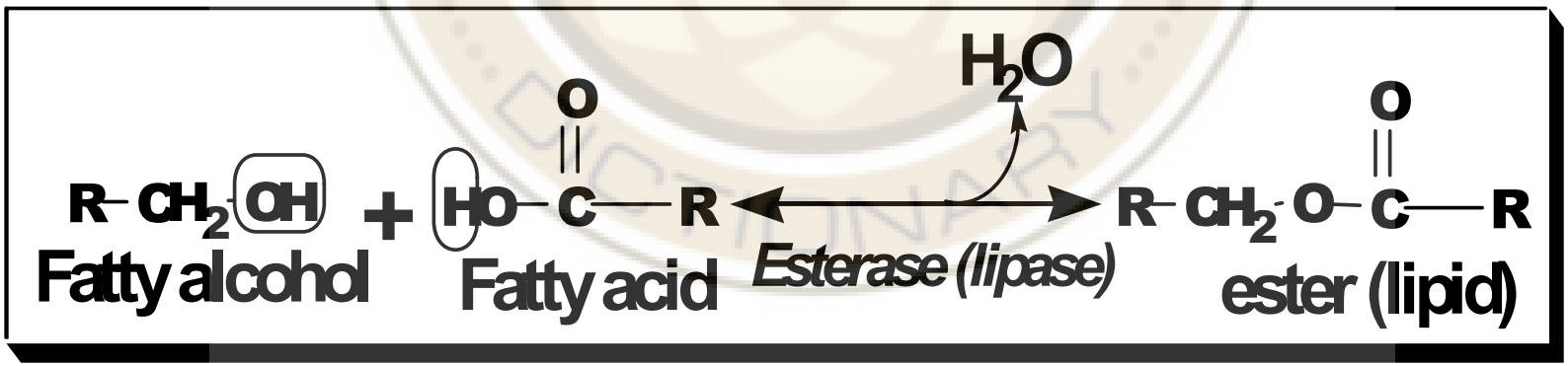
Chemistry of Lipids

Definition:

- **- Lipids are organic compounds formed mainly from alcohol and fatty acids combined together by ester linkage.**



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

Biological Importance of Lipids:

1. They are more palatable and storable to unlimited amount compared to carbohydrates.
2. 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.
3. Supply the essential fatty acids that cannot be synthesized by the body.
4. Supply the body with fat-soluble vitamins (A, D, E and K).
5. They are important constituents of the nervous system.
6. Tissue fat is an essential constituent of cell membrane and nervous system. It is mainly phospholipids in nature that are not affected by starvation.

7-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.

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

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

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

Classification of Lipids

1. Simple lipids (Fats & Waxes)
2. Compound or conjugated lipids
3. Derived Lipids
4. Lipid-associating substances

COSMETICS INCI-DIC DICTIONARY

Fatty alcohols

1-Glycerol:

- It is a trihydric alcohol (i.e., containing three OH groups) and has the popular name glycerin.
- It is synthesized in the body from glucose.
- It has the following properties:

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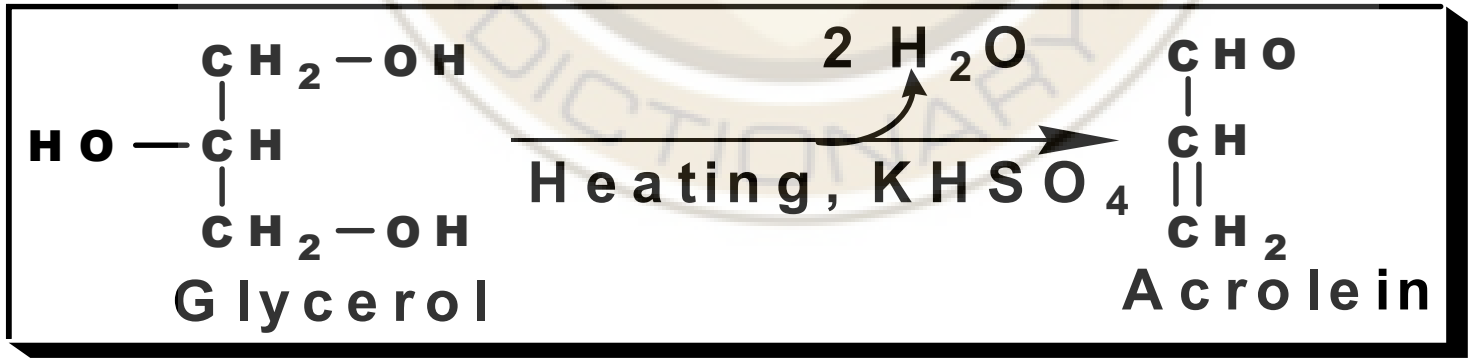
1. Colorless viscous oily liquid with sweet taste.
2. On heating with sulfuric acid or KHSO4 (dehydration) it gives acrolein that has a bad odor. This reaction is used for detection of free glycerol or any compound containing glycerol.



3-It combines with three molecules of nitric acid to form trinitroglycerin (TNT) that is used as explosive and vasodilator.

4-On esterification with fatty acids it gives:

- Monoglyceride or monoacyl-glycerol: one fatty acid + glycerol.
- Diglyceride or diacyl-glycerol: two fatty acids + glycerol.
- Triglyceride or triacyl-glycerol: three fatty acids + glycerol.

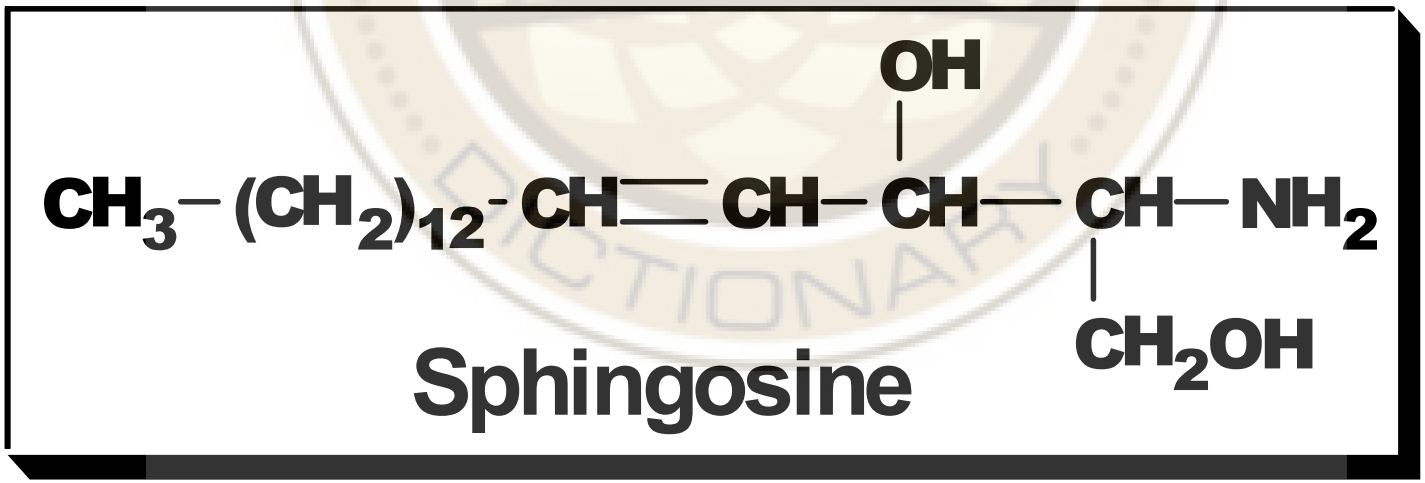
5-It has a nutritive value by conversion into glucose and enters in structure of phospholipids.

Uses of Glycerol:

1. Glycerol enters in pharmaceutical and cosmetic preparations.
2. Reduces brain edema in cerebrovascular disease.
3. Nitroglycerin is used as vasodilator especially for the coronary arteries, thus it is used in treatment of angina pectoris. Also, enters in explosives manufacturing.
4. Glycerol is used in treatment of glaucoma (increased intraocular pressure)due to its ability to dehydrate the tissue from its water content.

2-Sphingosine:

- - It is the alcohol(monohydric) present in sphingolipids.
- - It is synthesized in the body from serine and palmitic acid.
- It is not positive with acrolein test.



Sphingosine

Fatty Acids

Definition:

- **Fatty acids are aliphatic mono-carboxylic acids that are mostly obtained from the hydrolysis of natural fats and oils.**
- **Have the general formula $R\text{-}(CH_2)_n\text{-}COOH$ and mostly have straight chain (a few exceptions have branched and heterocyclic chains). In this formula "n" is mostly an even number of carbon atoms (2-34) with a few exceptions that have an odd number.**
- **Fatty acids are classified according to several bases as follows:**

I. According to presence or absence of double bonds they are classified into:

- **A-Saturated Fatty Acids**
- **they contain no double bonds with 2-24 or more carbons.**
- **They are solid at room temperature except if they are short chained.**
- **They may be even or odd numbered.**
- **They have the following molecular formula, $C_nH_{2n+1}COOH$.**

Saturated fatty acids (no double)

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

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

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

B-Long chain Saturated F.A.(more the10 carbon)

a-Volatile short-chain fatty acids:

- They are liquid in nature and contain (1-6) carbon atoms.
- water-soluble and volatile at room temperature, e.g., acetic, butyric, and caproic acids.
- Acetic F.A. (2C) CH_3-COOH.
- Butyric F.A. (4C) CH_3-$(CH_2)_2$-COOH.
- Caproic F.A. (6C) CH_3-$(CH_2)_4$-COOH.

b-Non-volatile short-chain fatty acids:

- They are solids at room temperature and contain 7-10 carbon atoms.
- They are water-soluble and non-volatile at room temperature 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-Long-chain fatty acids:

- They contain more than 10 carbon atoms.
- They occur in hydrogenated oils, animal fats, butter and coconut and palm oils.
- They are non-volatile and water-insoluble
- Include palmitic, stearic, and lignoceric F.A.

- palmitic(16C) $CH_3-(CH_2)_{14}-COOH$
- stearic (18 C) $CH_3-(CH_2)_{16}-COOH$
- lignoceric (24C) $CH_3-(CH_2)_{22}-COOH$

B-Unsaturated Fatty Acids

They contain double bond

- **monounsaturated**

they contain one double bonds .

(C_nH_{2n-1} COOH)

- **polyunsaturated**

they contain more the one double bond (C_nH_{2n- more than 1 COOH).

1-Monounsaturated 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.**

$$CH_3\text{-}(\ CH_2\ )_5CH\ =CH\text{-}(CH_2)_7\text{–}COOH$$

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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.**

$$CH_3\text{-}(CH_2)_7\text{-}\ CH{=}CH\ -\ (CH_2)_7\text{-}COOH$$

3-Nervonic acid

(Unsaturated lignoceric acid).

- **It is found in cerebrosides.**
- **It is C24:1Δ15, i.e., has 24 carbons and one double bond located at carbon number 15 and involving carbon 16.**

$$CH_3 - (CH_2)_7\ CH = CH - (CH_2)_{13}\text{-}\ COOH$$

2-Polyunsaturated fatty acids :

(Essential fatty acids):

- **Definition:**
- **They are essential fatty acids that can not 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.
- Its symptoms include: poor growth and health with susceptibility to infections, dermatitis, decreased capacity to reproduce, impaired transport of lipids, fatty liver, and lowered resistance to stress.

- **Function of Essential Fatty Acids:**

1. They are useful in the treatment of atherosclerosis by help transporting blood cholesterol and lowering it and transporting triglycerides.
2. The hormones are synthesized from them.
3. They enter in structure of all cellular and subcellular membranes and the transporting plasma phospholipids.
4. They are essential for skin integrity, normal growth and reproduction.
5. They have an important role in blood clotting (intrinsic factor).
6. Important in preventing and treating fatty liver.
7. Important role in health of the retina and vision.
8. They can be oxidized for energy production.

1-Linoleic:

- **C18:2Δ9, 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:

- **C18:3Δ9, 12, 15,**
- **in corn, linseed, peanut, olive, cottonseed and soybean oils.**

$$CH_3\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}(CH_2)_7\text{-}COOH$$

3-Arachidonic acid:

- **C20:4Δ5, 8, 11, 14.**
- **It is an important component of phospholipids in animal and in peanut oil from which prostaglandins are synthesized.**

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

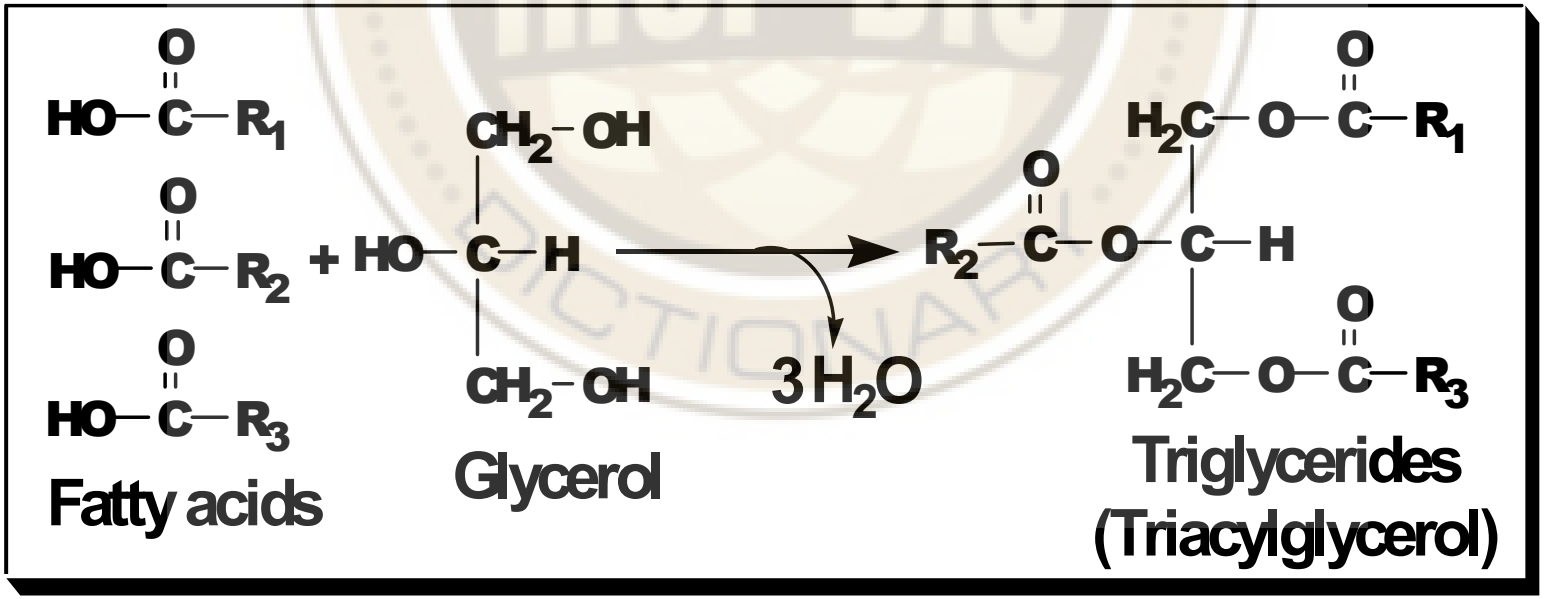
1-Simple Lipids

A-Neutral Fats and oils (Triglycerides)

Definition:

- **- They are called neutral because they are uncharged due to absence of ionizable groups in it.**
- **The neutral fats are the most abundant lipids in nature. They constitute about 98% of the lipids of adipose tissue, 30% of plasma or liver lipids, less than 10% of erythrocyte lipids.**

- They are esters of glycerol with various fatty acids. Since the 3 hydroxyl groups of glycerol are esterified, the neutral fats are also called "Triglycerides".
- Esterification of glycerol with one molecule of fatty acid gives monoglyceride, and that with 2 molecules gives diglyceride.

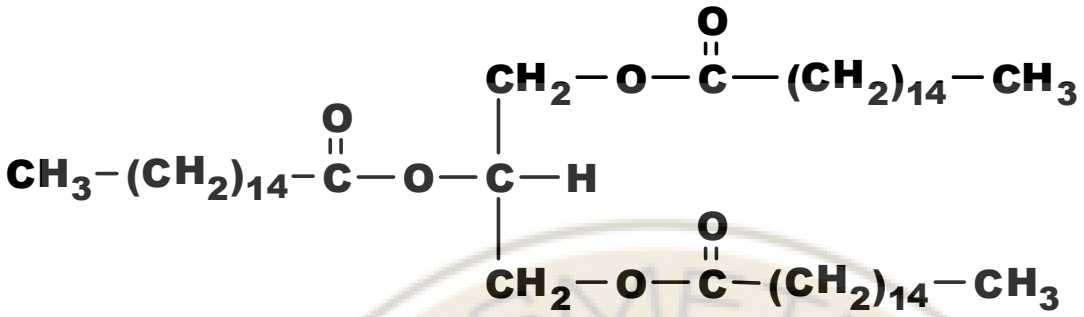


Types of triglycerides

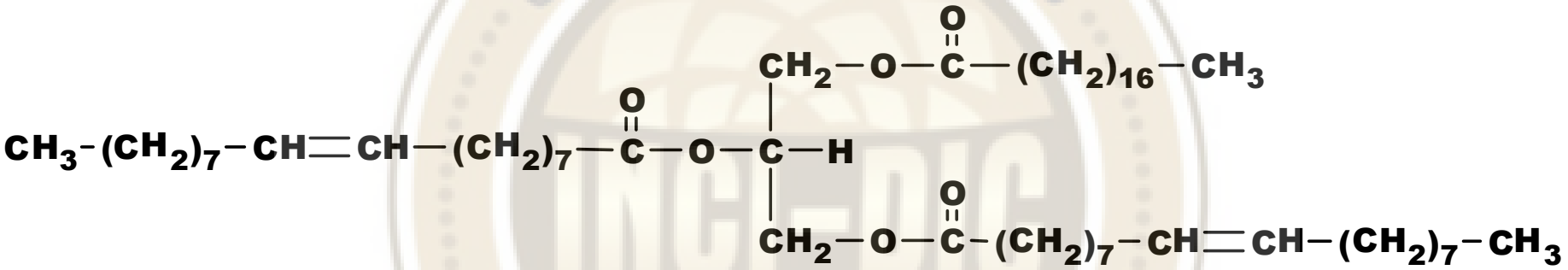
1-Simple triglycerides: If the three fatty acids connected to glycerol are of the same type the triglyceride is called simple triglyceride, e.g., tripalmitin.

2-Mixed triglycerides: if they are of different types, it is called mixed triglycerides, e.g., stearo-diolein and palmito-oleo-stearin.

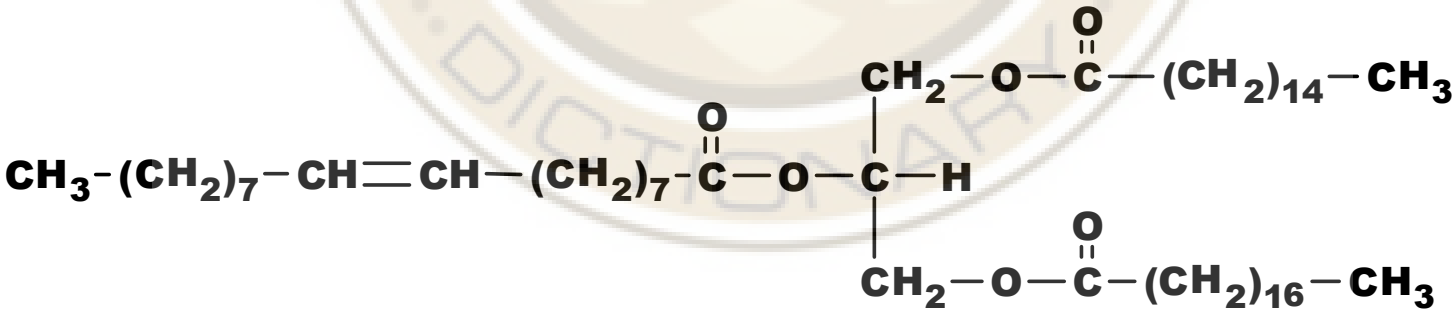
- **Natural fats are mixtures of mixed triglycerides with a small amount of simple triglycerides.**



Tripalmitin
(simple triacylglycerol)



1-Stearo-2,3-diolein
(mixed triacylglycerol)



1-palmito-2-oleo-3-stearin
(mixed triacylglycerol)

- 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.

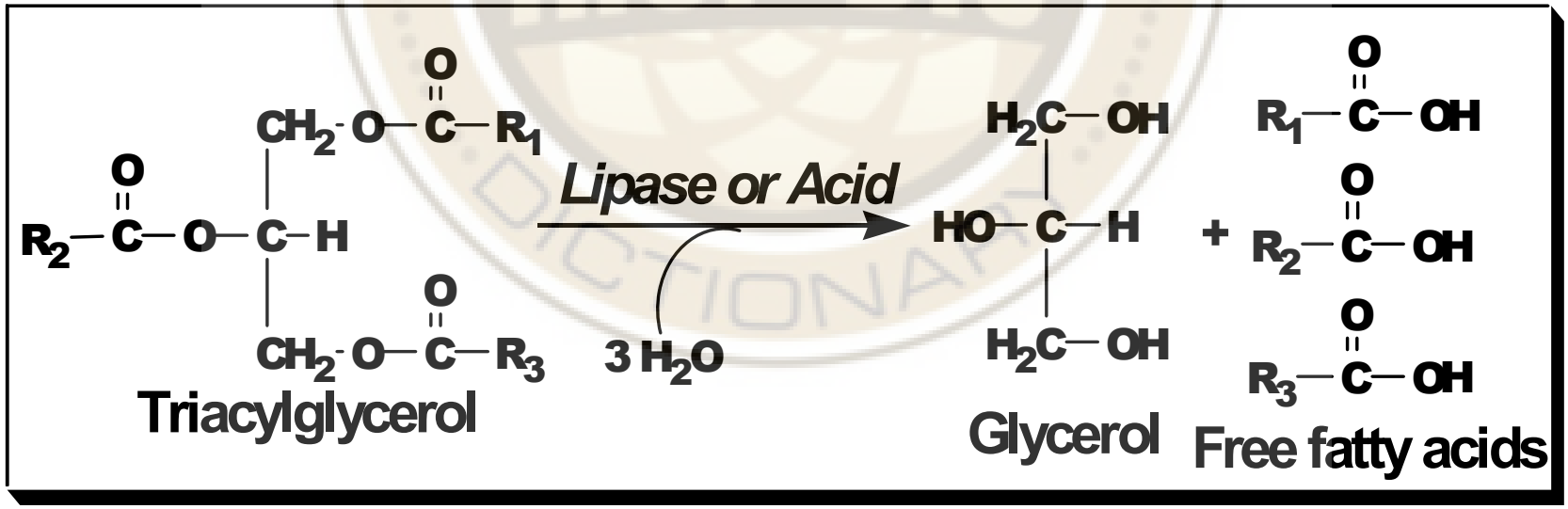
Physical properties of fat and oils:

1. Freshly prepared fats and oils are colorless, odorless 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).
2. Fats have specific gravity less than 1 and, therefore, they float on water.
3. Fats are insoluble in water, but soluble in organic solvents as ether and benzene.
4. Melting points of fats are usually low, but higher than the solidification point,

Chemical Properties of fats and oils:

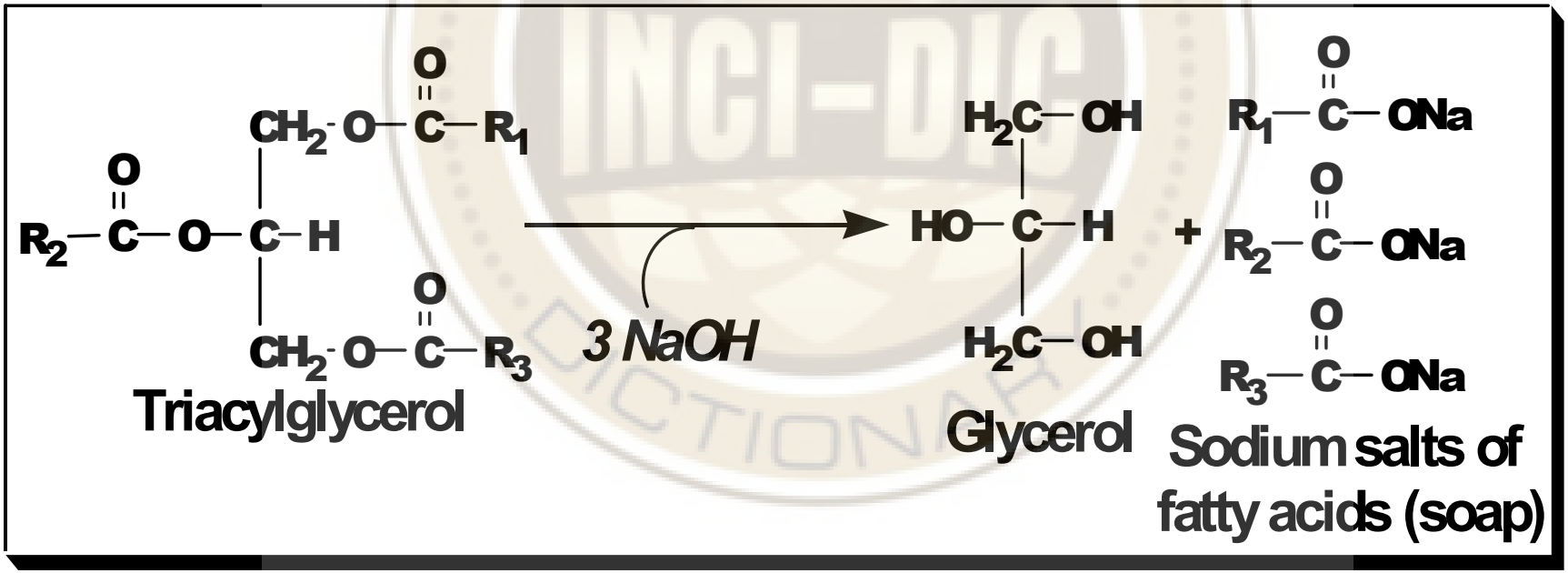
1-Hydrolysis:

- They are hydrolyzed into their constituents (fatty acids and glycerol) by the action of super heated steam, acid, alkali or enzyme (e.g., lipase of pancreas).
- - During their enzymatic and acid hydrolysis glycerol and free fatty acids are produced.



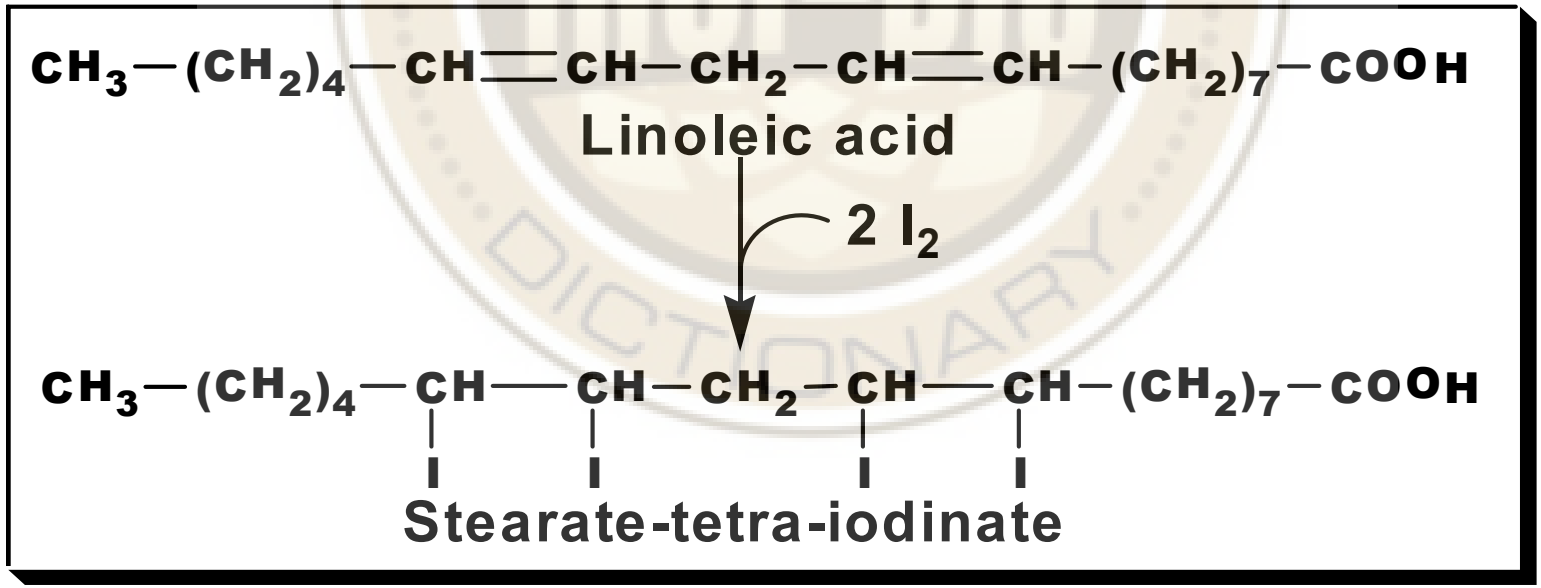
2-Saponification. Alkaline hydrolysis produces glycerol and salts of fatty acids (soaps).

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



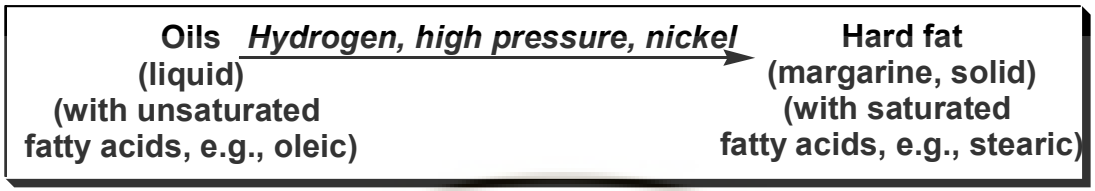
3-Halogenation

- **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.**
- **- It is a very important property to determine the degree of unsaturation of the fat or oil that determines its biological value**



4-Hydrogenation or hardening of oils:

- **It is a type of addition reactions accepting hydrogen at the double bonds of unsaturated fatty acids.**
- **The hydrogenation is done under high pressure of hydrogen and is catalyzed by finely divided nickel or copper and heat.**
- **It is the base of hardening of oils (margarine manufacturing), e.g., change of oleic acid of fats (liquid) into stearic acid (solid).**
- **It is advisable not to saturate all double bonds; otherwise margarine produced will be very hard, of very low biological value and difficult to digest.**



Advantages for hydrogenated oil or fat are as follows:

1. **It is more pleasant as cooking fat.**
2. **It is digestible and utilizable as normal animal fats and oils.**
3. **It is less liable to cause gastric or intestinal irritation.**
4. **It is easily stored and transported and less liable to rancidity.**

Disadvantages of hydrogenated

- **fats include lack of fat-soluble vitamins (A, D, E and K) and essential fatty acids**

5-Oxidation(Rancidty)

- This toxic reaction of triglycerides leads to unpleasant odour or taste of oils and fats developing after oxidation by oxygen of air, bacteria, or moisture.
- Also this is the base of the drying oils after exposure to atmospheric oxygen.

Example is linseed oil, which is used in paints and varnishes manufacturing

Rancidity

Definition:

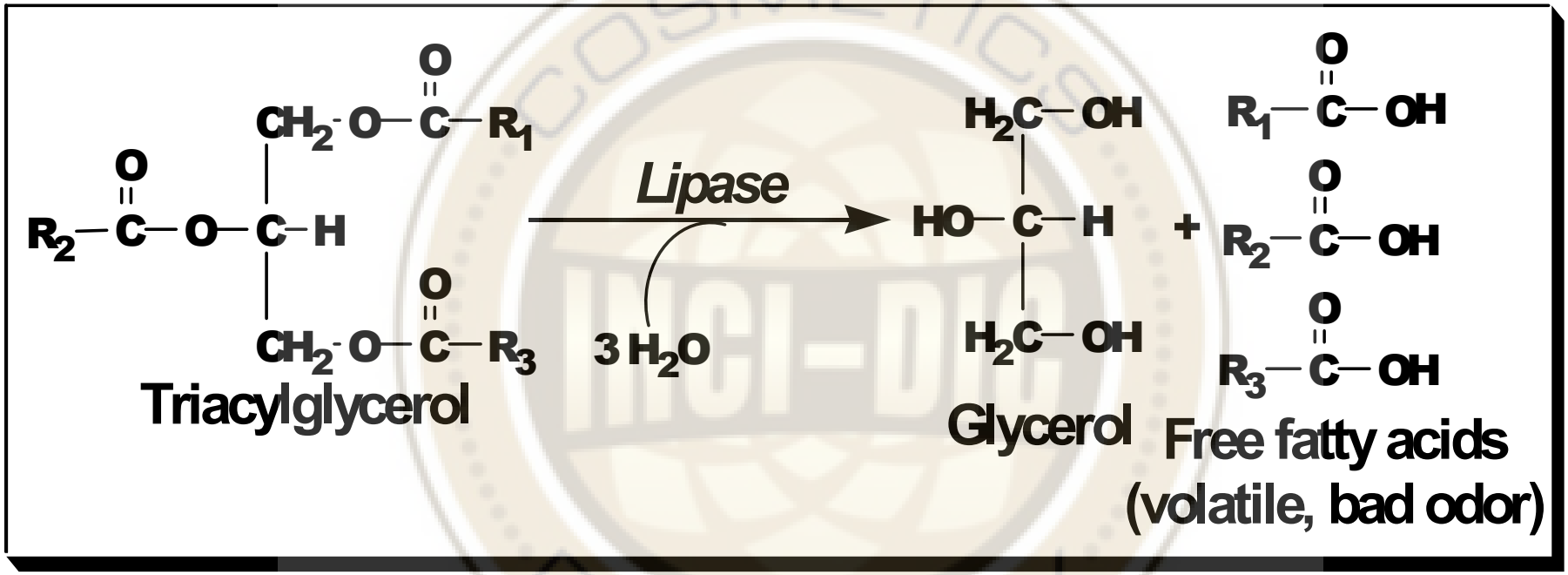
- It is a physico-chemical change in the natural properties of the fat leading to the development of unpleasant odor or taste or abnormal color particularly on aging after exposure to atmospheric oxygen, light, moisture, bacterial or fungal contamination and/or heat.
- Saturated fats resist rancidity more than unsaturated fats that have unsaturated double bonds.

Types and causes of Rancidity:

1. Hydrolytic rancidity
2. Oxidative rancidity
3. Ketonic rancidity

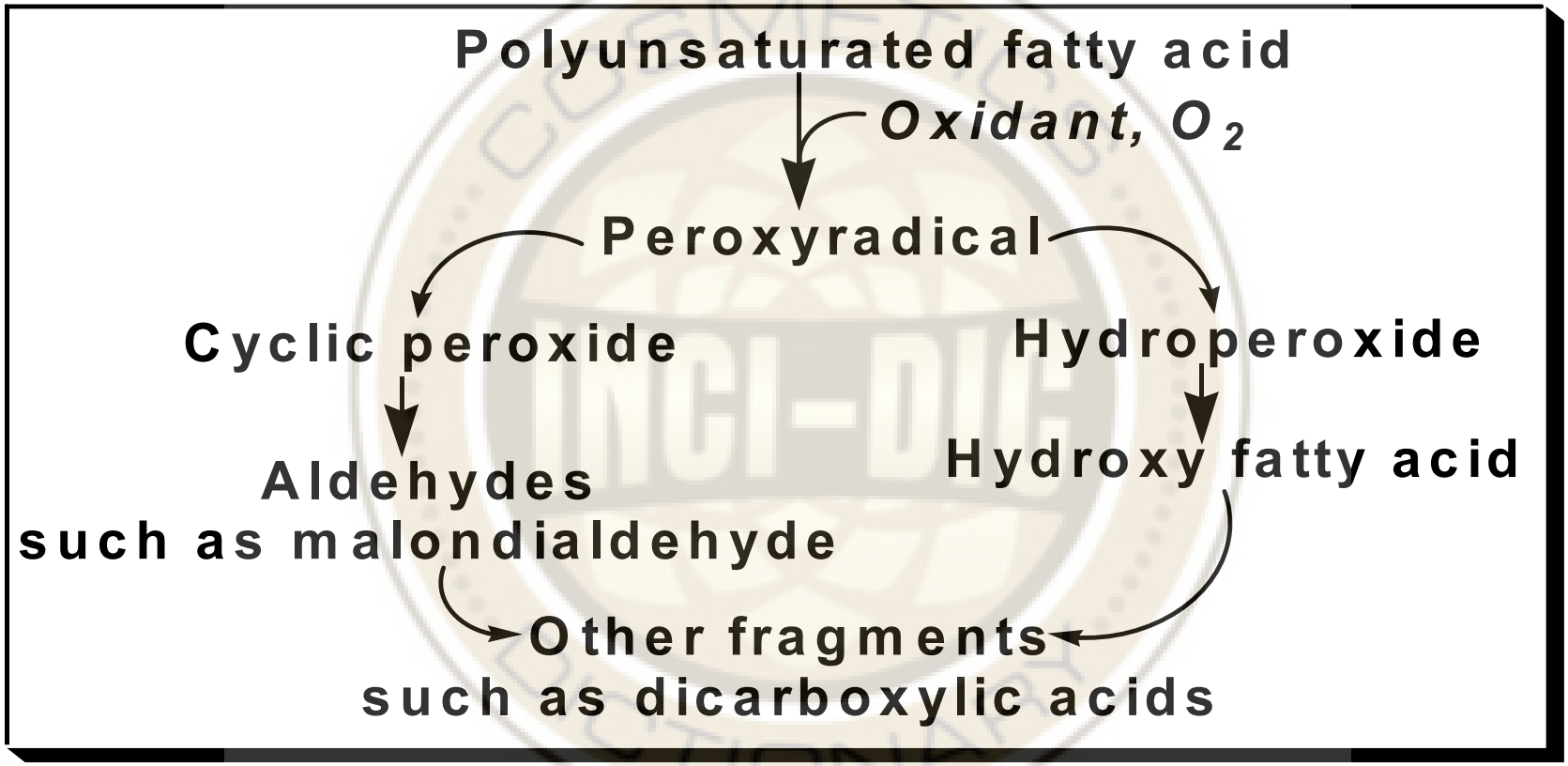
1-Hydrolytic rancidity:

- It results from slight hydrolysis of the fat by lipase from bacterial contamination leading to the liberation of free fatty acids and glycerol at high temperature and moisture.
- Volatile short-chain fatty acids have unpleasant odor.


Lipase
3 H2O
Triacylglycerol
Glycerol
Free fatty acids
(volatile, bad odor)

2-Oxidative Rancidity:

- It is oxidation of fat or oil catalyzed by exposure to oxygen, light and/or heat producing peroxide derivatives which on decomposition give substances, e.g., peroxides, aldehydes, ketones and dicarboxylic acids that are toxic and have bad odor.
- This occurs due to oxidative addition of oxygen at the unsaturated double bond of unsaturated fatty acid of oils.


Polyunsaturated fatty acid
Oxidant, O_2
Peroxyradical
Cyclic peroxide
Hydroperoxide
Aldehydes
such as malondialdehyde
Hydroxy fatty acid
Other fragments
such as dicarboxylic acids

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*.

Hazards of Rancid Fats:

1. The products of rancidity are toxic, i.e., causes food poisoning and cancer.
2. Rancidity destroys the fat-soluble vitamins (vitamins A, D, K and E).
3. Rancidity destroys the polyunsaturated essential fatty acids.
4. Rancidity causes economical loss because rancid fat is inedible.

Analysis and Identification of fats and oils

(Fat Constants)

- **Fat constants or numbers are tests used for:**

1. **Checking the purity of fat for detection of adulteration.**
2. **To quantitatively estimate certain properties of fat.**
3. **To identify the biological value and natural characteristics of fat.**
4. **Detection of fat rancidity and presence of toxic hydroxy fatty acids.**

1-Iodine number (or value):

- Definition: **It is the number of grams of iodine absorbed by 100 grams of fat or oil.**
- Uses: **It is a measure for the degree of unsaturation of the fat, as a natural property for it.**
- **Unsaturated fatty acids absorb iodine at their double bonds, therefore, as the degree of unsaturation increases iodine number and hence biological value of the fat increase.**
- **It is used for identification of the type of fat, detection of adulteration and determining the biological value of fat.**

2-Saponification number (or value):

- **Definition: It is the number of milligrams of KOH required to completely saponify one gram of fat.**
- **Uses:**
- **Since each carboxyl group of a fatty acid reacts with one mole of KOH during saponification, therefore, the amount of alkali needed to saponify certain weight of fat depends upon the number of fatty acids present per weight.**
- **Thus, fats containing short-chain acids will have more carboxyl groups per gram than long chain fatty acids and consume more alkali, i.e., will have higher saponification number.**

3-Acids Number (or value):

- **Definition:**
- **It is the number of milligrams of KOH required to neutralize the free fatty acids present in one gram of fat.**
- **Uses:**
- **It is used for detection of hydrolytic rancidity because it measures the amount of free fatty acids present.**

4-Reichert- Meissl Number (or value):

- **Definition: It is the number of milliliters of 0.1 N KOH required to neutralize the water-soluble fatty acids distilled from 5 grams of fat. Short-chain fatty acid (less than 10 carbons) is distillated by steam.**
- **Uses: This studies the natural composition of the fat and is used for detection of fat adulteration.**
- **Butter that has high percentage of short-chain fatty acids has highest Reichert-Meissl number compared to margarine.**

5-Acetyl Number (or value):

- **Definition: It is number of milligrams of KOH needed to neutralize the acetic acid liberated from hydrolysis of 1 gram of acetylated fat (hydroxy fat reacted with acetic anhydride).**
- **Uses: The natural or rancid fat that contains fatty acids with free hydroxyl groups are converted into acetylated fat by reaction with acetic anhydride.**
- **Thus, acetyl number is a measure of number of hydroxyl groups present.**
- **It is used for studying the natural properties of the fat and to detect adulteration and rancidity.**

B-Waxes

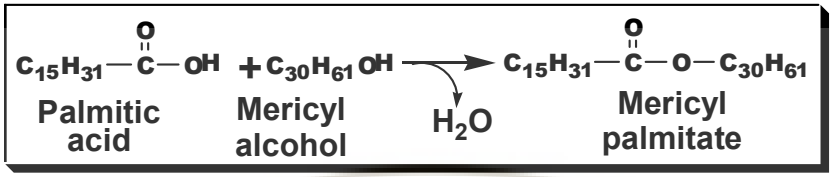
- **Definition**: **Waxes are solid simple lipids containing a monohydric alcohol (with a higher molecular weight than glycerol) esterified to long-chain fatty acids. Examples of these alcohols are palmitoyl alcohol, cholesterol, vitamin A or D.**
- **Properties of waxes: Waxes are insoluble in water, 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.**

Type of Waxes:

- - Waxes are widely distributed in nature such as the secretion of certain insects as bees-wax, protective coatings of the skins and furs of animals and leaves and fruits of plants. They are classified into true-waxes and wax-like compounds as follows:

A-True waxes: include:

- **Bees-wax** is secreted by the honeybees that use it to form the combs. It is a mixture of waxes with the chief constituent is mericyl palmitate.



B-Wax-like compounds:

- **Cholesterol esters: Lanolin (or wool fat) is prepared from the wool-associated skin glands and is secreted by sebaceous glands of the skin.**
- **It is very complex mixture, contains both free and esterified cholesterol, e.g., cholesterol-palmitate and other sterols.**

Differences between neutral lipids and waxes:

	Waxes	Neutral lipids
1.Digestibility:	Indigestible (not hydrolyzed by lipase).	Digestible (hydrolyzed by lipase).
2-Type of alcohol:	Long-chain monohydric alcohol + one fatty acid.	Glycerol (trihydric) + 3 fatty acids
3-Type of fatty acids:	Fatty acid mainly palmitic or stearic acid.	Long and short chain fatty acids.
4-Acrolein test:	Negative.	Positive.
5-Rancidability:	Never get rancid.	Rancidible.
6-Nature at room temperature.	Hard solid.	Soft solid or liquid.
7-Saponification	Nonsaponifiable.	Saponifiable.
8-Nutritive value:	No nutritive value.	Nutritive.
9-Example:	Bee & carnuba waxes.	Butter and vegetable oils.

2-Compound Lipids

Definition:

- 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:

1. Phospholipids
2. Glycolipids.
3. Lipoproteins
4. Sulfolipids and amino lipids.

A-Phospholipids

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

Importance:

1. They are present in large amounts in the liver and brain as well as blood. Every animal and plant cell contains phospholipids.
2. The membranes bounding cells and subcellular organelles are composed mainly of phospholipids. Thus, the transfer of substances through these membranes is controlled by properties of phospholipids.
3. They are important components of the lipoprotein coat essential for secretion and transport of plasma lipoprotein complexes. Thus, they are lipotropic agents that prevent fatty liver.
4. Myelin sheath of nerves is rich with phospholipids.

5-Important in digestion and absorption of neutral lipids and excretion of cholesterol in the bile.

6-Important function in blood clotting and platelet aggregation.

7-They provide lung alveoli with surfactants that prevent its irreversible collapse.

8-Important role in signal transduction across the cell membrane.

9-Phospholipase A2 in snake venom hydrolyses membrane phospholipids into hemolytic lysolecithin or lysocephalin.

10-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:

1. **Fatty acids** (a saturated and an unsaturated fatty acid).
2. **Nitrogenous base** (choline, serine, threonine, or ethanolamine).
3. **Phosphoric acid.**
4. **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:**

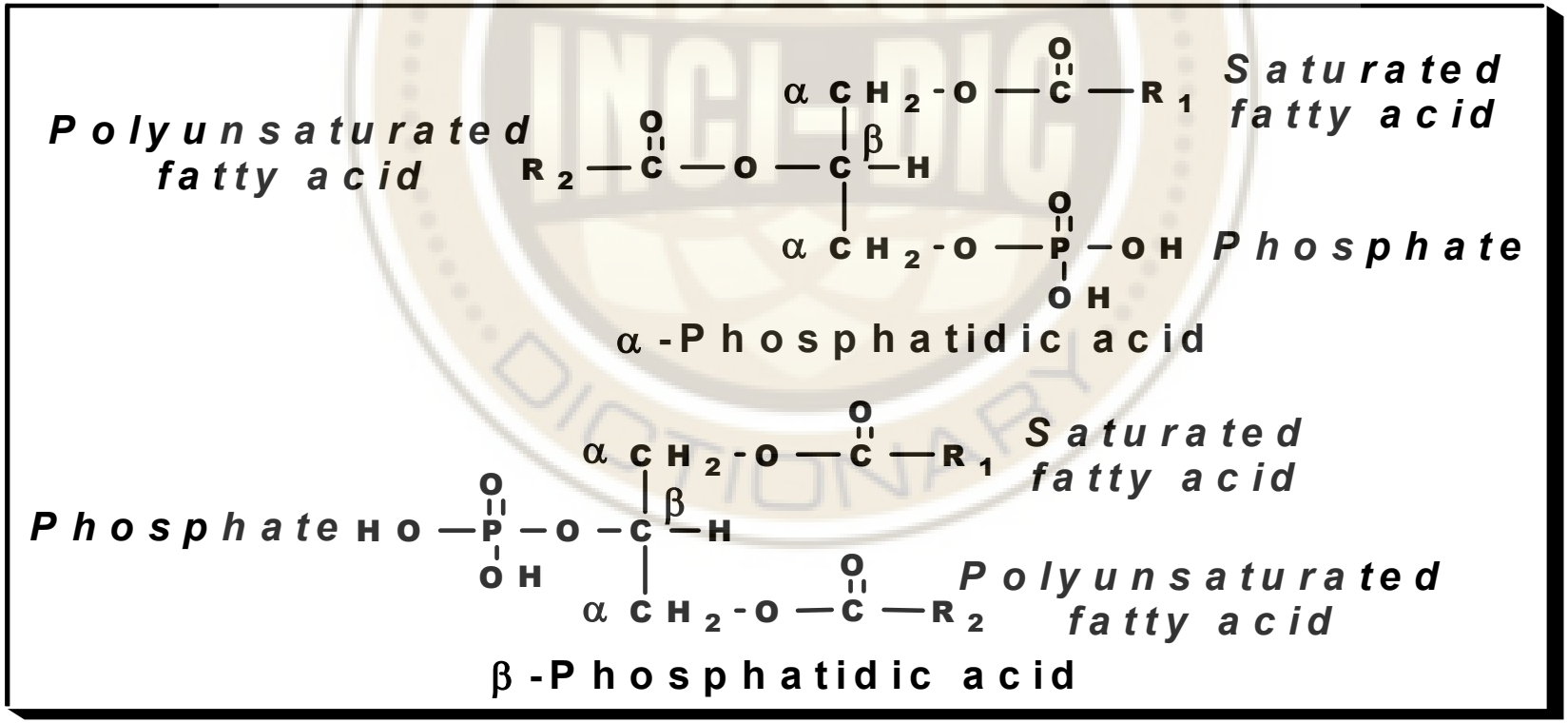
A-**Glycerophospholipids: They are regarded as derivatives of phosphatidic acids that are the simplest type of phospholipids and include:**

1. **Phosphatidic acids.**
2. **Lecithins**
3. **Cephalins.**
4. **Plasmalogens.**
5. **Inositides.**
6. **Cardiolipin.**

B-Sphingophospholipids: They contain sphingosine as an alcohol and are named Sphingomyelins.

A-Glycerophospholipids

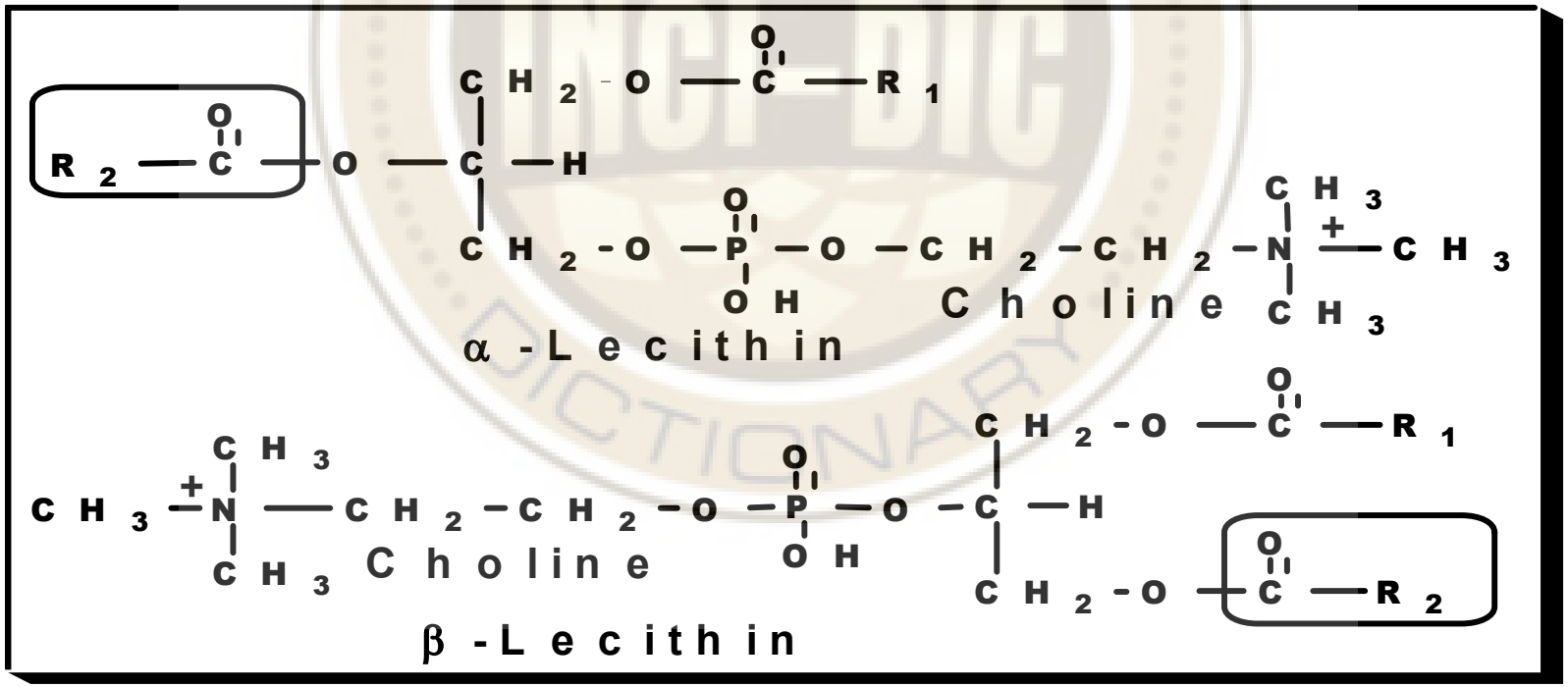
1-Phosphatidic acids: They are metabolic intermediates in synthesis of triglycerides and glycerophospholipids in the body and may have function as a second messenger. They exist in two forms according to the position of the phosphate



2-Lecithins:

- **Definition**: Lecithins are glycerophospholipids that contain choline as a base beside phosphatidic acid. They exist in 2 forms α- and β-lecithins. Lecithins are a common cell constituent obtained from brain (α-type), egg yolk (β-type), or liver (both types). Lecithins are important in the metabolism of fat by the liver.
- **Structure:** Glycerol is connected at C2 or C3 with a polyunsaturated fatty acid, at C1 with a saturated fatty acid, at C3 or C2 by phosphate to which the choline base is connected. The common fatty acids in lecithins are stearic, palmitic, oleic, linoleic, linolenic, clupandonic or arachidonic acids.

Lysolecithin causes hemolysis of RBCs. This partially explains toxic the effect of snake venom,. The venom contains lecithinase, which hydrolyzes the polyunsaturated fatty converting lecithin into lysolecithin. Lysolecithins are intermediates in metabolism of phospholipids.

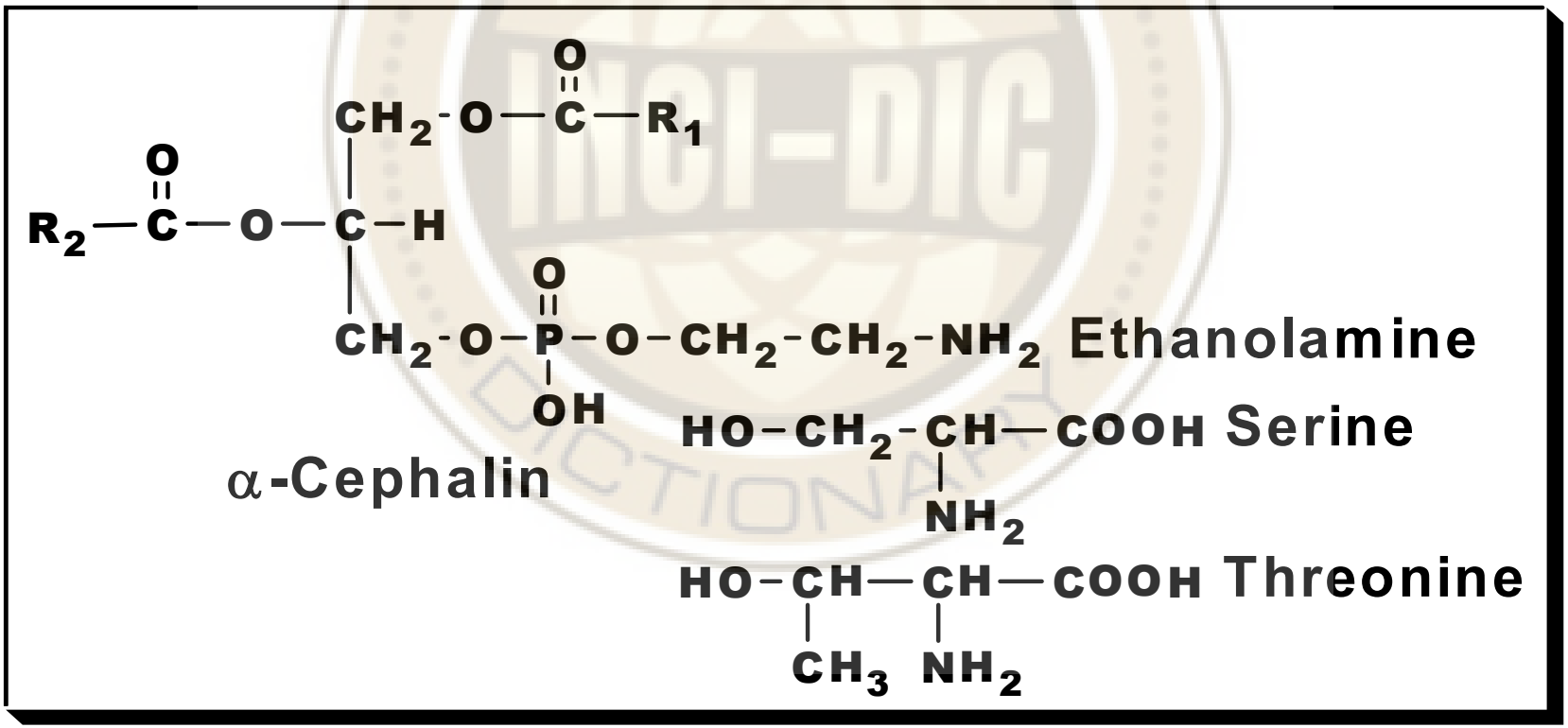


- **Lung surfactant**
- **Is a complex of dipalmitoyl-lecithin, sphingomyelin and a group of apoproteins called apoprotein A, B, C, and D.**
- **It is produced by type II alveolar cells and is anchored to the alveolar surface of type II and I cells.**
- **It lowers alveolar surface tension and improves gas exchange besides activating macrophages to kill pathogens.**
- **In premature babies, this surfactant is deficient and they suffer from respiratory distress syndrome.**
- **Glucocorticoids increase the synthesis of the surfactant complex and promote differentiation of lung cells.**

3-Cephalins (or Kephalins):

- **Definition**: They are phosphatidyl-ethanolamine or serine. Cephalins occur in association with lecithins in tissues and are isolated from the brain (Kephale = head).
- **Structure**: Cephalins resemble lecithins in structure except that choline is replaced by ethanolamine, serine or threonine amino acids.

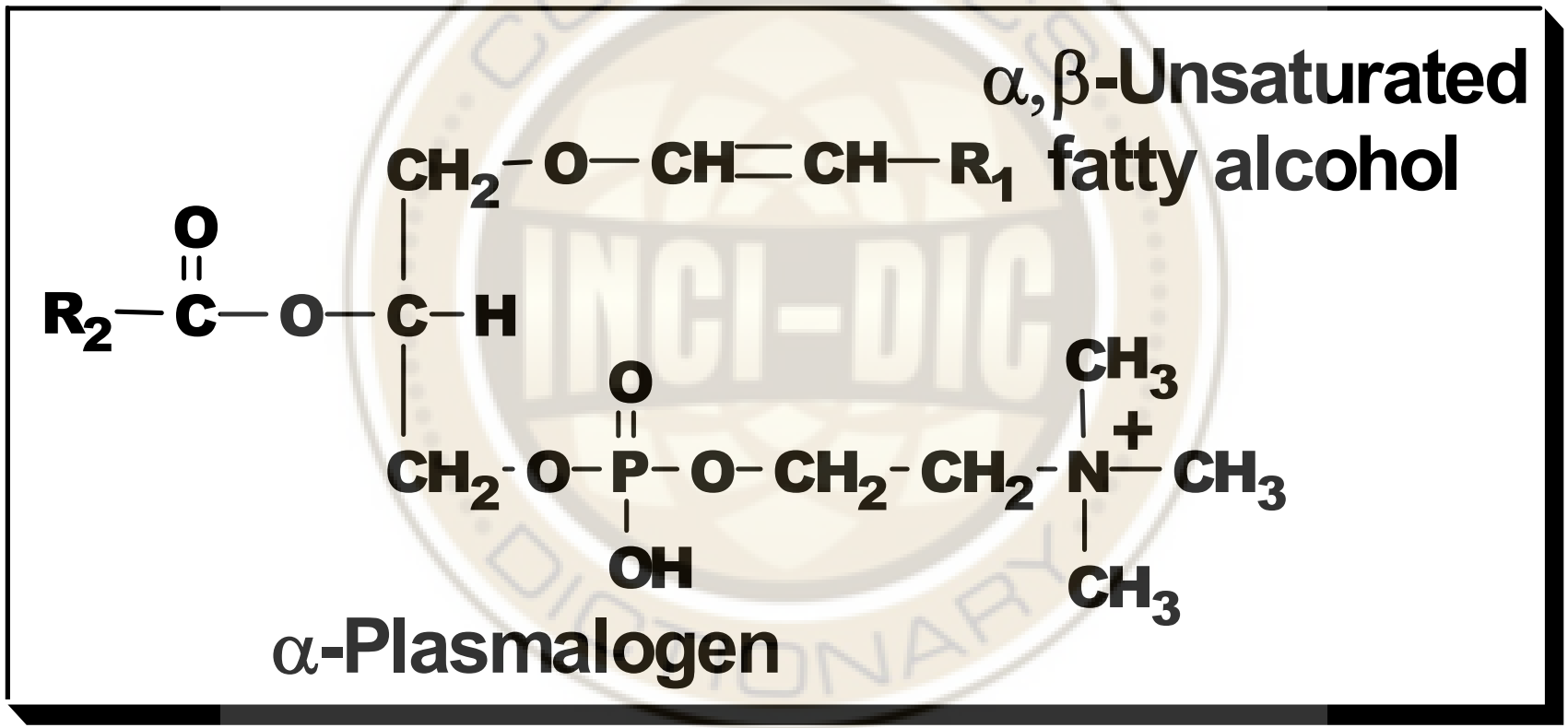
- **Certain cephalins are constituents of the complex mixture of phospholipids, cholesterol and fat that constitute the lipid component of the lipoprotein "thromboplastin" which accelerates the clotting of blood by activation of prothrombin to thrombin in presence of calcium ions.**



4-Plasmalogens:

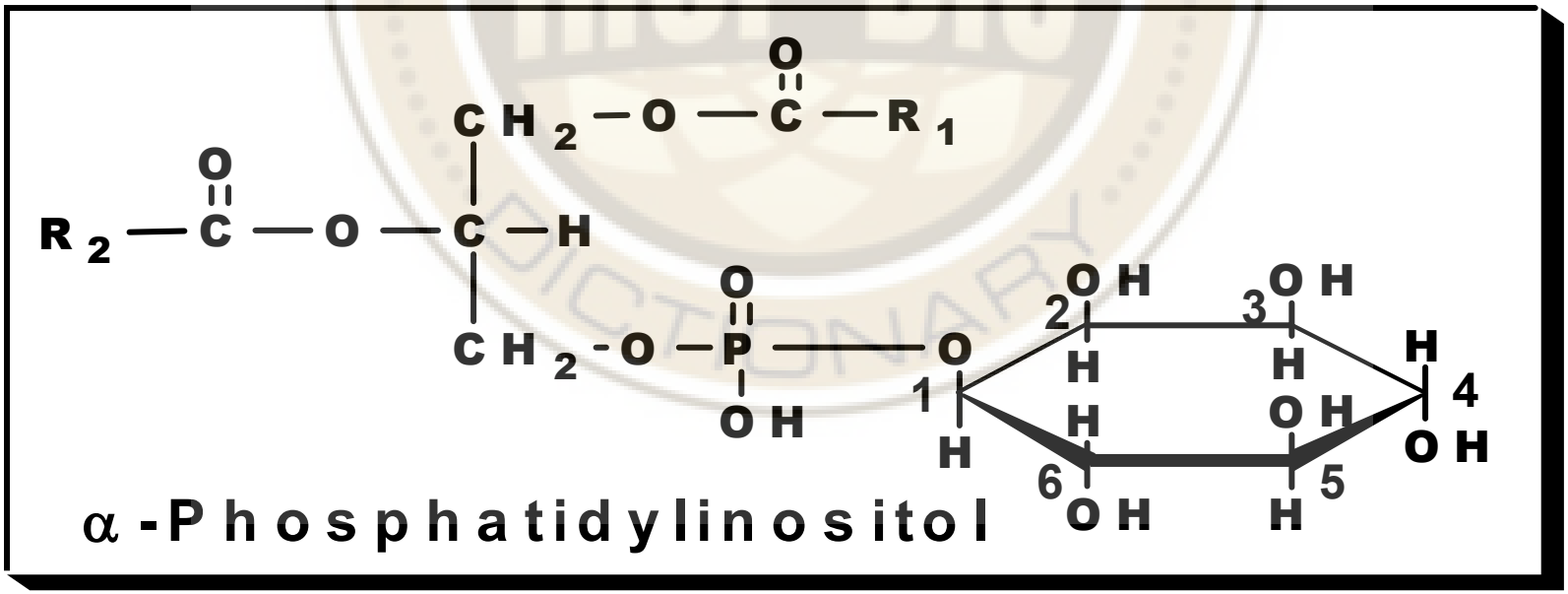
- **Definition:** Plasmalogens are found in the cell membrane phospholipids fraction of brain and muscle (10% of it is plasmalogens), liver, semen and eggs.
- **Structure**: Plasmalogens resemble lecithins and cephalins in structure but differ in the presence of α,β-unsaturated fatty alcohol rather than a fatty acid at C1 of the glycerol connected by ether bond.
- At C2 there is an unsaturated long-chain fatty acid, however, it may be a very short-chain fatty acid

- **Properties**: Similar to lecithins.



5-Inositides:

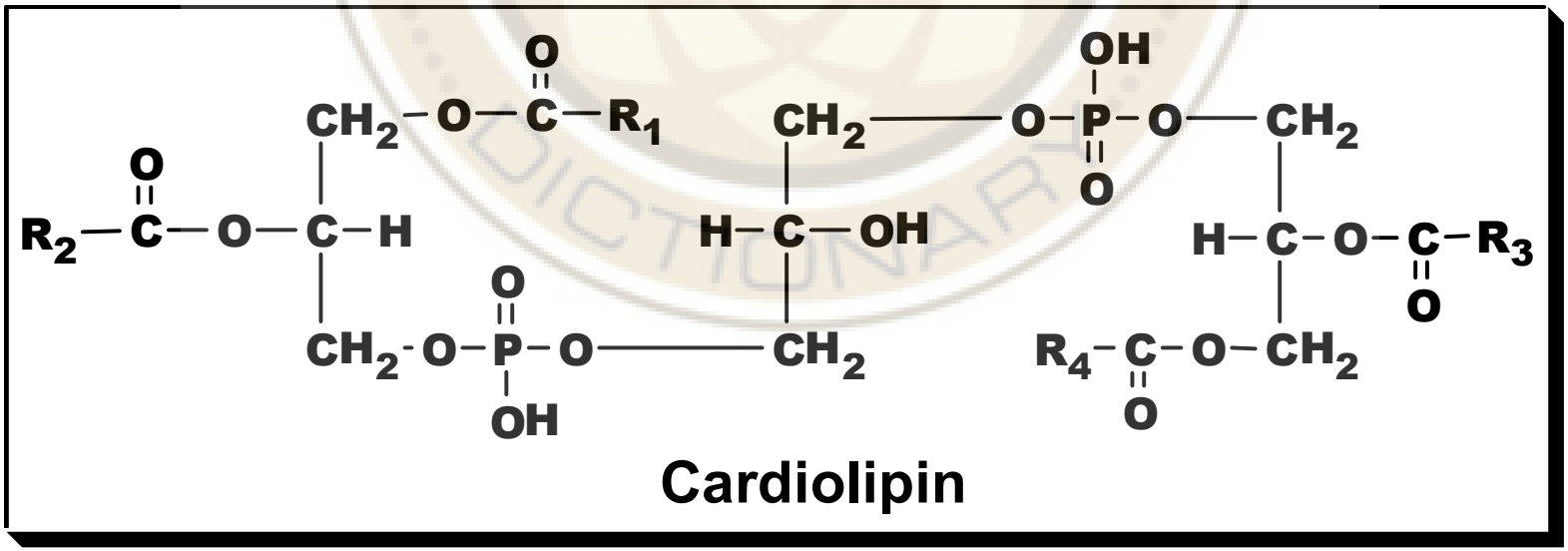
- **Definition:**
- - **They are phosphatidyl inositol.**
- **Structure: They are similar to lecithins or cephalins but they have the cyclic sugar alcohol, inositol as the base. They are formed of glycerol, one saturated fatty acid, one unsaturated fatty acid, phosphoric acid and inositol**



- **Source**: Brain tissues.
- **Function**:
- **Phosphatidyl inositol is a major component of cell membrane phospholipids particularly at the inner leaflet of it.**
- **They play a major role as second messengers during signal transduction for certain hormone..**
- **On hydrolysis by phospholipase C, phosphatidyl-inositol-4,5-diphosphate produces diacyl-glycerol and inositol-triphosphate both act to liberate calcium from its intracellular stores to mediate the hormone effects.**

6-Cardiolipins:

- **Definition**: They are diphosphatidyl-glycerol. They are found in the inner membrane of mitochondria initially isolated from heart muscle (cardio). It is formed of 3 molecules of glycerol, 4 fatty acids and 2 phosphate groups.
- **Function**: Used in serological diagnosis of autoimmunity diseases.



Cardiolipin

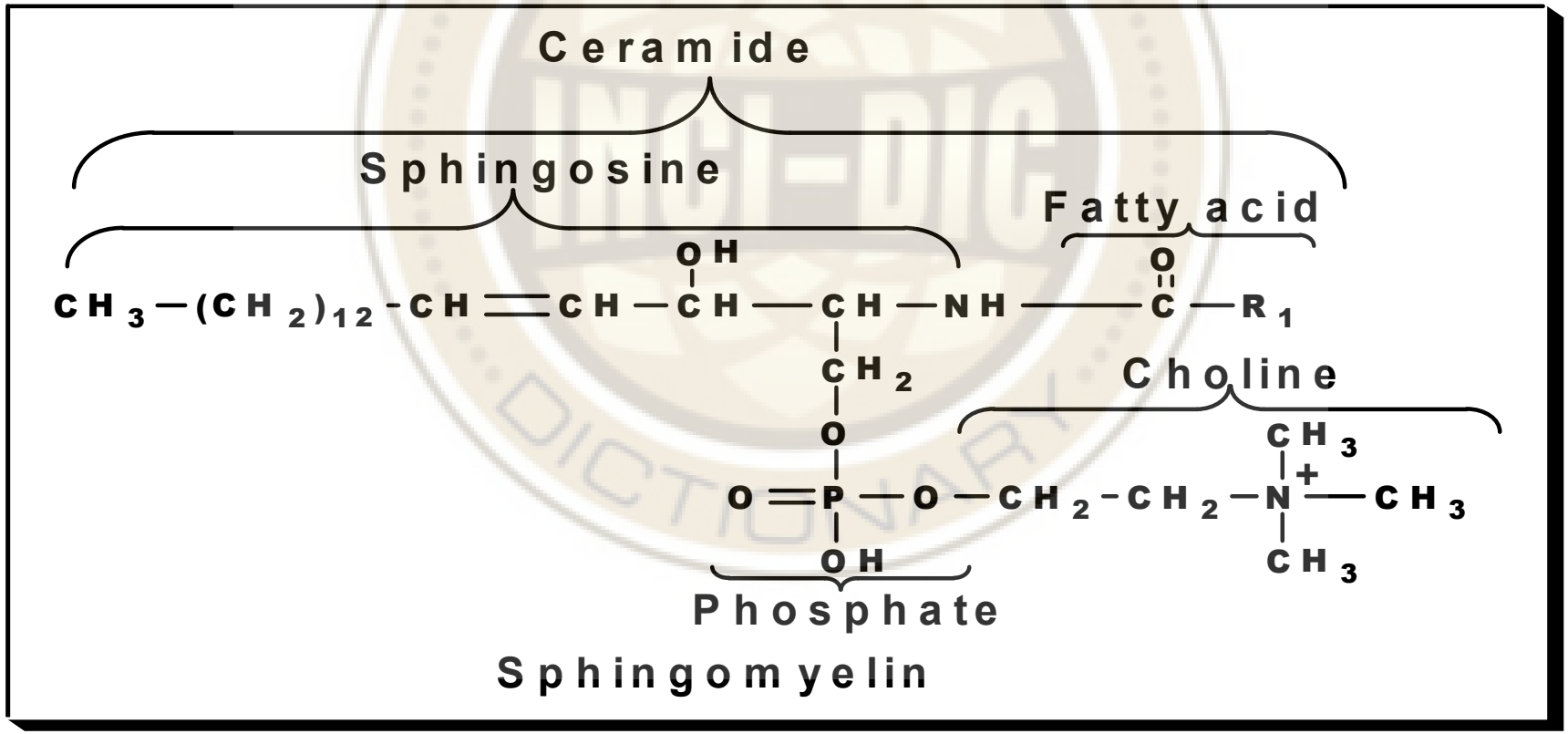
B-Sphingophospholipids

1-Sphingomyelins

- **Definition:** Sphingomyelins are found in large amounts in brain and nerves and in smaller amounts in lung, spleen, kidney, liver and blood.

- **Structure:** 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.
- Thus, sphingomyelins contain sphingosine base, one long-chain fatty acid, choline and phosphoric acid.
- To the amino group of sphingosine the fatty acid is attached by an amide linkage.

- **Ceramide** This part of sphingomyelin in which the amino group of sphingosine is attached to the fatty acid by an amide linkage.
- Ceramides have been found in the free state in the spleen, liver and red cells.



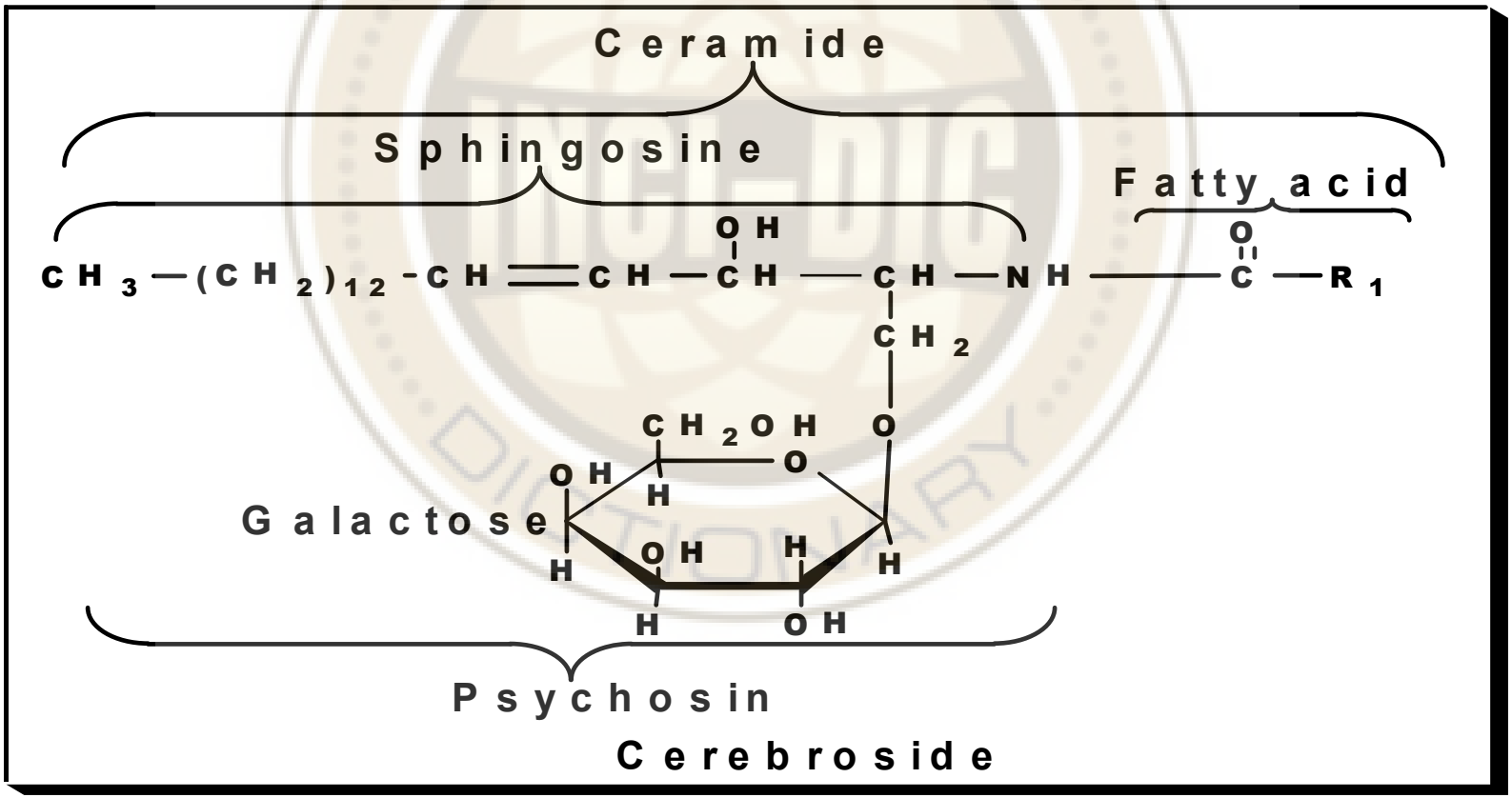
B-Glycolipids

- **Definition**: They are lipids that contain carbohydrate residues with sphingosine as the alcohol and a very long-chain fatty acid (24 carbon series).
- They are present in cerebral tissue, therefore are called cerebrosides
- **Classification**: According to the number and nature of the carbohydrate residue(s) present in the glycolipids the following are

1. **Cerebrosides.** They have one galactose molecule (galactosides).
2. **Sulfatides.** They are cerebrosides with sulfate on the sugar (sulfated cerebrosides).
3. **Gangliosides.** They have several sugar and sugaramine residues.

1-Cerebrosides:

- **Occurrence:** They occur in myelin sheath of nerves and white matter of the brain tissues and cellular membranes. They are important for nerve conductance.
- **Structure:** They contain sugar, usually β-galactose and may be glucose or lactose, sphingosine and fatty acid, but no phosphoric acid.

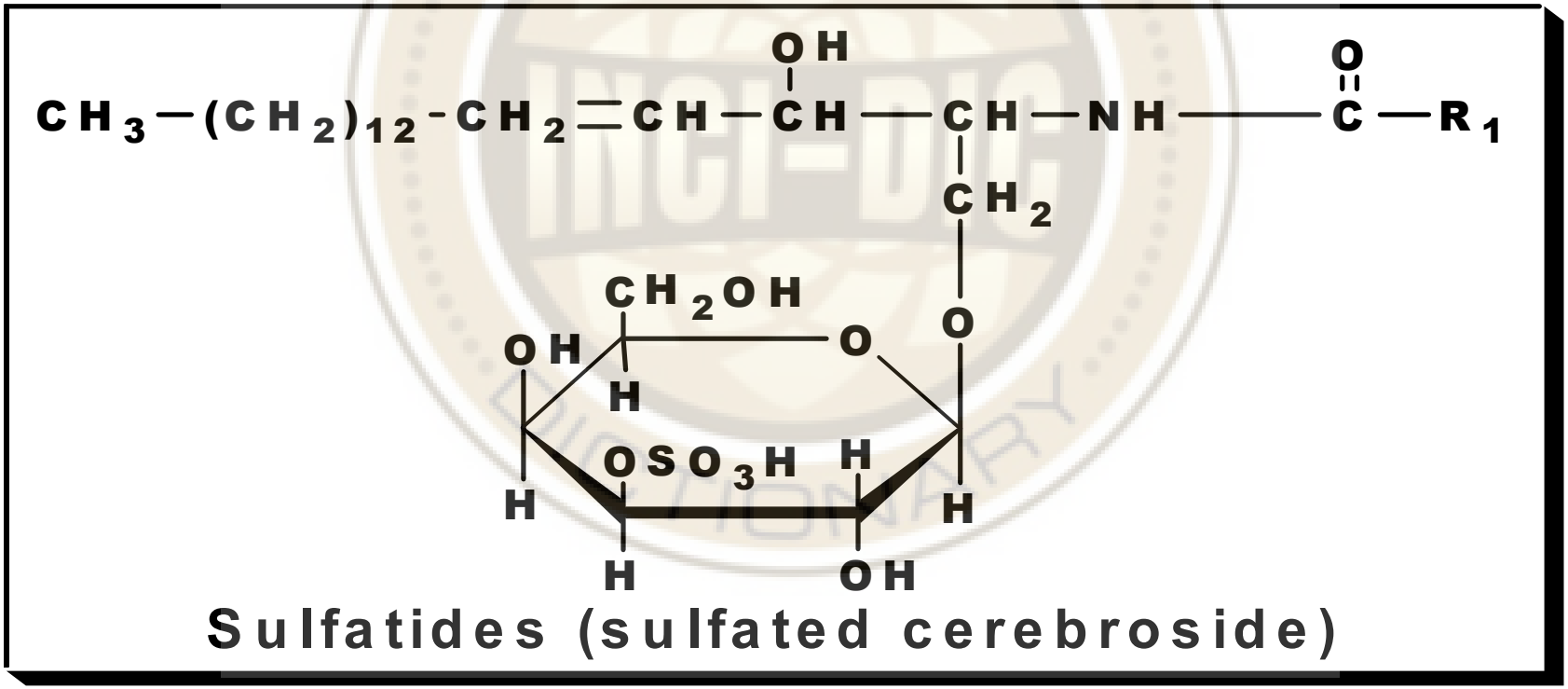


- **Types: According to the type of fatty acid and carbohydrate present, there are 4 different types of cerebrosides isolated from the white matter of cerebrum and in myelin sheaths of nerves. Rabbit cerebrosides contain stearic acid.**

1. **Kerasin contains lignoceric acid (24 carbons) and galactose.**
2. **Cerebron (Phrenosin) contains cerebronic acid (2-hydroxylignoceric acid) and galactose.**
3. **Nervon contains nervonic acid (unsaturated lignoceric acid at C15) and galactose.**
4. **Oxynervon contains oxynervonic acid (2-hydroxynervonic acid) and galactose.**

2-Sulfatides:

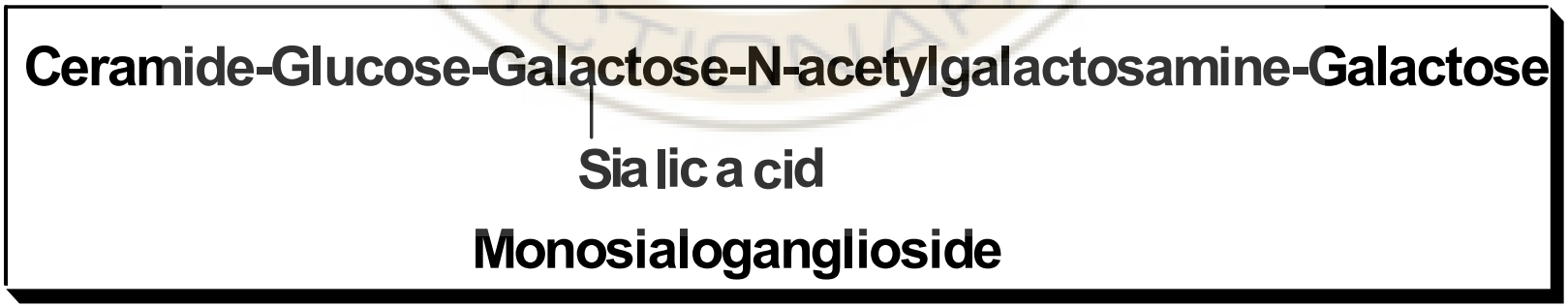
- They are sulfate esters of kerasin or phrenosin in which the sulfate group is usually attached to the –OH group of C3 or C6 of galactose. Sulfatides are usually present in the brain, liver, muscles and testes.



Sulfatides (sulfated cerebroside)

3-Gangliosides:

- They are more complex glycolipids that occur in the gray matter of the brain, ganglion cells, and RBCs. They transfer biogenic amines across the cell membrane and act as a cell membrane receptor.
- Gangliosides contain sialic acid (N-acetylneuraminic acid), ceramide (sphingosine + fatty acid of 18-24 carbon atom length), 3 molecules of hexoses (1 glucose + 2 galactose) and hexosamine. The most simple type of it the monosialoganglioside,. It works as a receptor for cholera toxin in the human intestine.



C-Lipoproteins

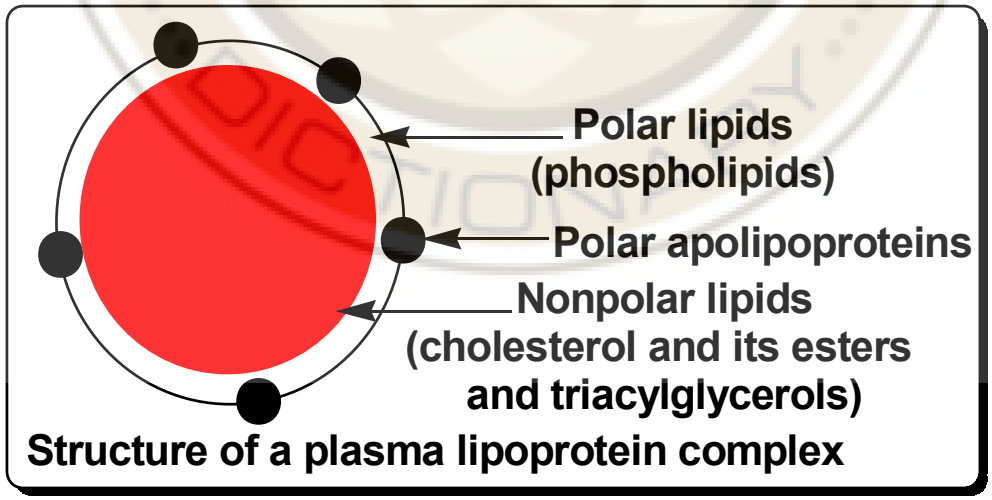
- **Definition: Lipoproteins are lipids combined with proteins in the tissues. The lipid component is phospholipid, cholesterol or triglycerides. The holding bonds are secondary bonds.**
- **They include:**

1. **Structural lipoproteins: These are widely distributed in tissues being present in cellular and subcellular membranes. In lung tissues acting as a surfactant in a complex of a protein and lecithin. In the eye, rhodopsin of rods is a lipoprotein complex.**

- **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). As the lipid content increases, the density of plasma lipoproteins decreases**

- **Plasma lipoproteins can be separated by two methods:**

1. **Ultra-centrifugation: Using the rate of floatation in sodium chloride solution leading to their sequential separation into chylomicrons, very low density lipoproteins (VLDL or pre-β-lipoproteins), low density lipoproteins (LDL or β-lipoproteins), high density lipoproteins (HDL or α-lipoproteins) and albumin-free fatty acids complex.**
2. **Electrophoresis: is the migration of charged particles in an electric field either to the anode or to the cathode. It sequentially separates the lipoproteins into chylomicrons, pre-β-, β-, and α-lipoprotein and albumin-free fatty acids complex.**



Structure of a plasma lipoprotein complex

a) Chylomicrons: They have the largest diameter and the least density. They contain 1-2% protein only and 98-99% fat. The main lipid fraction is triglycerides absorbed from the intestine and they contain small amounts of the absorbed cholesterol and phospholipids.

b) Very low-density lipoproteins (VLDL) or pre-β-lipoproteins: Their diameter is smaller than chylomicrons. They contain about 7-10% protein and 90-93% lipid. The lipid content is mainly triglycerides formed in the liver. They contain phospholipid and cholesterol more than chylomicrons.

c**) Low-density lipoproteins (LDL) or β-lipoproteins**: They contain 10-20% proteins in the form of apolipoprotein B. Their lipid content varies from 80-90%. They contain about 60% of total blood cholesterol and 40% of total blood phospholipids. As their percentage increases, the liability to atherosclerosis increases.

d) **High-density lipoproteins (HDL) or α-Lipoproteins**: They contain 35-55% proteins in the form of apolipoprotein A. They contain 45-65% lipids formed of cholesterol (40% of total blood content) and phospholipids (60% of total blood content). They act as cholesterol scavengers, as their percentage increases, the liability to atherosclerosis decreases. They are higher in females than in males. Due to their high protein content they possess the highest density.

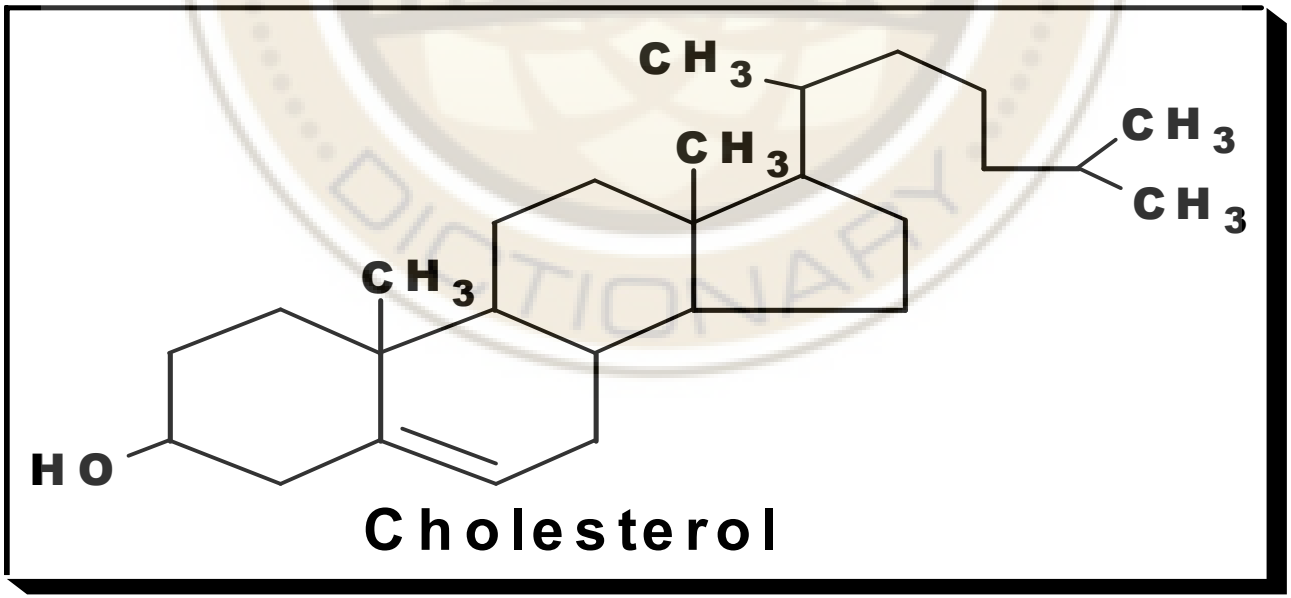
e) **Albumin-free fatty acids complex:** It is a proteolipid complex with 99% protein content associated with long-chain free fatty acids for transporting them.

Cholesterol:

- **Importance: -**
- **It is the most important sterol in animal tissues as free alcohol or in an esterified form (with linoleic, oleic, palmitic acids or other fatty acids).**
- **Steroid hormones, bile salts and vitamin D are derivatives from it.**
- **Tissues contain different amounts of it that serve a structural and metabolic role, e.g., adrenal cortex content is 10%, whereas, brain is 2%, others 0.2-0.3%.**
- **Source: - It is synthesized in the body from acetyl-CoA (1gm/day, cholesterol does not exist in plants) and is also taken in the diet (0.3 gm/day as in, butter, milk, egg yolk, brain, meat and animal fat).**

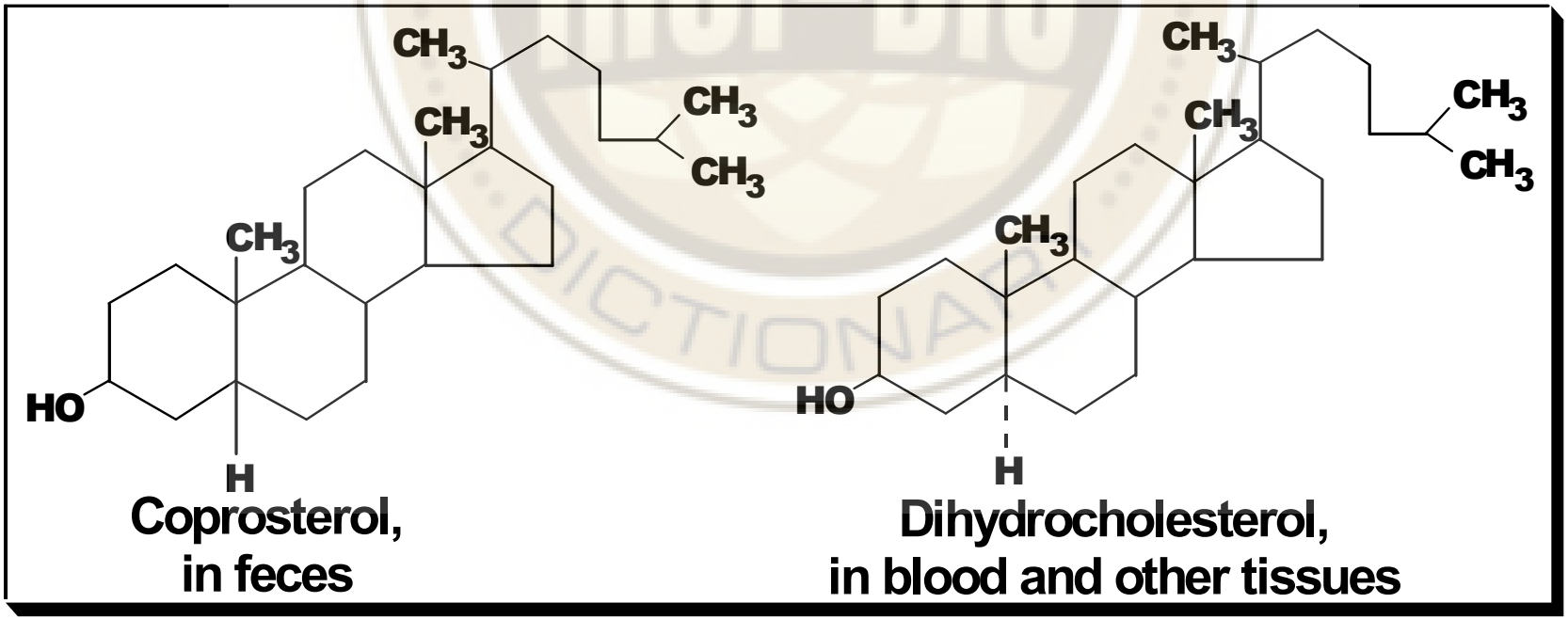
Physical propeties: It has a hydroxyl group on C3, a double bond between C5 and C6, 8 asymmetric carbon atoms and a side chain of 8 carbon atoms.

- It is found in all animal cells, corpus luteum and adrenal cortex, human brain (17% of the solids).
- In the blood (the total cholesterol amounts about 200 mg/dL of which 2/3 is esterified, chiefly to unsaturated fatty acids while the remainder occurs as the free cholesterol.

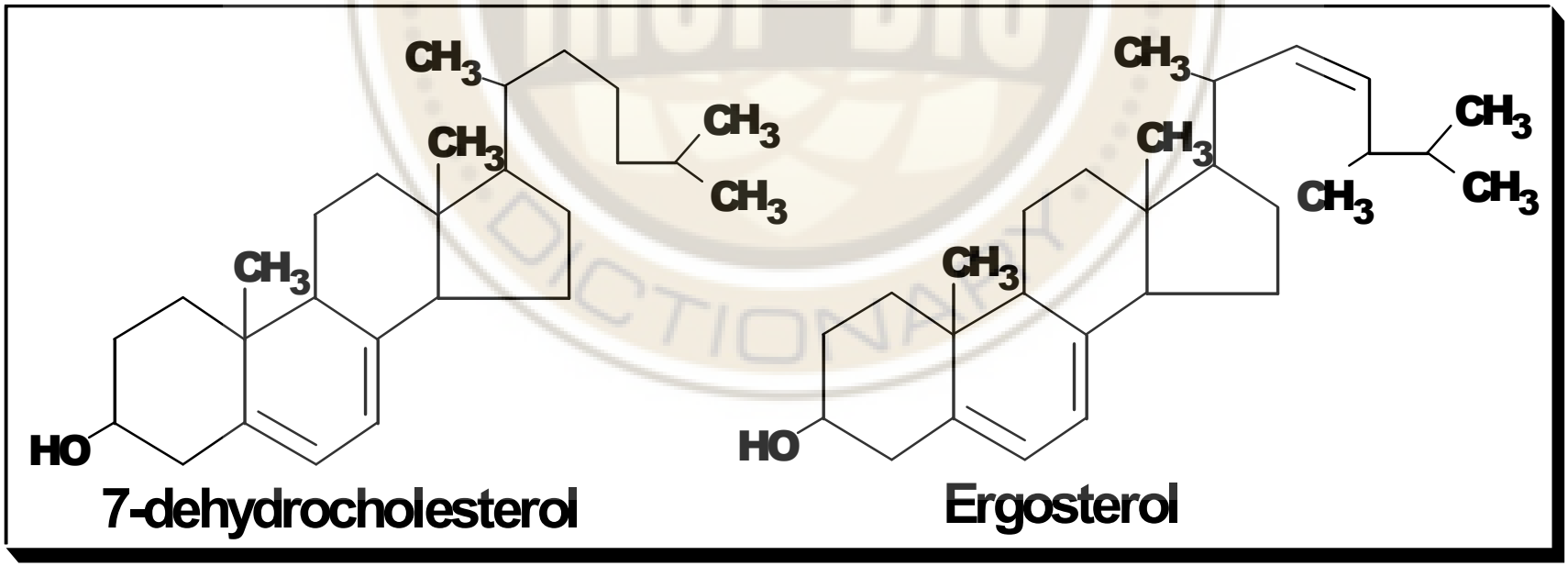


Cholesterol

- **Chemical properties** Intestinal bacteria reduce cholesterol into coprosterol and dihydrocholesterol.
- - It is also oxidized into 7-Dehydrocholesterol and further unsaturated cholesterol with a second double bond between C7 and C8. When the skin is irradiated with ultraviolet light 7-dehydrocholesterol is converted to vitamin D3. This explains the value of sun light in preventing rickets.



- **Ergosterol** differs from 7-dehydrocholesterol in the side chain. Ergosterol is converted to vitamin D2 by irradiation with UV Ergosterol and 7- dehydrocholesterol are called Pro-vitamins D or precursors of vitamin D.
- - It was first isolated from ergot, a fungus then from yeast. Ergosterol is less stable than cholesterol (because of having 3 double bonds).



Steroids

- Steroids constitute an important class of biological compounds.
- Steroids are usually found in association with fat. They can be separated from fats after saponification since they occur in the unsaponifiable residue.
- They are derivatives of cholesterol that is formed of steroid ring or nucleus.
- Biologically important groups of substances, which contain this ring, are:

1. Sterols.
2. Adrenal cortical hormones.
3. Male and female sex hormones.
4. Vitamin D group.
5. Bile acids.
6. Cardiac glycosides.

- **General consideration about naturally occurring steroids**:

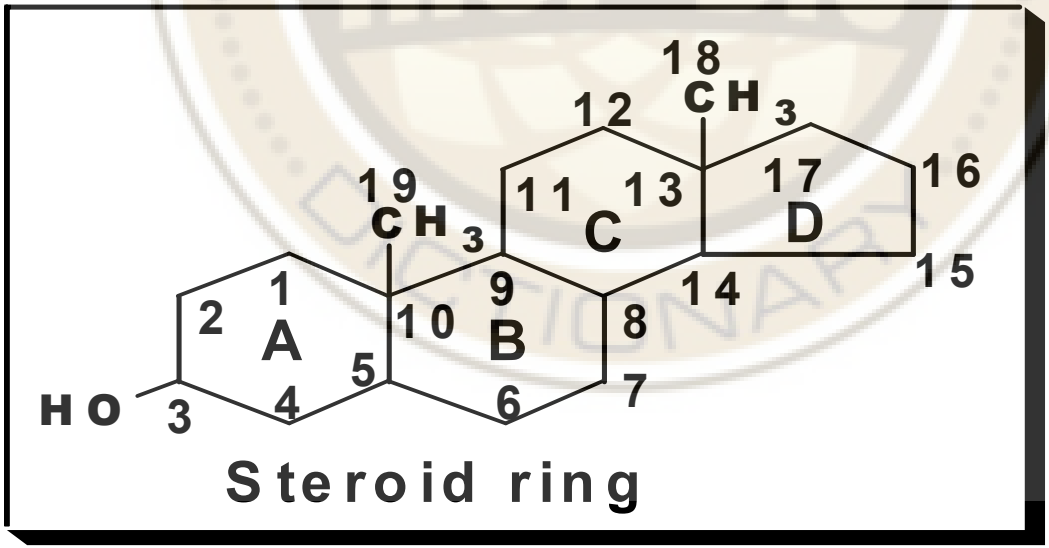
A typical member of this group is cholesterol. Certain facts have to be considered when drawing steroid formula:

1) There is always oxygen in the form of hydroxyl or ketone on C3.

2) Rings C and D are saturated (stable).

3) Methyl groups at C18 C19. In case of vitamin D, the CH3 group at C19 becomes a methylene group (=CH2) and the ring B is opened, whereas, this methyl group is absent in female sex hormones (estrogens).

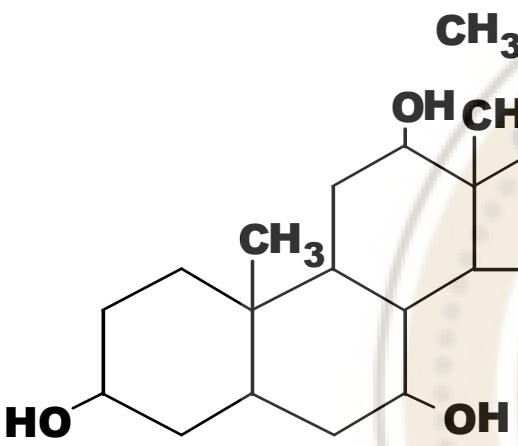
4) In estrogens (female sex hormones) ring A is aromatic and there is no methyl group on C10.

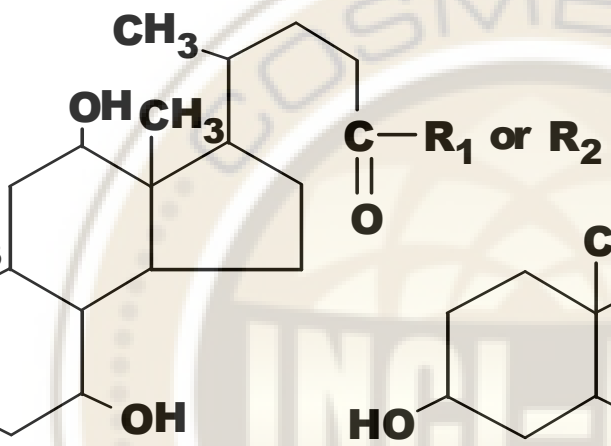


Steroid ring

- **Bile acids**:
- **They are produced from oxidation of cholesterol in the liver producing cholic and chenodeoxycholic acids that are conjugated with glycine or taurine to produce glycocholic, glycochenodeoxycholic, taurocholic and taurochenodeoxycholic acids. They react with sodium or potassium to produce sodium or potassium bile salts.**
- **Their function is as follows**:

1. **Emulsification of lipids during digestion.**
2. **Help in digestion of the other foodstuffs.**
3. **Activation of pancreatic lipase.**
4. **Help digestion and absorption of fat-soluble vitamins.**
5. **Solubilizing cholesterol in bile and prevent gall stone formation.**
6. **Choleretic action (stimulate their own secretion).**
7. **Intestinal antiseptic that prevent putrefaction**

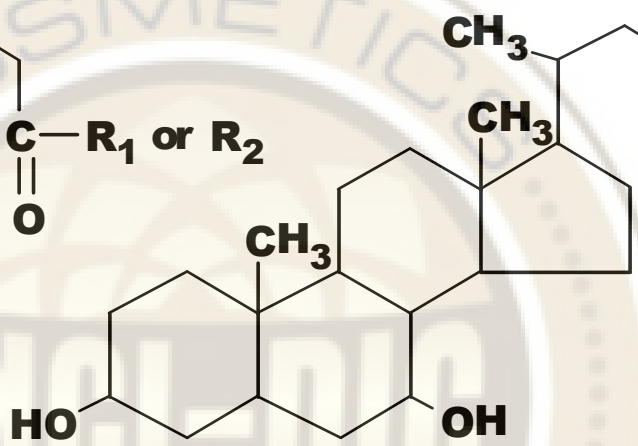


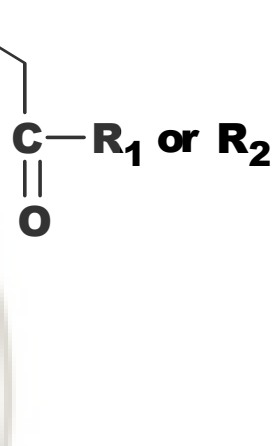


Sodium-tauro or glyco-cholate

R_1 $H_2N-CH_2-COO^-Na^+$

Sodium glycate





Sodium-tauro or glyco-chenodeoxycholate

R_2 $H_2N-(CH_2)_2-SO_3^-Na^+$

Sodium taurate