Biochemistry of dietary, functional and structural lipids

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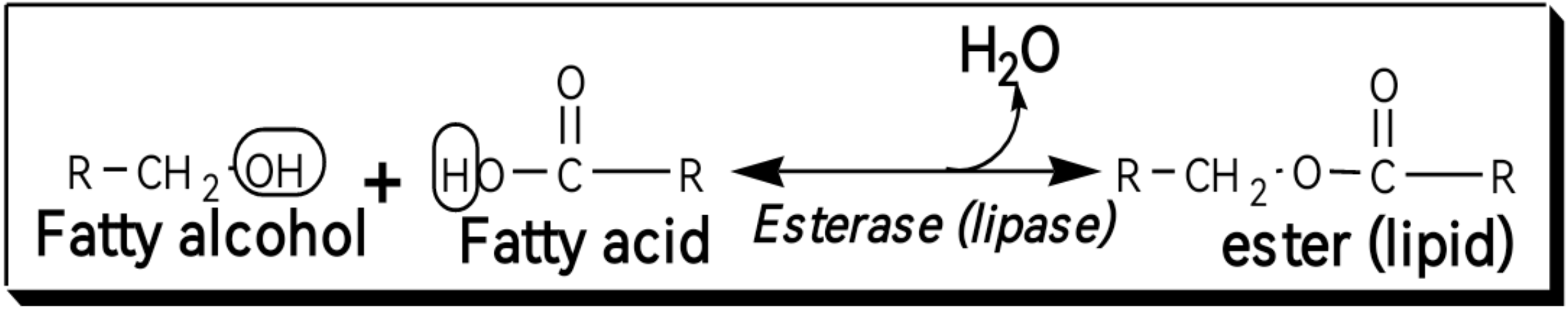
Objectives

- Classification & Biological importance of fat
- Discuss structure and function of fatty acids, fatty alcohols, and their derivatives
- Discuss Structure and function of phospholipids, glycolipids with special emphasis on cell membrane
- Discuss Structure and function of lipoproteins

Definition of lipids

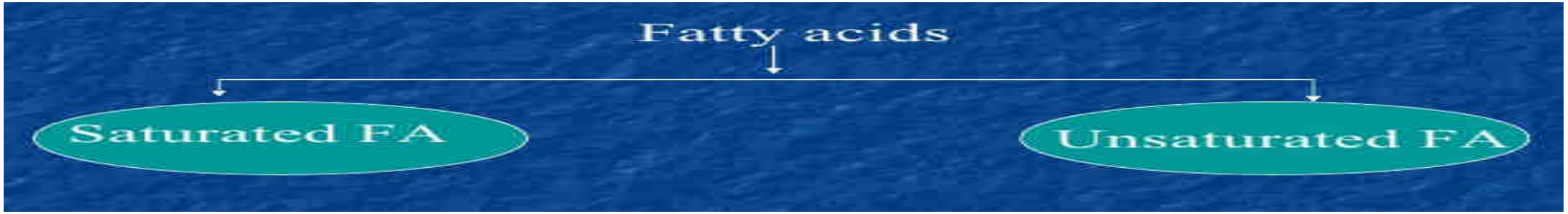
- **Lipids (or fats) are organic compounds formed mainly from alcohol and fatty acids combined together by ester linkage.**
- **Lipids include fats, oils, waxes and related compounds.**



Fatty Acids

- **Definition:** Fatty acids are aliphatic mono-carboxylic acids.
- They have the general formula R-$(CH_2)_n$-COOH and mostly have straight chain (with few exceptions).
- In this formula "**n**" is mostly an even number of carbon atoms (2-34) with a few exceptions that have an odd number or zero in acetic acid.

Fatty acids can be classified as follows:



I) **Saturated,** i.e., they contain no double bonds.

- They are solid at room temperature except if they are short chained. Examples are butyric, palmitic and stearic acids.

II) **Unsaturated,** i.e., they contain one (**monounsaturated**) or more double bonds (**polyunsaturated**).

TYPES OF FATTY ACIDS
(according to the number of double bonds)

Saturated (No bond)

Monounsaturated (1 bond)

Polyunsaturated (>1 bond)

Polyunsaturated fatty acids (Essential fatty acids or polyenoic):

- **Definition:** They are essential fatty acids that can not be synthesized in the human body (due to lack of enzymes that can form more than one double bond) and must be taken in adequate amounts in the diet. They are important for normal growth and metabolism. They are liquids at room temperature.

Function

1. They are useful in the treatment of atherosclerosis by help the transport of blood cholesterol and lowering it.
2. The hormone-like eicosanoids are synthesized from them.
3. They participate in the structure of all cellular and subcellular membranes and lipoproteins.
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. They have an important role in the health of the retina and vision.
8. They can be oxidized for energy production.

- **Deficiency:** Their deficiency in the diet leads to nutritional 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.
- **Source:** vegetable oils such as corn oil, peanut oil, olive oil, cottonseed oil, soybean oil and many other plant oils, cod liver oil and animal fats.

Examples: Include:

- **Linoleic:** C18:2$\Delta^{9, 12}$. **CH_3-$(CH_2)_4$-CH=CH-CH_2-CH=CH-$(CH_2)_7$-COOH**
- **α-Linolenic acid:** C18:3$\Delta^{9, 12, 15}$, in corn, peanut, olive, cottonseed and soybean oils.
- **γ-Linolenic acid:** is an isomer for α-Linolenic acid, C18:3$\Delta^{6, 9, 12}$.
- **Arachidonic acid:** C20:4$\Delta^{5, 8, 11, 14}$. It is an important component of phospholipids in animal and in peanut oil. It is synthesized in the body from linoleic acid.
- **Clupandonic acid:** 22:5$\Delta^{7, 10, 13, 16, 19}$. It is present in fish oils and brain phospholipids.

III- Hydroxy fatty acids

-They contain one or more hydroxyl groups, e.g., dihydroxy-stearic acids (18: dihydroxy at C_9 and C_{10}), cerebronic acidfound in brain glycolipids.

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

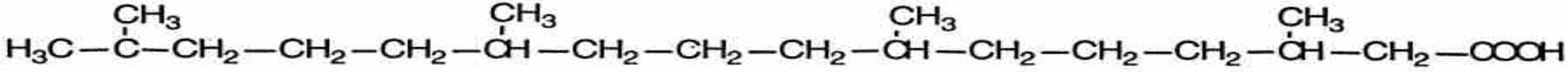
$$\quad\ |\qquad\ |$$

$$\quad OH\quad OH$$

Dihydroxy-stearic

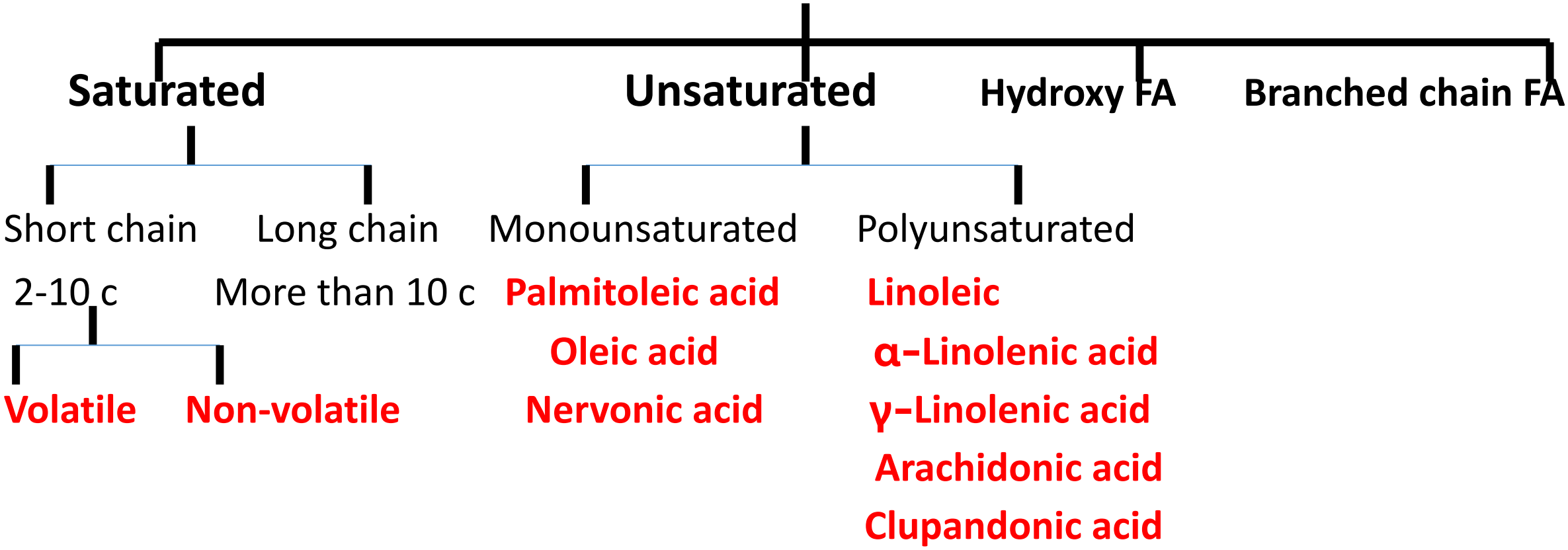
IV- Branched chain fatty acids:

- There are fatty acids with branched chains such as **phytanic acid**. If it is **not oxidized** in the body it will be **toxic** (Refsum's disease).



Phytanic acid

Fatty Acids

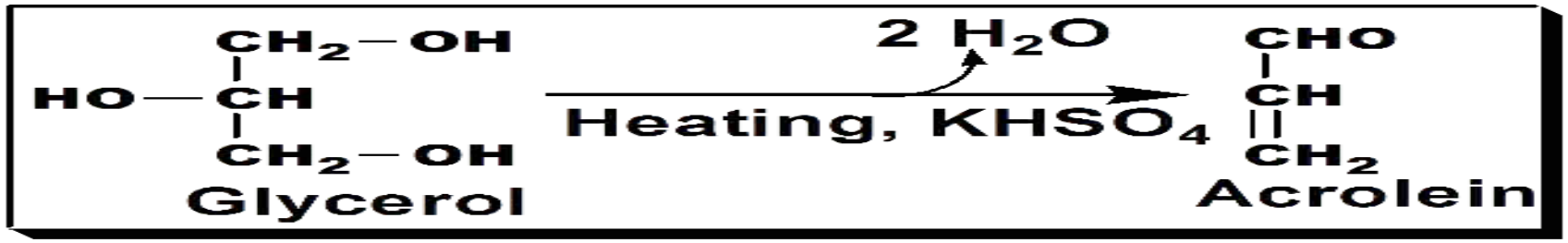

Saturated
Unsaturated
Hydroxy FA
Branched chain FA
Short chain
Long chain
Monounsaturated
Polyunsaturated
2-10 c
More than 10 c
Palmitoleic acid
Linoleic
Oleic acid
α-Linolenic acid
Volatile
Non-volatile
Nervonic acid
γ-Linolenic acid
Arachidonic acid
Clupandonic acid

Alcohols

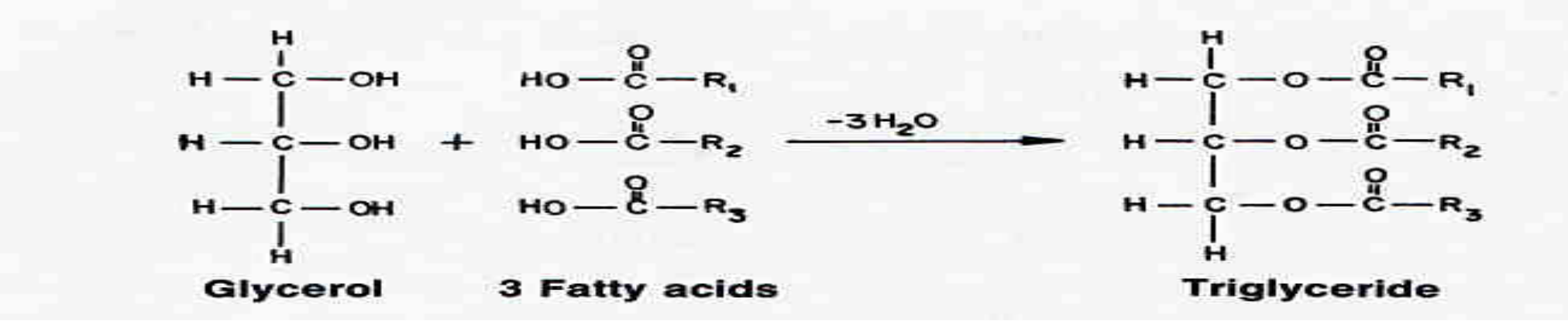
- **Alcohols associated with lipids include:** glycerol, cholesterol sphingosine and higher alcohols.

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.
- On heating with sulfuric acid or $KHSO_4$ (dehydration), it gives acrolein that has a bad odor. This reaction is used for detection of glycerol.

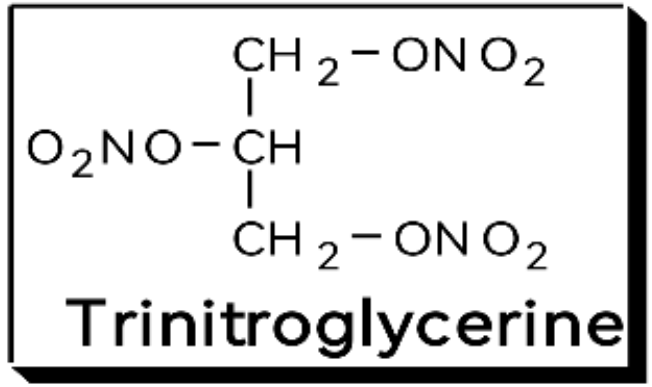


- On esterification with fatty acids it gives:
- Monoglyceride or monoacyl-glycerol: one fatty acid + glycerol.
- Diglyceride or diacyl-glycerol: two fatty acids + glycerol.
- Triglyceride or triacyl-glycerol: three fatty acids + glycerol.
- It has a nutritive value by conversion into glucose and enters in structure of phospholipids.



Uses of Glycerol:

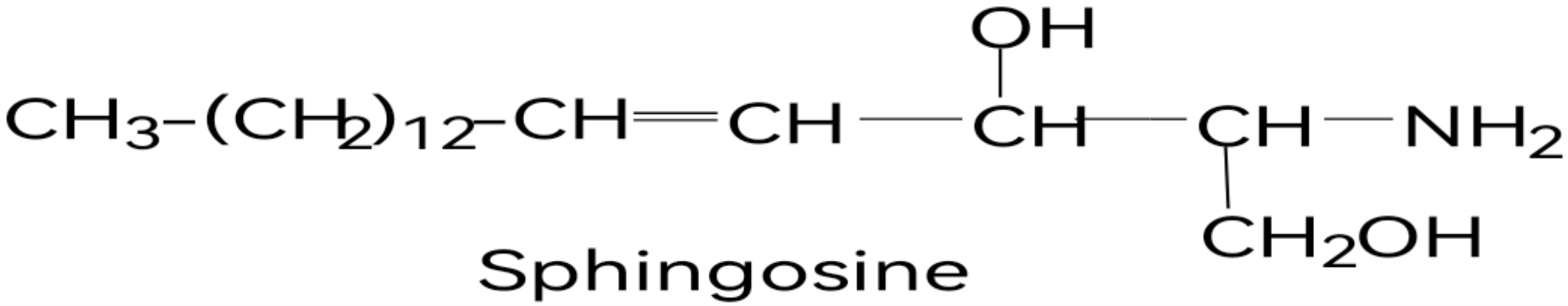
- Glycerol enters in pharmaceutical and cosmetic preparations (hygroscopic).
- Nitroglycerin is used as a vasodilator especially for the coronary arteries, thus it is used in treatment of angina pectoris.
- Glycerol is used in treatment of glaucoma (increased intraocular pressure) due to its ability to dehydrate the tissue from its water content.



Trinitroglycerine

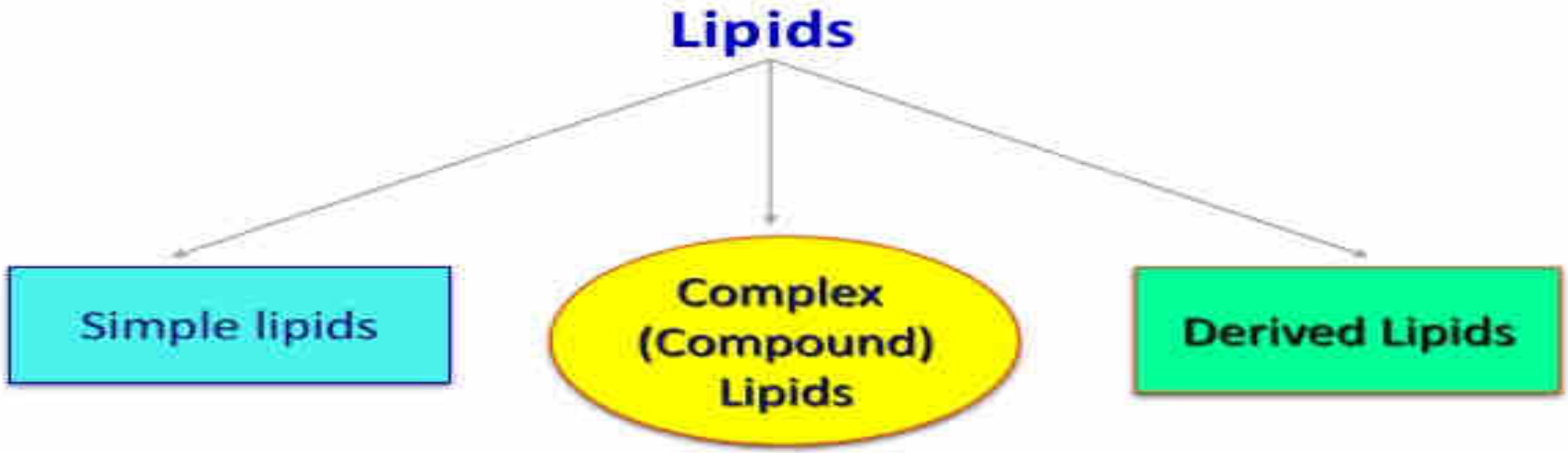
Sphingosine:

- It is the alcohol present in sphingolipids.
- It is negative with acrolein test.



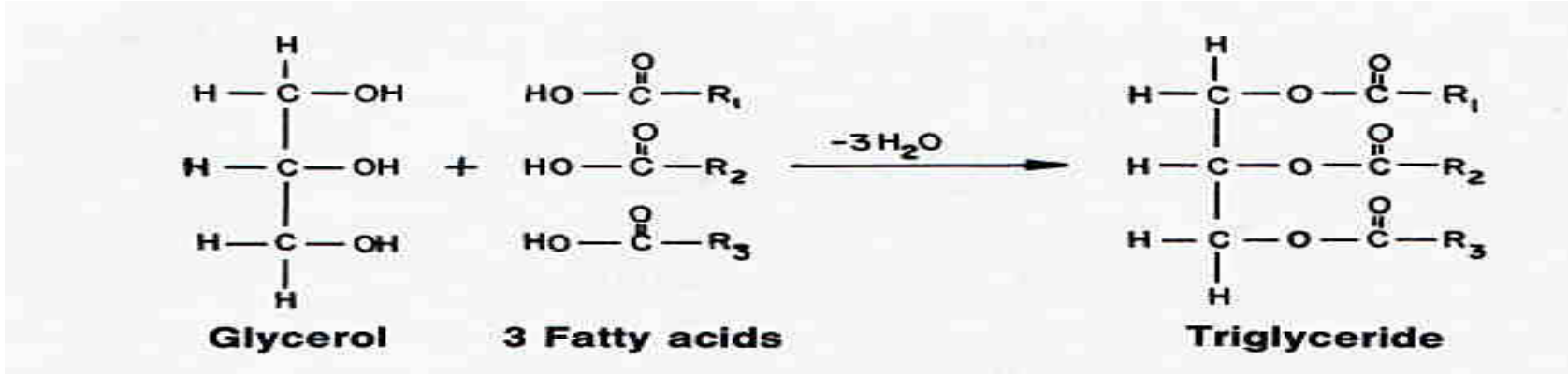
Sphingosine

Classification of lipids



I- Simple lipids:

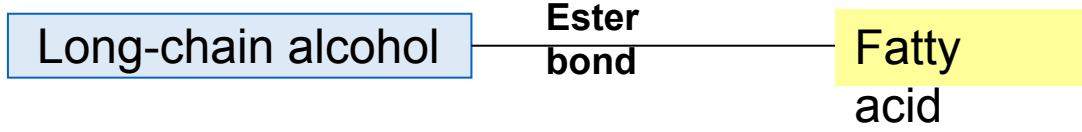
- They are esters of fatty acids with alcohol. It is neutral due to absence of ionizable groups (i.e., uncharged). They are classified according to the alcohol present into:
- **Neutral fats:** are esters of fatty acids with glycerol (triacylglycerols, or triglycerides or TAG).
- **Fats** are saturated fatty acids with glycerol. They are solid in nature.
- **Oils** are unsaturated fatty acids with glycerol. They are liquid in nature.



- **<u>Waxes:</u>** Esters of fatty acids with long-chain alcohols other than glycerol that is mostly monohydric.

- Cholesterol esters with any fatty acid are waxes.

- Esters of vitamin A and vitamin D with fatty acid are waxes, too.



II- Compound or conjugated lipids:

- They are **esters** of fatty acids and alcohols in addition to **other groups**. They include the following types:

- **Phospholipids (phosphatides):** Compound lipids containing fatty acids, alcohol, phosphoric acid and often a nitrogenous base. They are further classified according to the alcohol moiety into:

(a) Glycerophospholipids, where the alcohol is glycerol.

(b) Sphingophospholipids, where the alcohol is sphingosine.

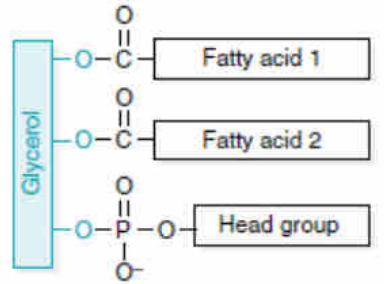
- **Glycolipids:** Compound lipids containing sphingosine, fatty acids, and carbohydrate, but not phosphoric acid nor glycerol.
- **Lipoproteins:** Compound lipids composed of a lipid part associating by secondary bonds with proteins as plasma and membranous lipoproteins.
- **Other compound lipids:** include:

Sulfolipids: containing sulfur.

Aminolipids: containing amino acids.

a) Phospholipids

- **Structure:** Phospholipids are compound lipids, which contain alcohol, fatty acids, nitrogenous base and phosphoric acid group.
- There are two classes of phospholipids according to the type of the alcohol present.

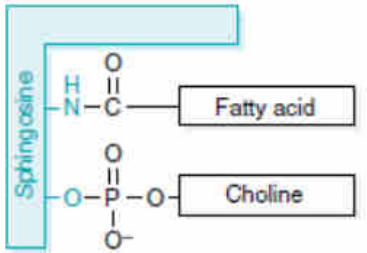


- **Glycerophospholipids (contain glycerol as alcohol)**

- Phosphatidate- Lecithins - Cephalins - Cardiolipin - Inositides - Plasmalogens

- **Sphingophospholipids (contain sphingosine as alcohol)**

- Sphingomyelins



Sphingomyelin

- **Functions:**

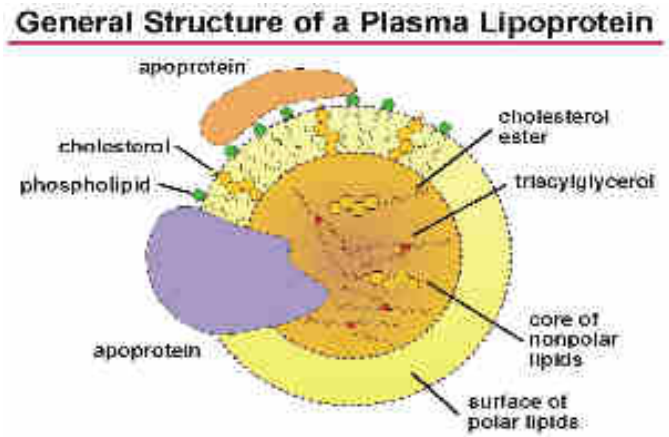
1. Phospholipids form the structural components of cell membranes and regulate membrane permeability.

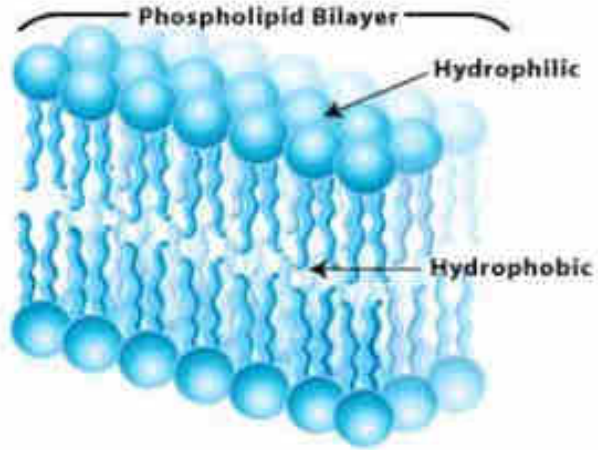
2.The subcellular organelles (endoplasmic reticulum, Golgi apparatus, mitochondria, nucleus, and lysosomes) are composed mainly of phospholipids.

3.They are important components of the lipoprotein coat help its transport and prevent fatty liver.

4.Myelin sheath of nerves is rich with phospholipids.

5.They have important functions in blood clotting and platelet aggregation (cephalin).



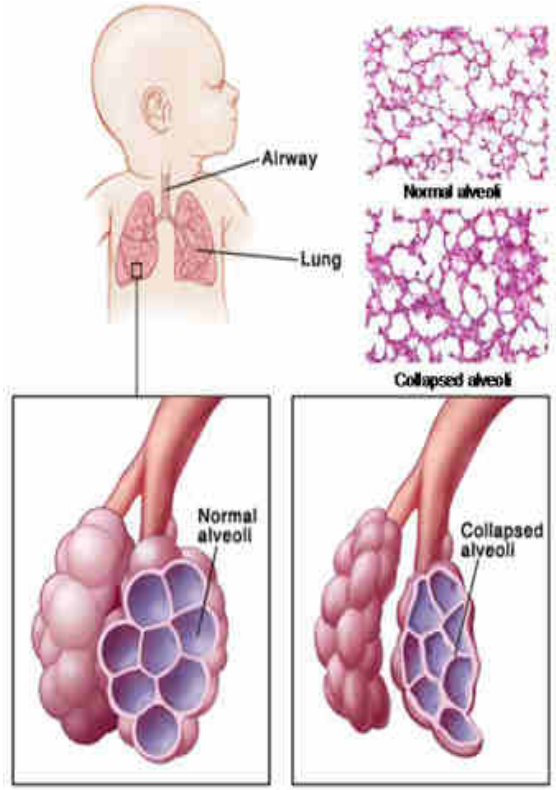


6.Dipalmitoyl Lecithin (major component of lung surfactant)

- Deficiency of lung surfactant in a newly born baby (preterm) will lead to collapse of alveoli causing Respiratory distress syndrome, that may cause death of the baby.

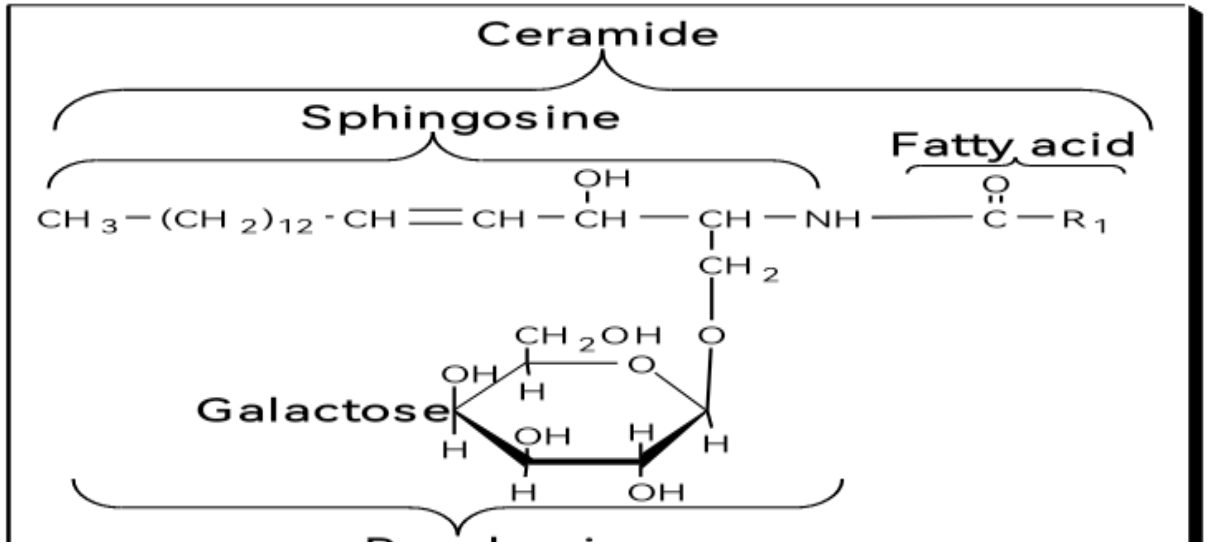
7. They have an important role in signal transduction across the cell membrane (second messenger) **(Phosphatidyl Inositol).**

8. They are source of polyunsaturated fatty acids for synthesis of eicosanoids



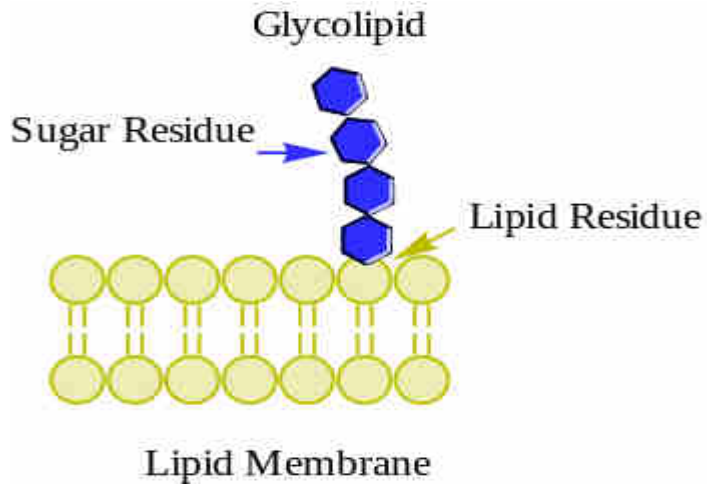
b) Glycolipids

- **structure:** 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. They are also referred as sphingogalactolipids or galactosides

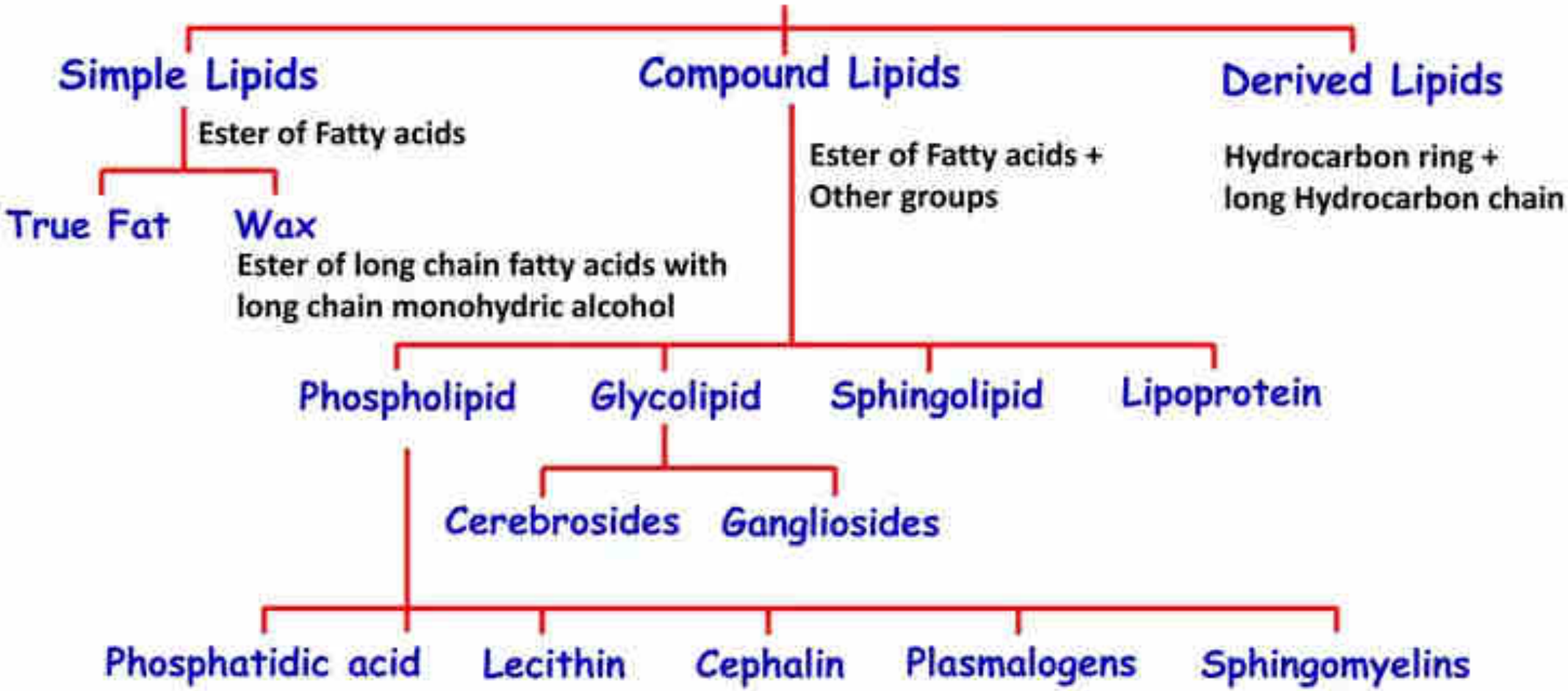


- **Classification:** According to the number and nature of the carbohydrate residue(s) present in the glycolipids, the following types exist:
- **Cerebrosides.** They have one galactose molecule (galactoside) or it may have one glucose (glucoside) or one lactose (lactoside) + ceramide.
- **Sulfatides.** They are cerebrosides with sulfate on the sugar (sulfated cerebrosides) + ceramide
- **Globosides:** two or more hexoses + ceramide.
- **Gangliosides.** They have several sugar & aminosuger residues + ceramide + sialic acid.

- **Functions:**
- Are an essential part of cell membranes
- Glycolipids (globosides) determine the blood group of the individuals.
- **Gangliosides** transfer biogenic amines across the cell membrane and **act as a cell membrane receptor for cholera and tetanus toxins**. This helps immune system to destroy and clear these pathogen from body.



Classification of Lipids



C- Lipoproteins

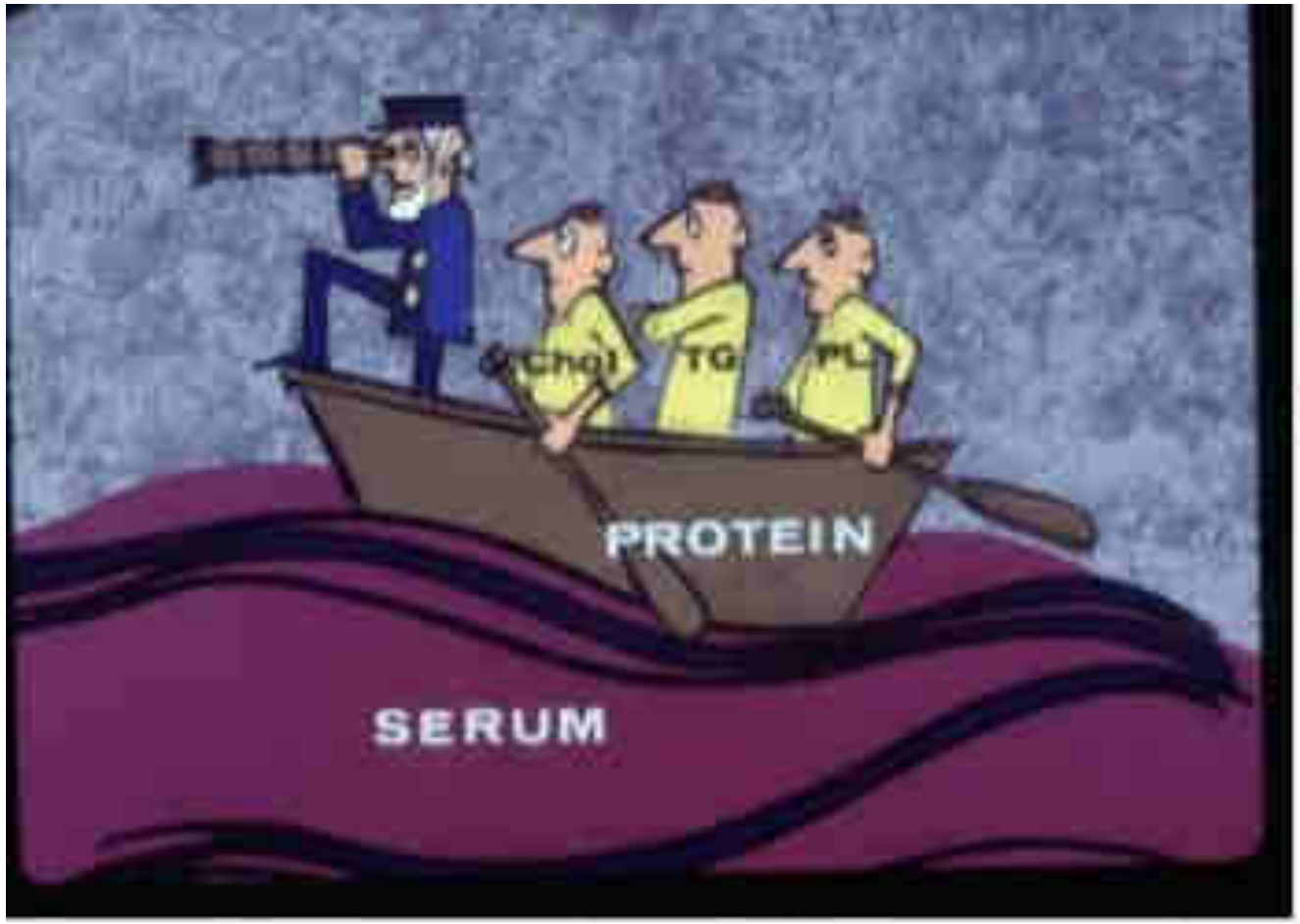
- **Definition:** spherical macromolecular complexes of lipids and specific protein called apo-protein.

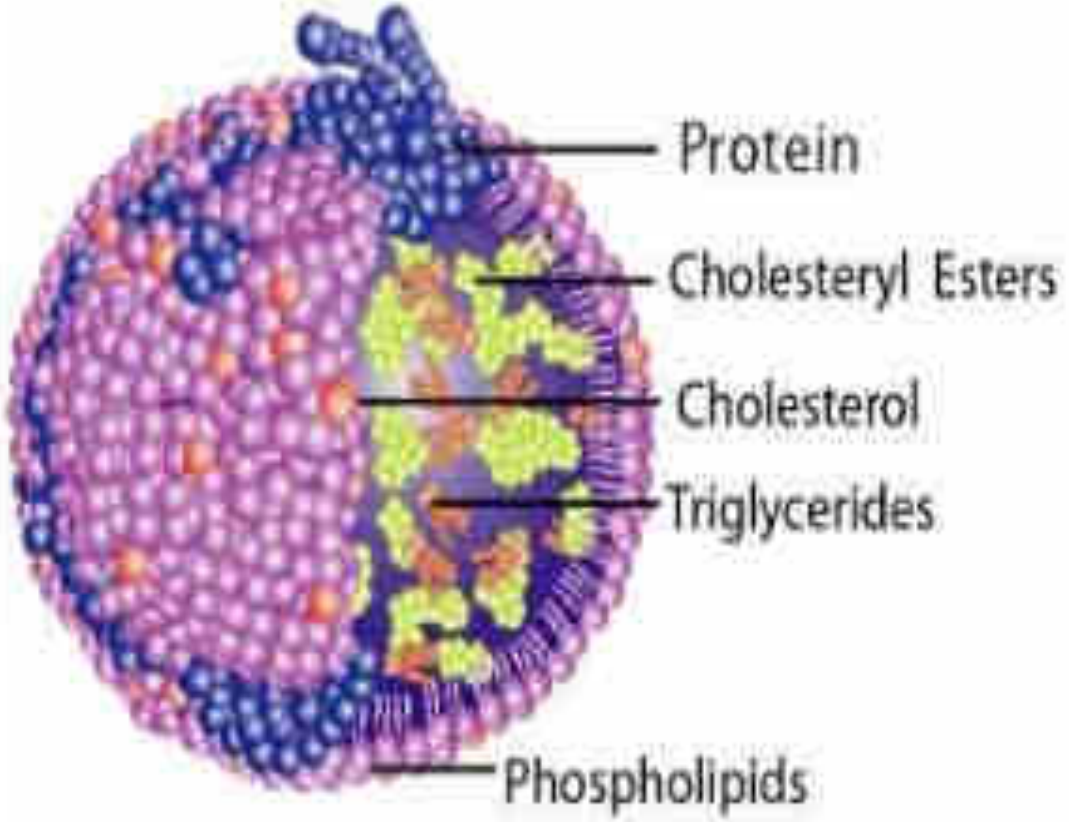
- **Functions of lipoproteins:**

1- They keep water insoluble lipids in solution of aqueous plasma.

2- Provide mechanism for transporting their lipid components to & from tissues.

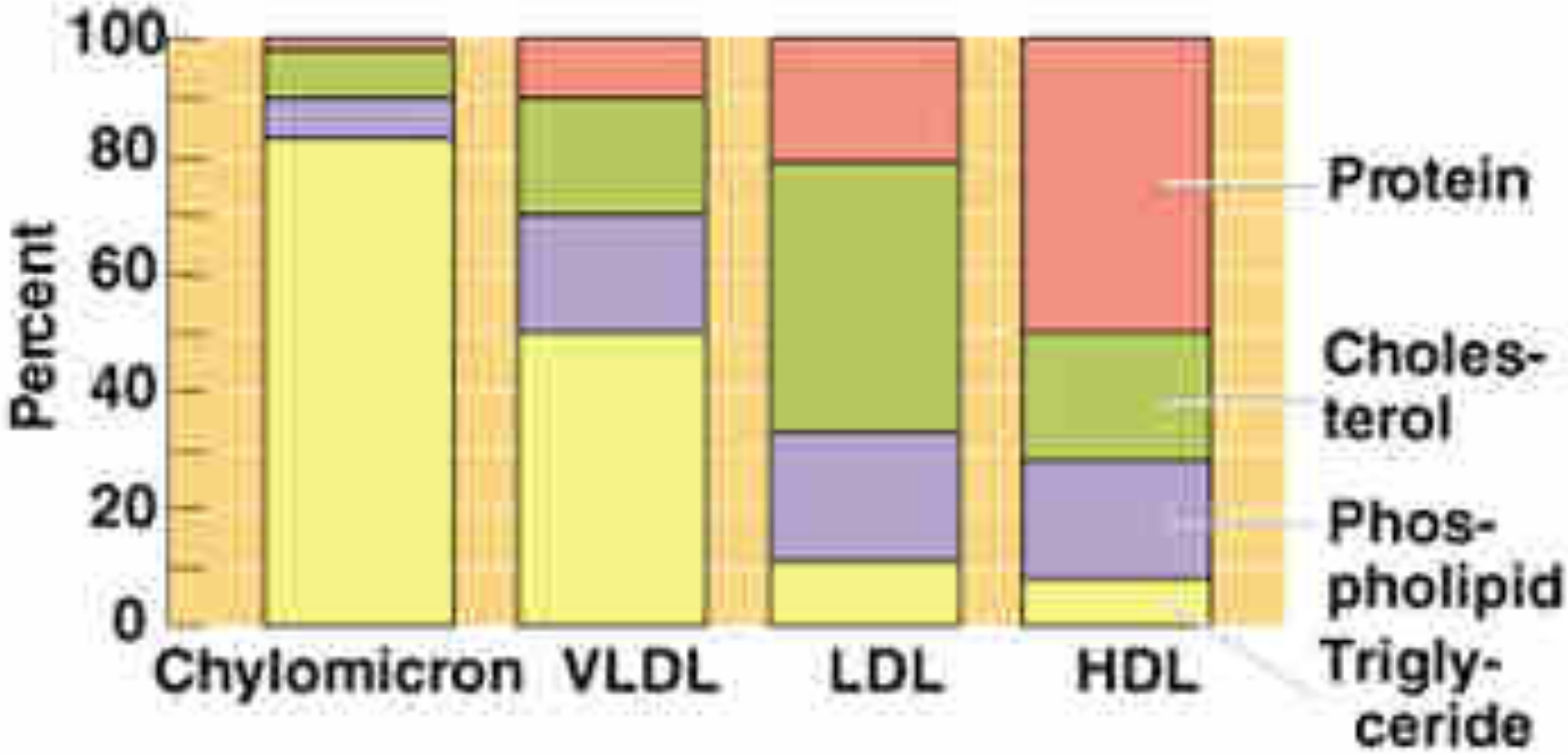
- **Classes of lipoproteins:**
- **1- Chylomicrons**
- **2- Very low density lipoproteins (VLDL)**
- **3- Low density lipoprotein (LDL or β–lipoprotein)**
- **4-High density lipoprotein (HDL or α–Lipoprotein)**
- **5-Free Fatty Acid – Albumin complex**





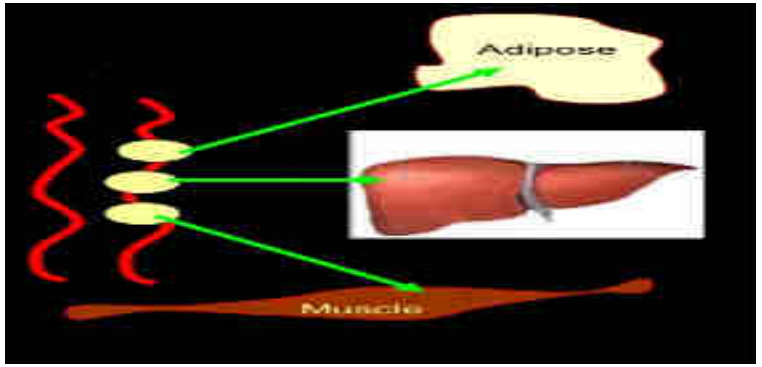
Lipoprotein

Apo-lipoprotein+ Lipid→Lipoprotein


100
80
60
40
20
0
Percent
Chylomicron
VLDL
LDL
HDL
Protein
Choles-
terol
Phos-
pholipid
Trigly-
ceride

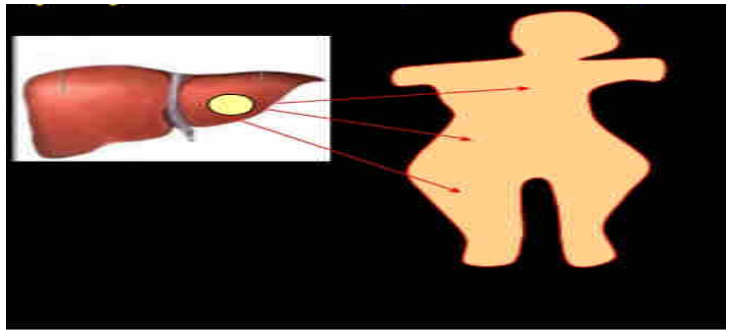
a) Chylomicrons:

- They contain 1-2% protein and 98-99% fat.
- Function: They carry triglyceride, cholesterol ester and phospholipids from the intestine to the peripheral tissues.



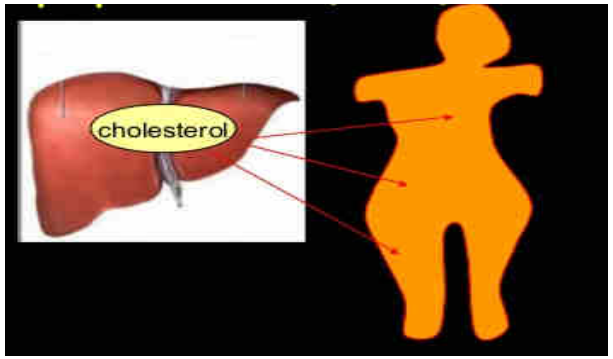
b) Very low-density lipoproteins (VLDL) or pre-β-lipoproteins:

- They contain about 7-10% protein and 90-93% lipid.
- Function: It carries triglycerides from the liver to extrahepatic tissues.



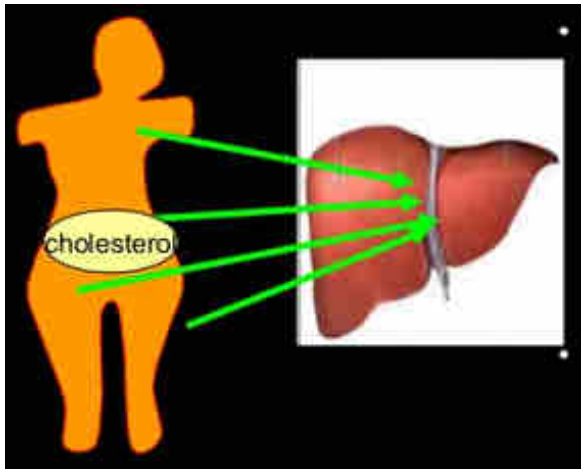
c) Low-density lipoproteins (LDL) or β–lipoproteins:

- They contain 10-20% proteins (apolipoprotein B) and 80-90% lipid.
- They contain about 60% of total blood cholesterol .
- Function: It carries cholesterol to various tissues.
- As their percentage increases in the blood, the liability to atherosclerosis increases.



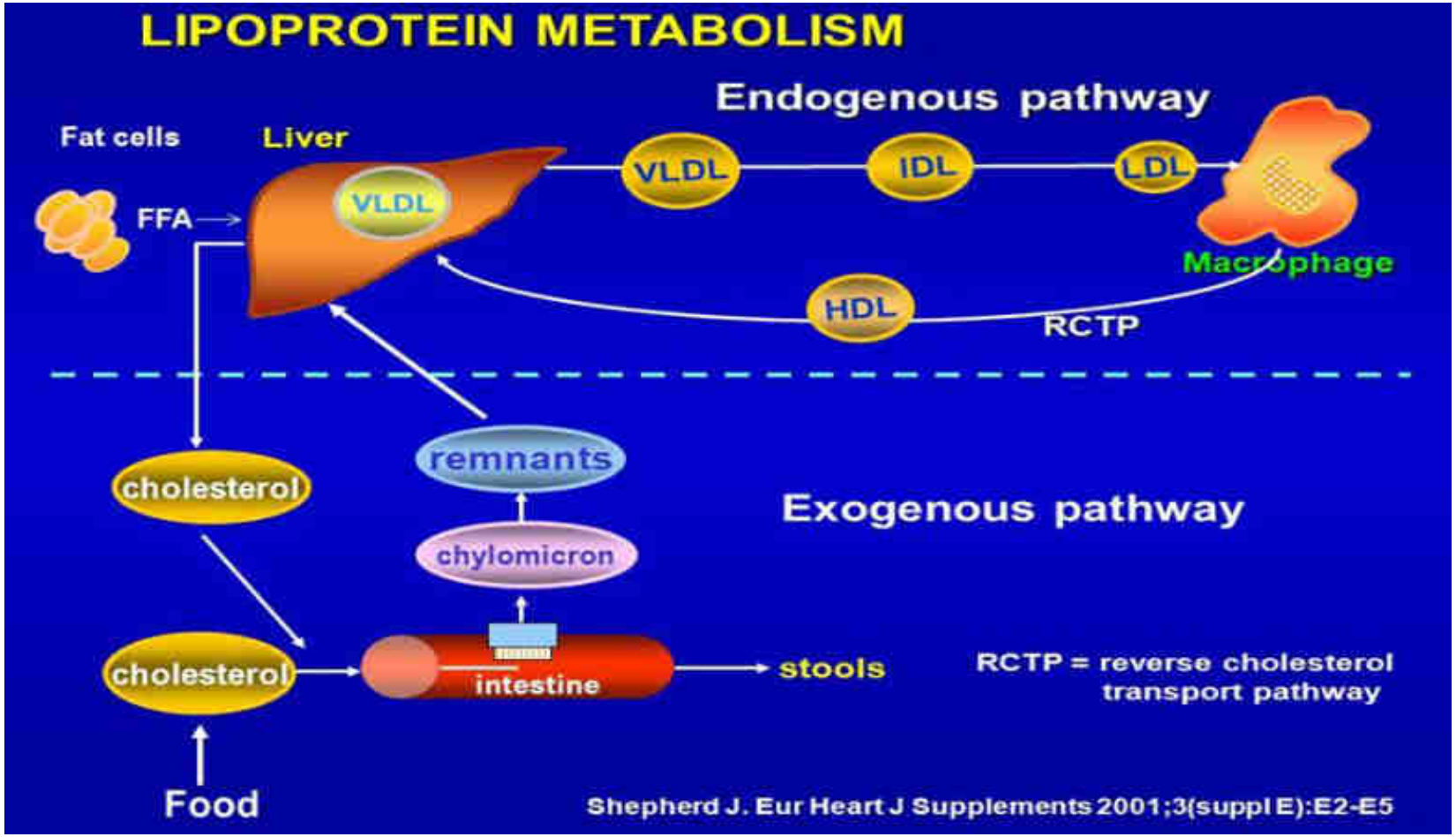
d) High-density lipoproteins (HDL) or α–Lipoproteins:

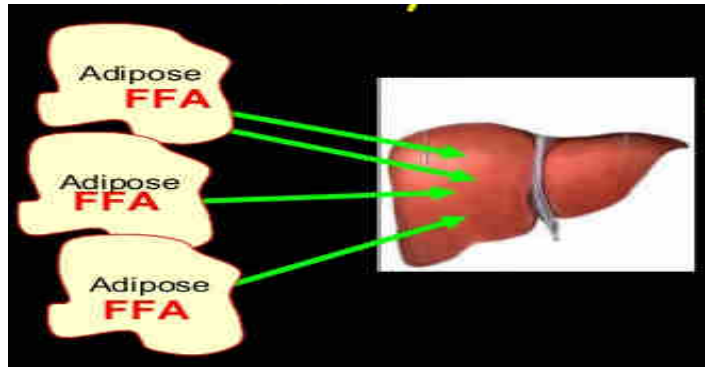
- They contain 40% proteins (apolipoprotein A) and 60% lipids.
- They contain 40% of total blood cholesterol.
- They act as cholesterol scavengers, as their percentage increases, the liability to atherosclerosis decreases.



e) Albumin-free fatty acids complex:

- It is a lipid carried on plasma albumin (99% protein +long-chain free fatty acids 1% for transporting them).
- **Summary:**





III- Derived Lipids:

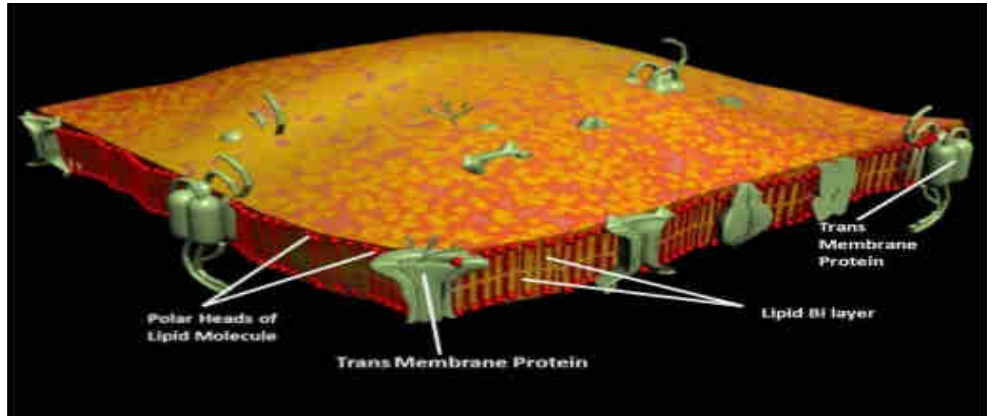
- They are products of hydrolysis of simple and compound lipids and/or their derivatives that still possess the general characteristics of lipids. They include:
- Fatty acids, monoglycerides and aldehydes.
- Alcohols including glycerol.
- steroids and hormonal derivatives of vitamin D.
- Eicosanoids (prostaglandins, leukotrienes and thromboxanes).
- Ketone bodies.

Biological Importance of Lipids

- They have a high-energy value (25% of body needs) and provide more energy/gram than carbohydrates and proteins.
- 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.
- Stored lipids "depot fat" are stored mainly in adipocytes. It is mainly triglycerides in nature and 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.

- Tissue fat “constant fat” is an essential constituent of cell membrane and nervous system. It is mainly phospholipids in nature that are not affected by starvation.



- Lipoproteins, 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 D_3 and bile acids.


Thank You
Have A Nice Day