Lipid Chemistry

Introduction to lipids:

a. Definition: Lipids Organic compounds related to fatty acids insoluble in water but soluble in organic solvents i.e. ether, benzene, acetone & chloroform.

b. The hydrophobic nature of lipids is due to the predominance of hydrocarbon chains (-CH2-CH2-CH2-) in their structure.

Biomedical Importance:

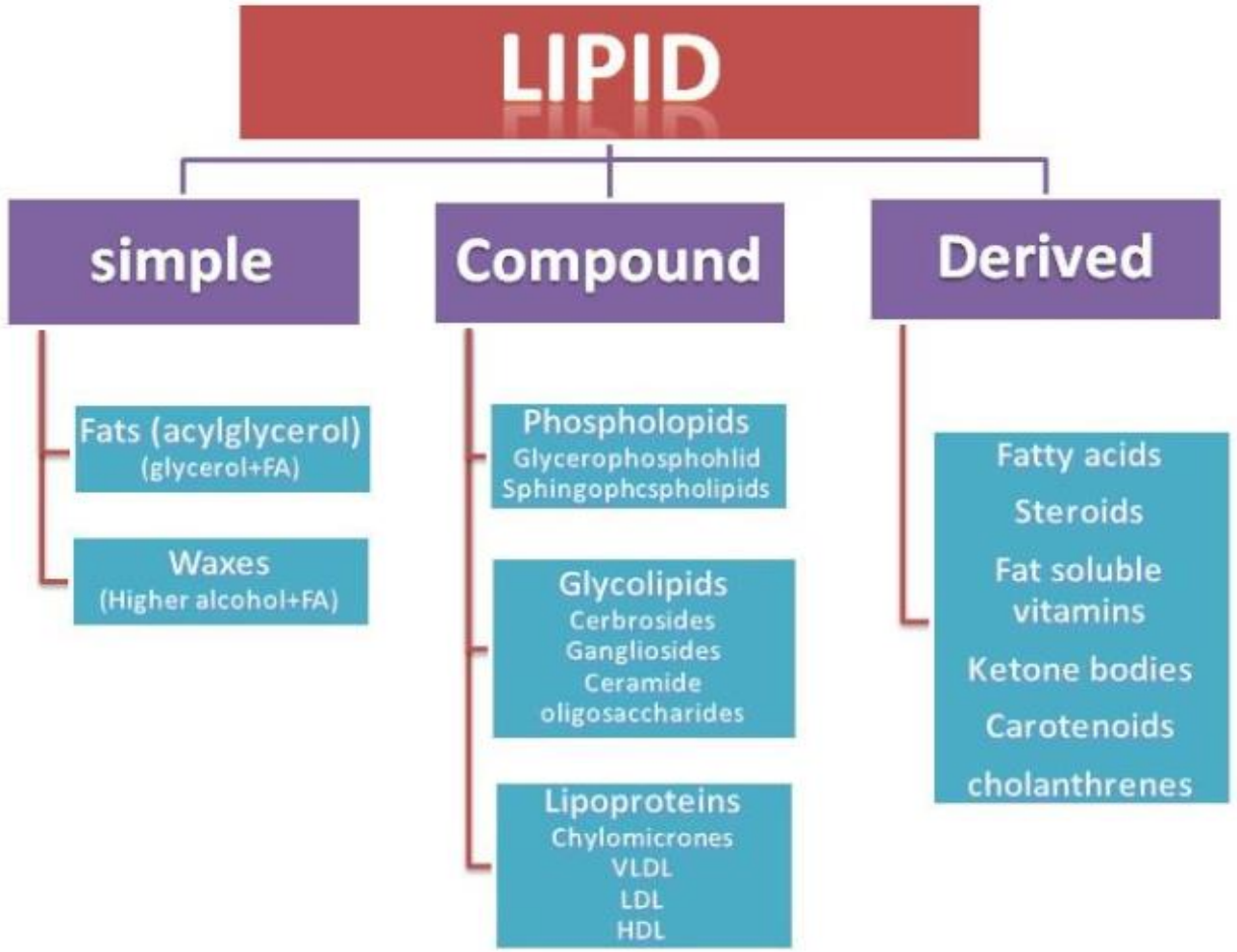
1. Source of energy: (Lipids have a high energy value)

2. Supply body e':

- Fat soluble vitamins (vit. K, E, D & A).

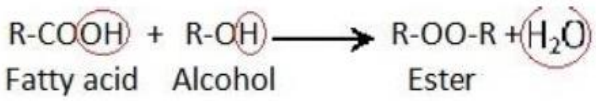
- Essential Fatty acid (a Linolenic & Linoleic acids).

Classification:



Simple lipids

- **Definition: Are esters of fatty acids with various alcohols. (Ester bond = -COO-). They are either fats or waxes.**



Fatty acids: R.COOH

- Fatty acids are water-insoluble "long chain hydrocarbons".
- They are mostly monocarboxylic i.e. having one carboxyl group at the end of the chain (-COOH).
- They are mostly aliphatic (i.e. not branched). A few branched chain fatty acids are present in **animals** and **plants.**
- Fatty acids may be Saturated: (no double bonds) or
  Unsaturated: (containing one or more double bonds).
- Fatty acids may be Essential: cannot be synthesized in the body or
  Nonessential: can be synthesized in the body.
- Fatty acids occur mainly as esters in natural fats and oils.
- Fatty acids may also present as free fatty acids (FFA) in the plasma carried on PP.
- **Short chain F.A :** less than 10 C , **long chain F.A:** more than 10 C

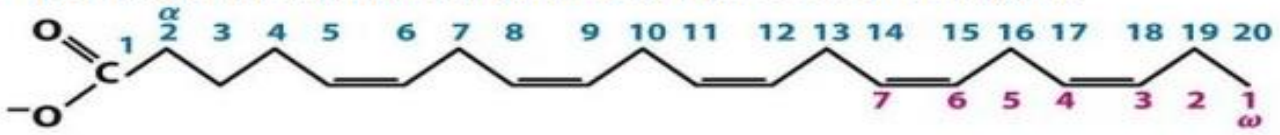
❖ **Numbering of carbon atoms:**

1. Starting from the carboxyl group:

- **1, 2, 3 system:** Give **COOH** No. 1 then proceed to the terminal CH_3.
- **α, β, system:** the 1st carbon following COOH is α then proceed to the terminal CH_3.

2. Starting from the terminal methyl group (omega "ω" carbon):

- The terminal methyl carbon is given ω_1 then proceeds to COOH group



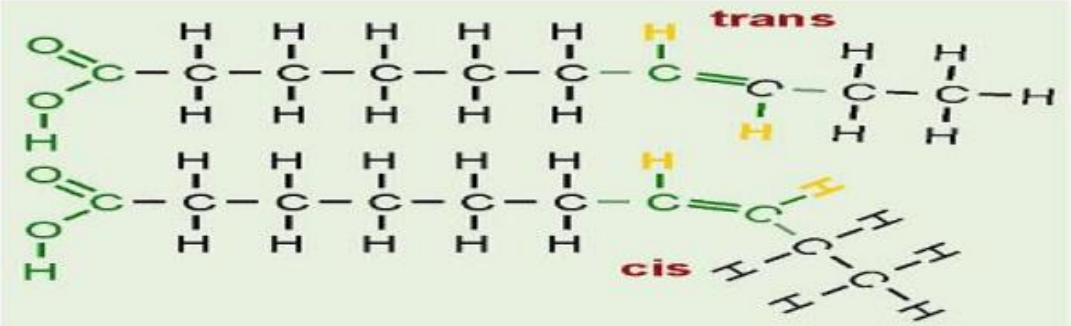
20:5($\Delta^{5,8,11,14,17}$) Eicosapentaenoic acid (EPA)

❖ **Position of double bonds:** The most commonly used systems for designating the Position of double bonds in unsaturated fatty acids are:

(1) **The delta (Δ) numbering system** e.g. palmitoleic acid **C 16:1 Δ^9** means that this acid contains 16 carbons (16) and one double bond (1) and the position of double bond is between carbon number **9** and carbon number **10** starting from **carboxyl carbon 1**

(2) **Omega (ω) system** e.g. the palmitoleic acid may be written as: **C 16:1 ω^7** which indicates a double bond on seventh carbon counting from the ω-carbon atom i.e. last **$-CH_3$** carbon.

- **Cis and Trans double bonds:** Double bonds in naturally occurring fatty acids in mammals are always in a **Cis** form (configuration) not as Trans form: polyunsaturated acids:
  - **a) Cis** form that the groups are on the **same** side.
  - **b) Trans** form means that the groups are on the **opposite** sides.
  - Trans fatty acid may be present in certain foods, during hydrogenation of oils to manufacture margarine.



❖ **Aliphatic & Branched chain fatty acids:**

Almost all fatty acids present in mammalian tissues are **aliphatic** i.e. straight chain. However, branched- chain fatty acids are found in nature.

A. **Phytanic acid (18C):**
- Some **milk** products contain branched chain fatty acids called **Phytanic acid** it contains 4 methyl groups at position 3, 7, 11 and 15 carbons.

B. **Refsum's disease:**
1. It is caused by inability of **oxidation** of Phytanic acid this leads to its accumulation in plasma and tissues.
2. Manifestations: nervous tissue damage in the form of **blindness** and **deafness.**

❖ **Saturated & Unsaturated fatty acids**

i. **Saturated fatty acids**
- Have no double bonds in the chain.
- Their general formula is **$CH3-(CH_2)_n-COOH$** where (n) equals the number of methylene (-CH2) groups between the methyl and carboxylic groups.
- The systemic name of saturated fatty acids ends by the suffix (-anoic) e.g. palmitic acid (16c) has systemic name hexadecanoic acid (Hexa =6, Deca =10).

- **Example of the formula of some saturated fatty acids:**
  - **Butyric acid (4c)** = $CH_3- CH_2- CH_2- COOH$
  - **Palmitic acid (16c)** = $CH_3 - (CH2)_{14} - COOH$
  - **Stearic acid (18c)** = $CH_3 - (CH2)_{16} – COOH$

Name	N.O of C	occurrence
Formic	1	Takes part in the metabolism of "C_1" units (formate)
Acetic	2	Major end product of carbohydrate fermentation by rumen organisms.
Propionic	3	
Butyric	4	In certain fats in small amounts (especially butter).
Palmitic acid	16	Common in all animal and plant fats
Stearic acid	18	
Arachidic	20	Peanut (arachis) oil

ii. Unsaturated fatty acids:

- The general formula is **(Cn- H_{2n-1}- COOH).**
- The systemic name of unsaturated fatty acids ends by the suffix **(-enoic)** e.g. **oleic acid** (18c) has systemic name octadecenoic acids.
- Unsaturated fatty acids are either **monounsaturated** or **polyunsaturated**.

❖ **Monounsaturated fatty acids** (**monoethenoic, monoenoic**) i.e. contain **one** double bond e.g. **palmitoleic** acid (16:1 Δ^9) and **oleic** acid (18:1 Δ^9).

ω9,C18:1 *or* n–9, 18:1

$$\overset{\omega}{\underset{n}{CH_3}}\overset{2}{\underset{17}{CH_2}}\overset{3}{CH_2}\overset{4}{CH_2}\overset{5}{CH_2}\overset{6}{CH_2}\overset{7}{CH_2}\overset{8}{CH_2}\overset{9}{\underset{10}{CH}}=\overset{10}{\underset{9}{CH}}(CH_2)_7\overset{18}{\underset{1}{COOH}}$$

Oleic acid.

❖ **Polyunsaturated fatty acids** **(essential fatty acids=polyethenoic =polyenoic fatty acids =PUFA)** Containing **more than one** double bond: e.g

- In polyunsaturated F.A. each 2 double bonds are separated by methylene group **($-CH_2$)**
- **PUFA** are classified according to the position of the 1st double bond in relation to ω carbon into ω_3, ω_6, ω_7 & ω_9 F.A.

▪ **ω_3 PUFA:**

i. PUFA having the 1st double bond at carbon **3** in relation to ω carbon
ii. E.X:
   1. α Linolenic acid (18:3) —> Parent FA
   2. Timnodonic acid (20 : 5)
   3. Cervonic acid (22 : 6)
      • α Linolenic is the precursor of other members of this group in the body.

- **ω_6 PUFA:**
  1. Linoleic acid (18:2) —> Parent FA
  2. γ Linolenic acid (18:3)
  3. Arachidonic acid (20:4)

a) **Linoleic** (**18:2** $\Delta^{9,12}$, ω^6) and lenolenic (**18:3** $\Delta^{9,12,15}$, ω^3):
   1. They are present in linseed oil.

b) **Arachidonic acid** (**20:4** $\Delta^{5,8,11,14}$, ω^6).
   1. It is present in peanut oil
   2. It is a component of phospholipids in animal.
   3. It is a precursor of a group of compounds called: **eicosanoids**.

Number of C Atoms and Number and Position of Double Bonds	Family	Common Name	Systematic Name	Occurrence
Monoenoic acids (one double bond)				
16:1;9	ω7	Palmitoleic	*cis*-9-Hexadecenoic	In nearly all fats.
18:1;9	ω9	Oleic	*cis*-9-Octadecenoic	Possibly the most common fatty acid in natural fats.
18:1;9	ω9	Elaidic	*trans*-9-Octadecenoic	Hydrogenated and ruminant fats.
Dienoic acids (two double bonds)				
18:2;9,12	ω6	Linoleic	all-*cis*-9,12-Octadecadienoic	Corn, peanut, cottonseed, soybean, and many plant oils.
Trienoic acids (three double bonds)				
18:3;6,9,12	ω6	γ-Linolenic	all-*cis*-6,9,12-Octadecatrienoic	Some plants, eg, oil of evening primrose, borage oil; minor fatty acid in animals.
18:3;9,12,15	ω3	α-Linolenic	all-*cis*-9,12,15-Octadecatrienoic	Frequently found with linoleic acid but particularly in linseed oil.
Tetraenoic acids (four double bonds)				
20:4;5,8,11,14	ω6	Arachidonic	all-*cis*-5,8,11,14-Eicosatetraenoic	Found in animal fats and in peanut oil; important component of phospholipids in animals.
Pentaenoic acids (five double bonds)				
20:5;5,8,11,14,17	ω3	Timnodonic	all-*cis*-5,8,11,14,17-Eicosapentaenoic	Important component of fish oils, eg, cod liver, mackerel, menhaden, salmon oils.
Hexaenoic acids (six double bonds)				
22:6;4,7,10,13,16,19	ω3	Cervonic	all-*cis*-4,7,10,13,16,19-Docosahexaenoic	Fish oils, phospholipids in brain.

❖ **Essential and nonessential fatty acids:**

A. Nonessential fatty acids:

1. These are fatty acids which **can be synthesized in the body**. Thus they are not necessary to be obtained from the diet.
2. They include all **saturated** and **monounsaturated** fatty acids as **palmitoleic** and **oleic acid**.
3. They can be synthesized from acetyl COA (active acetate) derived from glucose oxidation.

B. Essential fatty acids:

a) These are fatty acids that **cannot be synthesized in the body**. They must be obtained from the diet.

b) They include fatty acids that contain more than one double bond **(polyunsaturated fatty acids)** e.g. **lenoleic, lenolenic, arachidonic** acids.

c) The human body has enzyme system that can form only **one double bond** at the **ninth** carbon atom.

Sources:

a) Vegetable oils e.g. corn oil, soya bean oil, safflower oils, sunflower, linseed oil and cotton seed oil.

b) Fish oils: shark liver oils, which particularly contain the ω^3 polyunsaturated fatty acids.

Importance:

a) Normal growth.

b) They enter in the structure of phospholipids and cholesterol esters.

c) They enter in the structure of **cell membranes** and are required for the fluidity of membrane structure.

d) They protect against **atherosclerosis** and **coronary heart disease** by **decreasing** free cholesterol and LDL.

❖ Eicosanoids

A. **Definition:** These are **cyclic** compounds that derived from **arachidonic** acid (eicosatetraenoic)(20 C) after cyclization of its carbons chain to form a ring.

- Hormone like molecules produced by most mammalian cells
- Active within the cell in w' they are produced (autocrine) or on adjacent cells (paracrine)
- Have many physiological & pathological & Pharmacological actions

B. Components of eicosanoids:

1. **Prostanoids:** which comprise **prostaglandins, prostacyclins** and **thromboxanes.**
   a) **Prostaglandins (PG)**
      1) **PGE_2**: vaso**dilata**tion, relaxation of the uterus and intestine.
      2) **PGF_2** : vaso**constric**tion, **contraction** of the uterus and intestine.
   b) **prostacyclins**
      They cause **vasodilatation** and inhibit platelets aggregation
   c) **thromboxanes**
      They cause platelets aggregation

2. **Leukotriens (LT):**
   a) They are present in **leucocytes, platelets** and **mast cells.**
   b) They cause **chemotaxis** i.e. Collection of white blood cells at the site of inflammation (↑ vascular permeability).

❖ **Properties of fatty acids:**

A. Physical properties:

1. **Solubility:**
   a) **Short chain fatty acids** e.g. acetic (2C), butyric (4C) and caproic (6C) are **soluble in water**
   b) **Long chain fatty acids** are **insoluble in water** but soluble in nonpolar fat solvents.
2. **Melting point :** It depends on the **length** of the chain of fatty acids and the **degree of unsaturation**, so:
   a) **Short chain** and **unsaturated** fatty acids are **liquid** at room temperature.
   b) **Long chain saturated** fatty acids are **solid** at room temperature.

B. Chemical properties:

❖ **Properties due to "COOH" group:**

1. **Salt formation (soap):** Fatty acids form soap (salts) with **alkalies** as NaOH, KOH, $Ca(OH)_2$:

$$\underset{\text{Fatty acid}}{RCOOH} + \underset{\text{Sodium hydroxide}}{NaOH} \longrightarrow \underset{\text{Sodium salt}}{R.OOONa} + H20$$

2. **Ester formation:**
   a) Fatty acids form **esters (R.COO.R)** with **alcohols:**

$$R.COOH + R_1.OH \longrightarrow R.COOR_1 + H_2O$$

   1) Esters of fatty acids with glycerol ⟶ **Neutral fats (Acylglycerols).**
   2) Esters of fatty acids with higher alcohols ⟶ **waxes**
3. **Reduction:**

$$\text{Fatty acid (R-COOH)} \xrightarrow{2H,\ -H_2O} \text{F. aldehyde (R-CHO)} \xrightarrow{2H} \text{F. alcohol (R-CH}_2\text{OH)}$$

❖ **Properties due to double bond:**

2. **Hydrogenation, halogenation and oxidation:** These are

a) Hydrogenation: $-CH=CH- \xrightarrow{2H + Heat + Nickel} -CH_2 - CH_2-$

b) Halogenation: $-CH=CH- \xrightarrow{2\ I} -\overset{I}{C}H-\overset{I}{C}H-$

C) Oxidation: $-CH=CH- \xrightarrow{2\ O} -\overset{O-O}{C}H-\overset{O-O}{C}H-$ Peroxide

Alcohols: R.OH

I. Introduction: Alcohols associated with lipids include **glycerol, cholesterol and higher alcohols** (e.g. cetylalcohol, $C_{16}H_{33}OH$) usually found in the **wax.**

II. Glycerol: It is polyhydric alcohol containing 3 (-OH) groups:

- **Properties:**
  1. Glycerol is colorless, odorless, and hygroscopic and has sweet taste.
  2. It is soluble in **water and alcohol** insoluble in **nonpolar solvents**
  3. It combines with one fatty acid to form monoacylglycerol, and so on

- **Acrolein:** It is an aldehyde substance with a characteristic odour. It derives from glycerol by losing 2 water molecules.
- **Uses of Glycerol:**
  1. Nitroglycerol is used as a drug for dilatation of coronary artery.
  2. Glycerol enters in manufacturing of creams and lotions for dry skin

III Cholesterol: is an alcohol and derived lipids (see later)

IV. Higher alcohol: long chain contain **one (-OH)** group i.e. monohydric alcohols.

Simple lipids

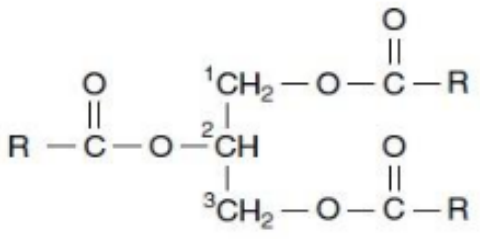
A. They are called simple because they are formed only from **alcohols** and **Fatty acids**. There are two classes of simple lipids (according to the type of alcohol): **acylglycerols** and **waxes**.

- **Acylglycerols** are esters of **one**, **two** or **three** fatty acids with **glycerol**

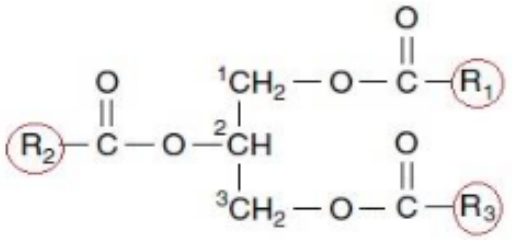
B. Numbering of carbons of glycerol is either: **α, β** and **γ** or **1, 2** and **3**. **Notice that** carbon **1** and **3** of glycerol in Triacylglycerols are not identical when viewed in 3 dimensions. Enzymes can differentiate between the two positions.

i.Triacylglycerols (triglycerides):

- They are called neutral fat because they carry **no** charge.
- **Body triacylglycerols:**
  - Location: They are stored mainly in cytoplasm of adipose tissue cells (which is located subcutaneously and around kidney and other organs).
  - Body fat is important source of energy. Each gram fat gives 9.3
  - Human fat is liquid at room temperature and contains high contents of oleic acid.
- **Dietary sources of triacylglycerols:**
  - In animals e.g. butter and lards.
  - In plants e.g. Cotton seed oil, linseed oil, sesame oil and olive oil.
  - Marine oils e.g. cod liver oil and shark liver oil.
- **Types of triacylglycerols:**
  - Simple triacylglycerols: similar 3 fatty acids are attached to **glycerol**.
  - Mixed triacylglycerols: 3 different fatty acids are attached to **glycerol**.



Simple triacylglycerols



Mixed triacylglycerols

❖ **properties of triacylglycerols:**

A. Physical properties:

a. **Solubility: All** triacylglycerols are insoluble in water, soluble in fat solvents.

b. **Melting point:**

- Triacylglycerols rich in unsaturated F.A. are **liquid** at room temperature. **"Oils"**.
- Triacylglycerols rich in saturated F.A. are **solid** at room temperature **"Fats"**.

c. **Specific gravity:** It is **less** than **one**. Specific gravity of water is one Therefore, triacylglycerols float on the surface of water.

d. **Grease stain test:** All Triacylglycerols give **+ve** grease stain test.

B. Chemical properties:

1. **Hardening (Reduction):**

Def: Hydrogenation of oils to form solid fat or margarine

As: USFA are converted to SEA

2. **Hydrolysis of TAG:**

a. **Acid Hydrolysis:**

Boiling TAG with acids ⟶ Glycerol + 3FAs

b. **Alkaline Hydrolysis (Saponification):**

- **Def:** Hydrolysis of TAG using alkalis
- **Produces:** Glycerol & Soap
- **Soap:** Alkaline salt of FA

TAG + 3KOH ⟶ Glycerol + 3RCOOK (K soap)

c. **Enzymatic Hydrolysis:**

TAG by lipase enzyme gives glycerol & 3 FAs

3. **Rancidity:**

Def: Development of toxic compound with bad flavor (odor & taste) of fats or oils duo to oxidation of USFA.

Types: Hydrolytic & oxidative.

1. Hydrolytic Rancidity:

Cause: Due to presence of **(H2O)** OR **Bacteria** (Contain lipase enzyme).

- Lipase causes release of short chain F.As which are volatile.

2. Oxidative Rancidity:

- Oils are more liable to develop this type of rancidity **why?**

As: they are rich in USFA.

- Oxidation at USFA → Peroxides, ketones & aldehydes → Bad flavor

Q: Addition of vit. E, phenols & quinones may prevent oxidative rancidity why?

As: They are antioxidants so protects USFA against oxidation.

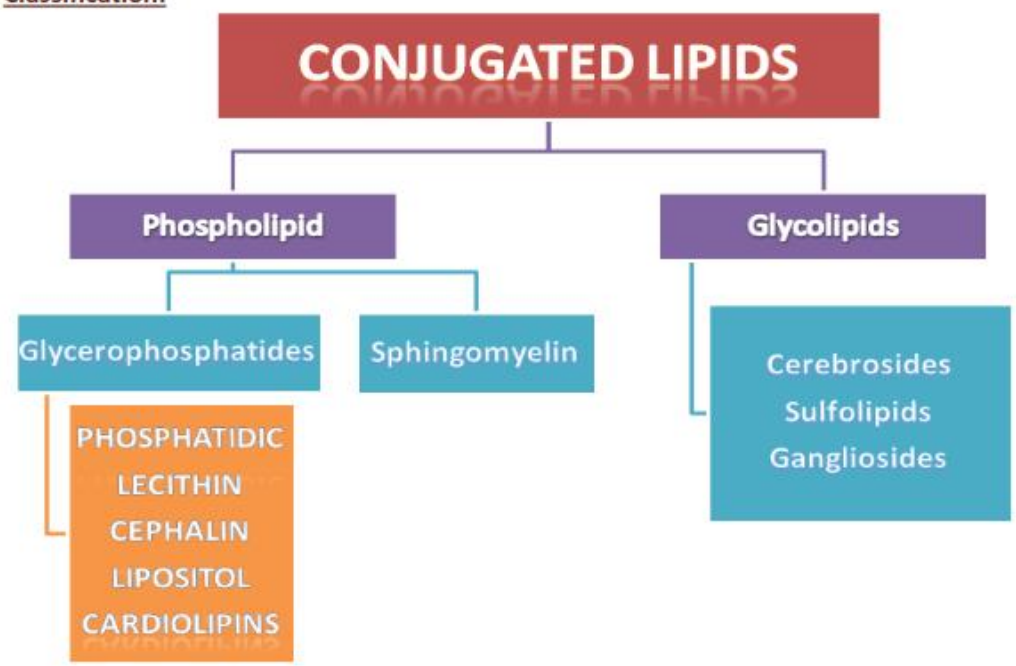
ii.Waxes

- **Def**: Esters of long chain FA **with** long chain alcohols contain **one (-OH)** group.
- **Site**: Trunks of trees & fur of animals
- **Function:** Acts as a protective coat
- **Examples**:
  1. **True wax (Bee's wax):** Esters of **palmitic** acid e' **mericyl** alcohol (C30)
  2. **Lanolin (in hair):** Esters of cholesterol derivatives
  3. **Vit A** (Retinol) esters
  4. **Vit D** (Calciferol) esters
- **Properties:**
  1. They have the same physical properties as fat.
  2. They give negative **Acrolein** test because they contain no glycerol.
  3. They are not digested by lipase enzyme. Thus they are not utilized.
  4. They are solids at room temperature.

	Triacylglycerols	Waxes
Composition	Contain glycerol i.e. give positive **Acrolein** test.	Contain no glycerol so, give negative **Acrolein** test.
Melting point	At room temperature: they are either solids or liquids	At room temperature, they are solids.
Rancidity	They may undergo rancidity.	They do not undergo rancidity.

Conjugated Lipids

- **Def:** Simple lipids conjugated with another group.
- **Classification:**



Phospholipids

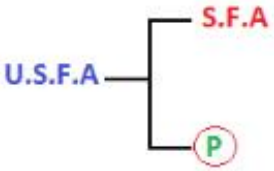
❖ **Classified according to the alcohol present into**

A. Glycerophosphatides (Phosphoglycerides): Containing **(glycerol)**

B. Sphingomyelin: Containing sphingosine **(sphingol)**

Glycerophosphatides (Phosphoglycerides)

- Phospholipids containing **glycerol** as alcohol
- They are derivatives of phosphatidic acid.



1. **Phosphatidic acid:**
   - Diacylglycerol phosphate
   - Formed during synthesis of TAG & phospholipid
   - FA at **position 1** is SFA & at **position 2** USFA
   - Other Phosphoglycerides are formed by conjugation of different groups to phosphate
2. **Lecithin (Phosphatidyl Choline):**
   - **Structure:** Formed of phosphatidic acid + Choline
   - **Functions:**

- Enters in the structure of **cell membrane**.
- Acts as **lipotropic** factor. I.e. prevent fatty liver.
- Forms cholesterol ester, Cholesterol esters are transported to the liver, and excreted with bile, This prevent **atherosclerosis**.

Lecithin + Cholesterol $\xrightarrow{\text{LCAT}}$ **Cholesterol ester + lysolecithin**

- Lecithin acts as body store of **Choline**. Choline is important for:

i- Nerve transmission. ii- Transmethylation: It acts as methyl donor

- **Dipalmityl lecithin** (i.e. lecithin which contains 2 palmitic acid residues) Act as a **surfactant in lung**

i- Dipalmityl lecithin is continuously secreted by the lung cells in the alveolar wall, forming a monolayer over the watery surface of the alveolus and so lowers the surface tension this helps expiration and inspiration

- **During expiration**, the surfactant becomes **solid** under pressure. This prevents the adherence of alveolar wall.
- **During inspiration,** The surfactant makes the lung easier to expand.

❖ **Respiratory distress syndrome** (hyaline membrane disease):

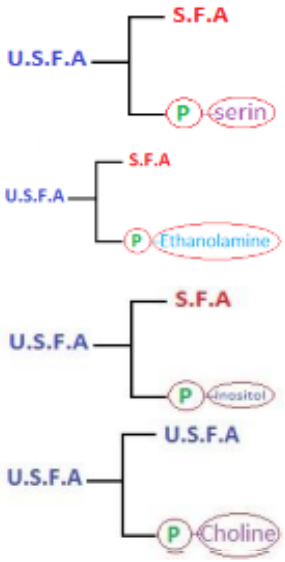
- In premature babies, lungs do not secrete enough surfactant. This leads to lung collapse and death from respiratory failure.

- **Treatment** of this case needs putting the premature babies in incubator and administration of surfactant locally in the lung.

3. **Phosphatidyl serine:**
   - Formed of phosphatidic acid + serine
4. **Cephalin (Phosphatidyl ethanolamine):**
   - **Structure:** Formed of phosphatidic acid + ethanolamine
   - **Functions:** coagulation mechanism activating factors
5. **Phosphatidyl Inositol (Lipositol):**
   - **Structure:** Formed of phosphatidic acid + Inositol
   - **Functions:** acts as precursor of 2nd messenger "IP_3"
6. **Plasmalogens:**
   - **Structure:** Same structure as lecithin but FA at position 1 is replaced by unsaturated fatty alcohol
   - **Functions:** present in brain & muscles "Lipophilic antioxidants".
7. **Cardiolipins (Diphosphatidyl glycerol):**
   - **Structure:** Formed of 2 molecules of phosphatidic acid connected by 1 molecule of glycerol
   - **Hydrolytic products:** 4FA + 3 Glycerol + 2 Phosphate
   - **Functions:**

   1. Cardiolipins is the major lipid in mitochondrial membrane.

   2. It stimulates antibody formation i.e. antigenic



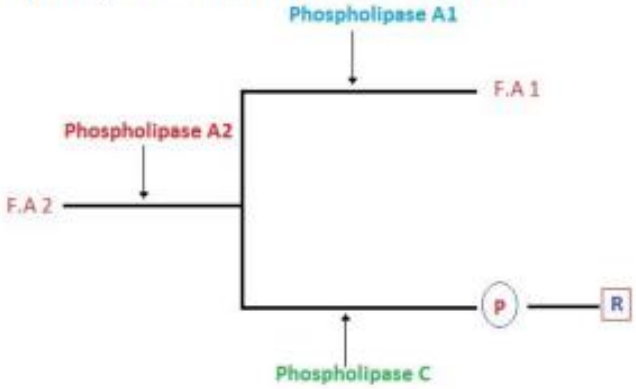
8. **Lysophospholipids:**
   - **Structure:** Like lecithin and Cephalin, but contains only **1** fatty acid in position**1**
   - **Functions:**

   1. **Lysolecithin** is important in metabolism.

   2. **Lysocephalin** is strong surface-active substance. It is used in manufacturing most types of chocolates.

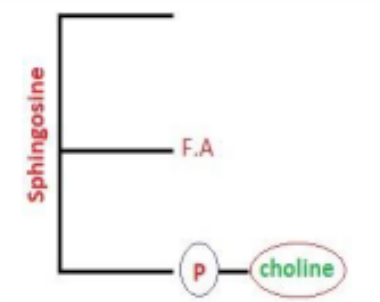
Hydrolysis of Glycerophosphatides

By Phospholipases: Hydrolyzes different phospholipids



Sphingomyelin

- **Structure:**
  1. Sphingosine.
  2. Fatty acid attached to amino group at position 2.
  3. Phosphate at position3.
  4. Choline base (attached to phosphate).



- **Functions:**
  - It is present in high concentrations in brain and nerve tissue
- **Niemann Pick's disease:**
  1. It is accumulation of large amounts of Sphingomyelin in liver due to deficiency of sphingomyelinase enzyme.
  2. It leads to mental retardation and death in early life.

GLYCOLIPIDS

- Formed of ceramide (Sphingosine + FA) attached to carbohydrates.
- Includes cerebrosides, Sulfolipids & Gangliosides.

1. **Cerebrosides:**
   - **Structure:** • Formed of **ceramide** + → Glucose (glucocerebroside). / Galactose (galactocerebroside).
     • FA contain **24** carbons → Cerebronic OR Nervonic
   - **Functions:**
     1- Cerebrosides are present in many tissues especially in the brain and myelin of nerve fibers.
     2- They act as insulators of nerve impulse.
   - **Gaucher's disease:**

   -Def: Accumulation of cerebrosides (sphingolipids) in phagocytes due to deficiency of "β glucocerebrosidase" enzyme.

   -Manifestations: mental retardation, hepatomegally and bone disorder.
2. **Gangliosides:**
   - **Structure:** Formed of ceramide + complex carbohydrate e.g. (NANA)
   - **Function:**
     1. They act as receptors at cell membrane.
   - **Degradation by:** **hexoaminidase** enzyme.
   - **Tay Sachs disease:**

   - Def: Accumulation of gangliosides in brain and intestine due to deficiency of **hexoaminidase** enzyme

   -Manifestations: mental retardation, hepatomegally and blindness.

3. **Sulfolipids (sulfatides):**
   - Formed of ceramide + galactose 3 sulfate.

❖ **Importance of glycolipids : Found in**
- Cell membranes
- Myelin sheath
- Receptors for hormones.

Q1- Enumerate sphingolipids:
- Sphingomyelin
- Glycolipids: (cerebrosides, Sulfolipids, Gangliosides)

Q2: Enumerate Choline containing lipids:
- Lecithin
- Plasmalogens
- Sphingomyelin

Lipoproteins

❖ These are complex lipids formed of lipids conjugated with protein.
❖ They are present in c.m, mitochondria and plasma (plasma lipoproteins).
❖ Plasma lipoproteins convert water **insoluble** lipids into water **soluble** complexes. This facilitates transport of lipids between blood and different tissues.
❖ The plasma lipids are triacylglycerols, phospholipids, cholesterol (free and esterified) and free fatty acids.
❖ Methods used for separation of plasma lipids:
These methods include: electrophoresis, Ultracentrifugation, gas liquid chromatography and thin layer chromatography
❖ The protein fractions are called **Apo lipoproteins**. **They include :**

FRACTION	SOURCE	MAIN LIPID	ptn Amount	Types
chylomicrons	Intestine	TG	2%	A, B_{48},C & E.
VLDL	Liver	TG	12%	B_{100}, C & E
LDL	Blood from chylomicrons and VLDL	Cholesterol, esters and phospholipids	22%	B_{100}
HDL	Liver	Cholesterol, esters and phospholipids	50%	A, C, D & E.
FFA.Albumin	Adipose tissue	FFA	99%	Albumin

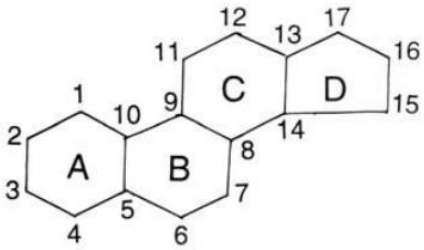
Derived Lipids

❖ **Def:**
Produced by **hydrolysis** of simple or conjugated lipids or associated with lipids in nature.

❖ **Includes:**
1. FA
2. Steroids
3. Carotenoids
4. Ketone bodies
5. Fat soluble vitamins (Vit. K, E, D & A)

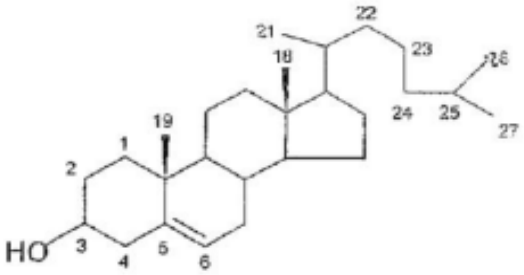
Steroids

- Compounds containing steroid nucleus **(cyclopentano-perhydro-phenanthrene "CPPP")**



❖ **Types of steroids and sterols are:**
1. Cholesterol (animal origin).
2. Ergosterol (plant origin).
3. Vitamin D group (D_2 and D_3).
4. Bile salts.
5. Steroid hormones:
   a) Male sex hormones.
   b) Female sex hormones.
   C) Adrenocortical hormones.
6. Digitalis glycosides.

Cholesterol



❖ **Structure:**
a. **cyclopentano-perhydro-phenanthrene** ring
b. -OH group at C_3 (so it is an alcohol).
c. 2 methyl groups at C_{10} & C_{13} (- CH_3 = I).
d. Long side chain at C_{17}.

❖ **Body cholesterol:**
a. It is present in everybody cell (cell membrane) especially in:
   - Adrenal cortex.
   - Liver and kidney.
   - Brain and nerve tissue.

b. Blood cholesterol:
   - It occurs in the blood in 2 forms: free form and esterified form (combined to fatty acids to form ester)
   - The level of blood cholesterol is normally less than 220 mg/dl. Any increase above this level is called: **hypercholesterolemia**

❖ **Properties:**

1. It is an alcohol, **in**soluble in water, soluble in fat solvents.
2. It forms characteristic crystals with broken corner.
3. It gives positive Lieberman's test which runs as follows
   cholesterol + Acetic acid + conc. sulphuric acid → Bluish green color.

❖ **Functions of cholesterol**: it is important for:

1. **It enters in the structure of everybody cell particularly:**
   a) Cell membranes.
   b) In nervous tissue.
2. **Synthesis of steroid hormones.**
3. **Synthesis of bile salts.**
4. **Synthesis of vitamin D3.**

Ergosterol

❖ **Structure:** Similar to cholesterol but differs in:

a) Extra double bond between C7 & C8.
b) The side chain is unsaturated and has extra methyl group.

❖ **Properties:** It is a plant sterol, poorly absorbed from small

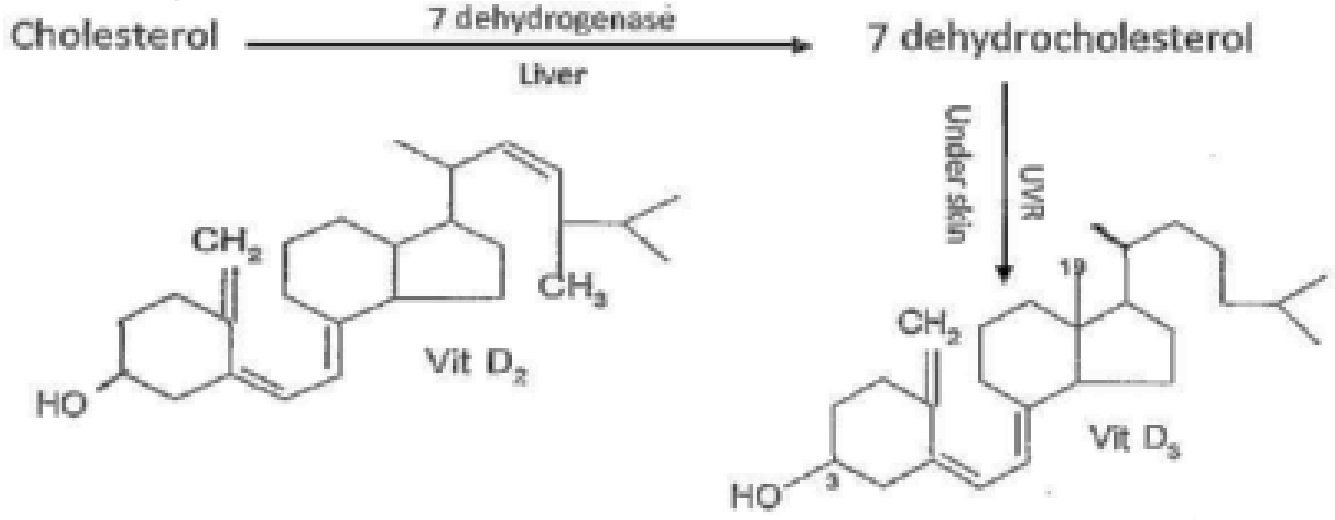
❖ **Functions:** It gives vitamin D_2 by ultraviolet rays.

Vitamin D group

❖ **Structure:**

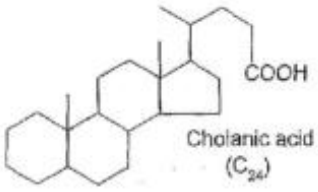
1. Vitamin D_3 is derived from 7-dehydrocholesterol by the rupture of second ring by ultraviolet rays.

2. Vitamin D_2 is derived from ergosterol by the rupture of second ring by ultraviolet rays.



Bile acids and salts

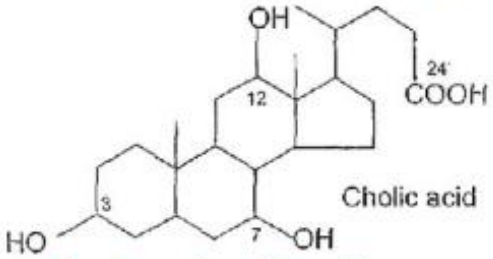
Bile acids are hydroxyl derivatives of C24 steroid termed **cholanic** acid

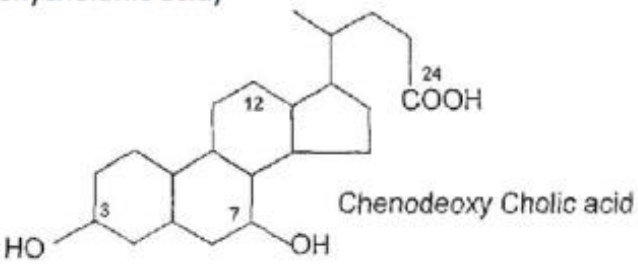


❖ **Types of bile acids:** Primary & Secondary bile acids

A. Primary bile acids

- Cholic acid (3, 7, 12 trihydroxy cholanic acid)
- Chenodexy cholic acid (3, 7 dihydroxycholanic acid)





B. Secondary bile acids

- 2ry bile acids are formed from 1ry bile acids by the action of intestinal bacteria (contain **7α dehydroxylase**).

2ry bile acids are:

- Deoxycholic acid (3, 12 dihydroxy cholanic acid).
- Lithocholic acid (3 monohydroxy cholanic acid).

C. Bile Salts

- Formed by & conjugation of bile acids with glycine or tourine then Na^+ or K^+ to form: • **Na glycocholate** • **Na taurocholate**
- Bile salts are excreted from **liver** & stored in **gall bladder**
- Bile salts pass to intestine during digestion of fat
- They are reabsorbed from intestine & back to liver (**Enterohepatic circulation**)

❖ **Importance of bile salts: MDAPS**

1. Main way for excretion of cholesterol.
2. Digestion of fat due to emulsification.
3. Absorption of fat due to formation of micelle.
4. Prevents precipitation of cholesterol & formation of cholesterol stones.

S. Stimulates liver cells to secrete more bile (Choleretic effect).

Steroid Hormones

Sex Hormones

Male Sex H (C_{19}) (Androgens)
1. Testosterone
2. Dihydrotestosterone
3. Androstendione

Female Sex H

Estrogens
1. Estradiol
2. Estrane

Progesterones
1. Progesterone
2. Pregnandiol

Corticoids (C_{21})

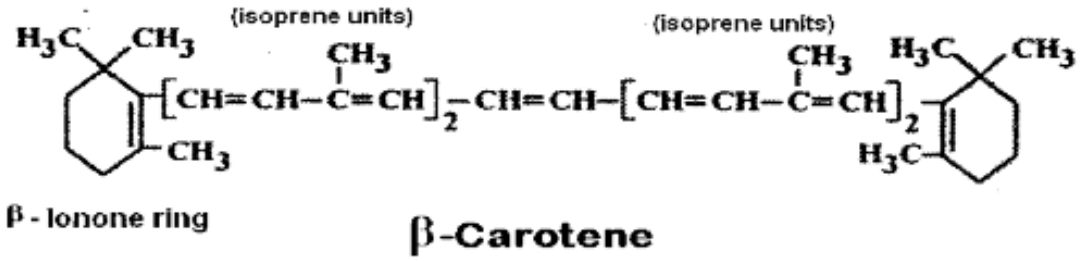
Glucocorticoids
1. Corticosterone
2. Cortisol
3. Cortisone

Mineralocorticoids
1. Aldosterone
2. 11deoxy-Corticosterone

Carotenoids (terpenes)

- **Definition:**
  a) Carotenoids are among the most common and most important natural Pigments.
  b) They have yellow to red color.
- **Types and structure:**
  a) Many types are present e.g. α, β and γ carotene.
  b) All are hydrocarbons formed only of carbons and hydrogen.
  c) Generally each carotene is formed of two ionone rings. Each ionone ring is connected to two isoprene units, both are interconnected by methane group (-CH=CH-).
- **Sources:**
  a) Plant sources: They are responsible for many colors of fruits and vegetables e.g. carrots, orange, apricot, apple and tomato.
  b) Animal sources: fats, butter, milk and egg yolk.
- **Functions:**

*** Antioxidant** *** Antimalignant** *** Provitamin A**



β - Ionone ring

β-Carotene