.**