

4.2. LIPIDS

The term 'lipid' was coined by **Bloor**, a German biochemist, in 1943, who defined lipids as follows :

"Lipids are naturally occurring compounds which are insoluble in water and soluble in one or more organic solvents such as benzene, chloroform, ether and acetone, the so-called fat solvents and on hydrolysis yield fatty acids which are utilized by the living organisms."

Lipids are thus **hydrophobic** in nature and are important constituents of plants and animals. In plants they are present in the seeds, nuts, fruits, protoplasm, cell membrane etc. while in the animals they are stored in adipose tissues, bone marrow, nervous tissues etc. Lipids are structurally diverse group of biomolecules including fats, oils and fatty substances and also occur alongwith carbohydrates and proteins. They contain a large proportion of carbon-hydrogen bonds and liberate a large amount of energy on breakdown. Lipids yield water soluble glycerol and fatty acids on alkaline hydrolysis.

Chemical composition = Carbon (C), hydrogen (H) and oxygen (O) (only three elements)

Other definitions

Lipids are a group of naturally occurring molecules that include fats, waxes, sterols, even fat-soluble vitamins (such as A, D, E and K), monoglycerides, diglycerides, triglycerides, phospholipids and others.

Or

Lipids may be broadly defined as **hydrophobic** or **amphiphilic** small molecules, the amphiphilic nature of some lipids allows them to form structures such as vesicles, multilamellar/unilamellar liposomes, or membranes in an aqueous environment.

The main biological functions of lipids include storing of energy, acting as structural component of cell membranes and signalling. Lipids have applications in the cosmetic and food industries and recently in **nanotechnology**.

I. Classification

A. On the basis of **chemical composition**, lipids are classified as follows :

1. **Simple Lipids or homolipids**. These are esters of fatty acids with various alcohols. Example (i) Fats and Oils (triglycerides, triacylglycerols), (ii) Waxes.

2. **Compound lipids or heterolipids**. These are esters of fatty acids with alcohol and possess additional groups like phosphate, carbohydrates etc.

Examples : (i) Phospholipids (with phosphoric acid, nitrogen bases).

(ii) Glycolipids (with carbohydrates and nitrogen).

3. **Derived Lipids**. These are derived from simple and compound lipids by hydrolysis. These include fatty acids, alcohols, mono- and di-glycerides, steroids, terpenes and carotenoids etc.

B. On the basis of function, lipids may be classified into :

1. **Storage lipids** : These lipids are mainly meant for storage e.g. fats, oils, elaioplasts of plants having storage lipids. Elaioplasts, a type of leucoplast, specialized in storing oil body deposits as rounded plastoglobuli.

2. **Structural lipids** : These lipids are responsible for structural architecture of the cell also possessing additional functional groups like phosphate etc. Example : phospholipids, phosphatidylinositol (having inositol as one component) etc.

C. Basing on the types of biochemical subunits or building-blocks i.e. ketoacyl and isoprene groups, lipids may be divided into the following eight categories. Biological lipids originate entirely or in part from these two distinct types of biochemical subunits.

As derived from condensation of ketoacyl subunits :

1. Fatty acids
2. Glycerolipids
3. Glycerophospholipids
4. Sphingolipids
5. Saccharolipids
6. Polyketides

As derived from condensation of isoprene subunits :

7. Sterol lipids
8. Prenol lipids

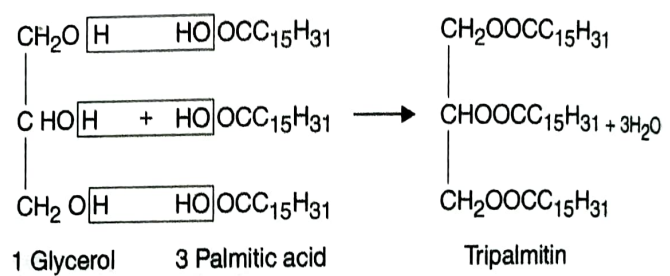
Although the term 'lipid' is sometimes used as a synonym for fats, fats are a sub group of lipids called triglycerides. Lipids also include molecules such as fatty acids and their derivatives (including tri-, di-, monoglycerides and phospholipids) as well as other sterol-containing metabolites such as cholesterol.

1. Simple Lipids or Storage Lipids

(i) **Fats and Oils.** Fats, oils, the simple lipids are triglycerides or triacylglycerols. They constitute about 98% of total dietary lipids and the remaining 2% constitute phospho-lipids, chlorosterol or its esters. They are the major components of storage or depot fats in plants and animals. They are also known as neutral lipids as they are nonpolar, hydrophobic and contain no electrically charged or highly polar functional groups. Commonly fats are solids and oils are liquid at room temperature.

Chemically, fats are esters of high molecular weight fatty acids and glycerol e.g. *Tripalmitin*, a common fat, is an ester of one glycerol and three palmitic acids, as follows.

Thus tripalmitin is a triglyceride or triacylglycerol.



Fats are poorer in oxygen in comparison to carbon. As they are insoluble in water, they can be stored in the cells without disturbing their osmotic relations. Fats are found in plants as reserve material in the form of intracellular oil droplets in storage organs like seeds, fruits e.g. groundnut, almond, castor, linseed, sesamum, coconut etc, and also in chloroplasts.

Animal fat and Plant Fat. Animal fats, such as those from meat, milk and eggs are relatively rich in saturated fatty acids and low in polyunsaturated fatty acids while in plant fats, a reverse trend is marked (Table 4.4).

Table 4.4. Fatty acid composition (%) of some important animal and plant fats.

Type of fat/oil	Saturated Fatty acids (%)	Monounsaturated Fatty acids (%)	Polyunsaturated Fatty acids (%)
<i>Animal fats</i>			
Chicken fat	34	44	21
Beef fat	53	44	2
Pork fat	59	39	2
Butter fat	60	36	4

Type of fat/oil	Saturated Fatty acids (%)	Monounsaturated Fatty acids (%)	Polyunsaturated Fatty acids (%)
<i>Plant fats</i>			
Soybean oil	14	24	53
Corn oil	15	31	53
Olive oil	20	26	54
Soft margarine	23	22	52

A differential account between animal fats and plant fats is presented in table 4.5.

Table 4.5. Differences between animal and plant fats

S.No.	Animal fats	Plant fats
1.	Animal fats are relatively rich in saturated fatty acids (mainly C ₁₆ and C ₁₈ fatty acids)	Plant fats are relatively rich in unsaturated fatty acids (mainly polyunsaturated)
2.	These are solid at ordinary room temperature.	These are liquid at ordinary room temperature.
3.	Exhibit low iodine number.	Usually high iodine number.
4.	Mainly stored in liver and bone marrow.	Mainly stored in seeds and fruits.
5.	Exhibit oxidative rancidity more frequently.	Exhibit oxidative rancidity less frequently
6.	Examples : Butter fat, beef fat, pork fat etc.	Examples : Olive oil, castor oil, soybean oil, corn oil etc.

(ii) **Waxes.** Biological waxes are esters of long chain (14-36 carbon atoms) saturated and unsaturated fatty acids with long chain (16-30 carbon atoms) monohydroxy alcohols. They have higher melting points (60° – 100°C) than triglycerides. Waxes are secreted by cutaneous glands in vertebrates as a protective coating to keep the skin water proof. The leaves of many plants are shiny because of the deposition of waxy coating. Waxes serve as the chief storage form of fuel in planktons. Biological waxes have a variety of applications in pharmaceutical, automobile and cosmetic industries.

2. Compound Lipids or Structural Lipids

(i) **Phospholipids.** *Phospholipids* or *phosphatids* are the most abundant membrane lipids. They are structural components of membranes and are never stored in large quantities. They contain *phosphoric acid groups*. Usually they possess one hydrophilic polar 'head' group and two hydrophobic non-polar 'tails'. For this, reason, they are often known as '**Polar lipids**'. Hence, phospholipids are *amphipathic* where as storage lipids (triglycerides and waxes) are not. For this property all biological membranes possess two layers of phospholipid molecules, spread over as sheets. The polar heads orient towards the outer cytoplasmic side and the non-polar tails orient towards the inner side forming the hydrophobic core of the membrane. Lecithin (Phosphatidyl cholines), plasmalogens (Phospho-glyceracetals), phosphosphingosides etc. are phospholipids.

(ii) **Glycolipids** (Cerebrosides or Glycosphingosides) : These compound lipids contain carbohydrates mainly monosaccharides groups. They are present on the outer face of the plasma membranes and are also important constituent of brain (8% of the solid matter). Galactose (a monosaccharide) is the head group in the plasma membrane of neural tissues

while glucose is the head group in non-neutral tissue. Glycosphingolipids act as cell surface recognition molecules (antigens), especially as of blood group substances.

3. Derived lipids

(i) **Steroids** (Gr. *Stereos* : Solid) : They do not contain fatty acids, thus they are *nonsaponifiable* i.e. cannot be hydrolyzed by heating with alkali to yield soaps of their fatty acid components. The steroids may be separated from the fat after the latter is saponified, because fats are saponifiable. All steroids are derivatives of a fused and fully saturated ring system called *Cyclopenta-noperhydrophenanthrene* or **Sterane**. This system consists of three cyclohexane rings i.e. A, B and C fused to a terminal cyclopentane ring i.e. ring D (Fig. 4.14). It is a 19 carbon structure.

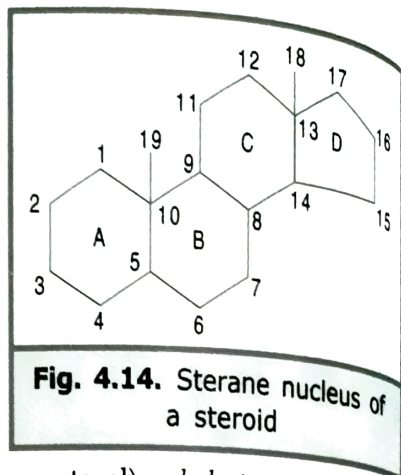


Fig. 4.14. Sterane nucleus of a steroid

Some common steroids are *cholesterol*, *coprostanol* (copro-sterol), *cholestanol*, *ergosterol*, *lanosterol* etc.

Cholesterol is the precursor of many other important steroids such as *bile acids* and various *steroid hormones*. Cholesterol is an important component of cell membrane and plasma lipoprotein. It is also present in nerve tissues and is the principal sterol of higher animals. However, cholesterol is not found in plant fats. It was first isolated from human gallstones. Cholesterol is a major cause of heart disease. Two types of cholesterol are there:

- Low density lipo-protein cholesterol* (LDL - C) - which is bad for health as it triggers heart trouble.
- High density lipoprotein cholesterol* (HDL - C) - which is good for health. Generally women have higher level of HDL-C than men, for which fewer women than men have heart attacks.

Ergosterol is present in ergot, yeast and *Neurospora*. Lanosterol is present in wool fat, liver, and yeast.

(ii) **Terpenes**. These are present in plants as many hydrocarbons (from terpenines). In general, these hydrocarbons and their derivatives have lesser than 40 carbon atoms. Terpenes with 40 carbon atoms (tetraterpenes) include compounds known as **carotenoids**. Carotenoids are coloured red or yellow e.g. pigments of tomato (**lycopene**), carrot (**α -and β -carotene**) are red and oxygen-containing carotenoids are yellow (**Xanthophyll**). Carotenoids are also called **lipochromes** or **chromolipids**.

II. FATTY ACIDS

A. Types and structure

Fatty acid is the principal component of lipids. Fatty acids are straight chain hydrocarbons containing even number of carbon atoms (commonly 12-24). Depending upon the saturation by hydrogen, fatty acids may be :

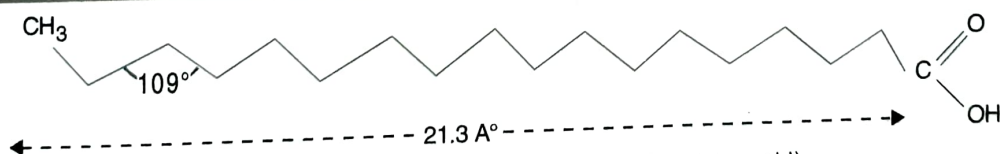
1. Saturated fatty acids. These fatty acids have carbon atoms which are fully saturated with hydrogen atoms.

Example : Lauric acid, palmitic acid, arachidic acid, stearic acid etc. These are found in plants. No double bond is present in these fatty acids.

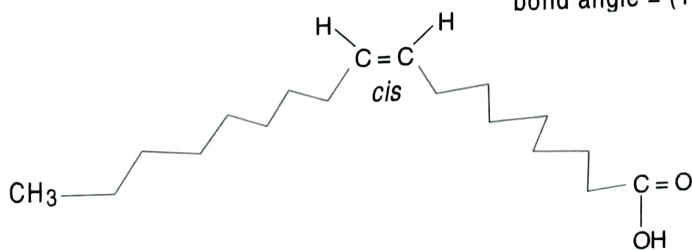
Table 4.6. Some important saturated and unsaturated fatty acids and their molecular structure and melting points.

S. No.	Fatty acid	No. of Carbon	Structure (Molecular)	Melting points in °C	Source
Saturated Fatty acids (C_nH_{2n}O₂)					
1.	Capric acid	10	CH ₃ (CH ₂) ₈ COOH	31.2	Cocount oil
2.	Lauric Acid	12	CH ₃ (CH ₂) ₁₀ COOH	43.6	Cocount oil
3.	Myristic Acid	14	CH ₃ (CH ₂) ₁₂ COOH	54.1	Cocount oil
4.	Palmitic Acid	16	CH ₃ (CH ₂) ₁₄ COOH	62.7	Animal & Vegetable fats
5.	Stearic Acid	18	CH ₃ (CH ₂) ₁₆ COOH	69.9	- do -
6.	Arachidic Acid	20	CH ₃ (CH ₂) ₁₈ COOH	75.2	Corn oil, peanut oil
7.	Cerotic Acid	26	CH ₃ (CH ₂) ₂₄ COOH	87.7	Wool fat
Unsaturated Fatty acids					
8.	Oleic Acid (<i>cis</i> form)	18	CH ₃ (CH ₂) ₇ CH = CH(CH ₂) ₇ COOH (One double bond)	13.4	All fats
9.	Elaidic Acid (<i>Trans</i> form)	18	CH ₃ (CH ₂) ₇ CH = CH(CH ₂) ₇ COOH (One double bond)	45	All fats
10.	Linolic Acid	18	C ₁₇ H ₃₁ COOH (Two double bonds)	-5.2	Linseed oil
11.	Linolenic Acid	18	C ₁₇ H ₂₉ COOH (Three double bonds)	-11.3	Linseed oil
12.	Arachidonic acid	20	C ₁₉ H ₃₁ COOH (Four double bonds)	-49.5	Peanut (<i>L.arachis</i>) oil

2. Unsaturated fatty acids. These fatty acids contain **one or more double bonds**, so that unsaturation of the carbon atoms occur.



A. Simplified structure of stearic acid (saturated fatty acid)
bond angle = (109°)



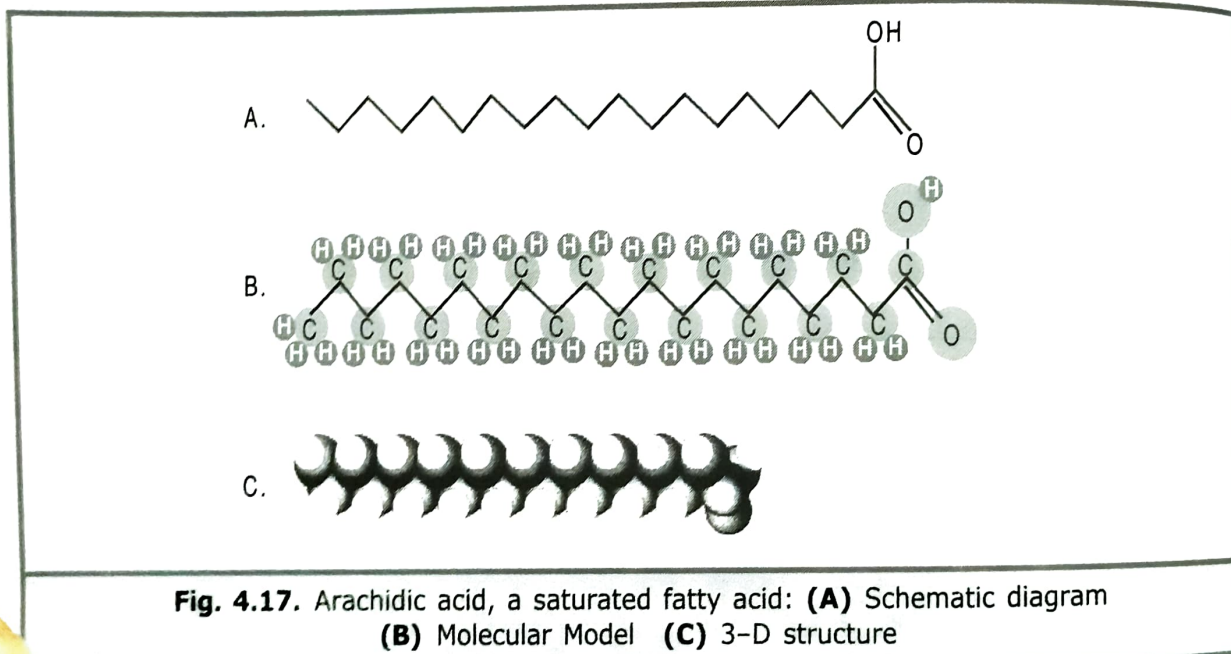
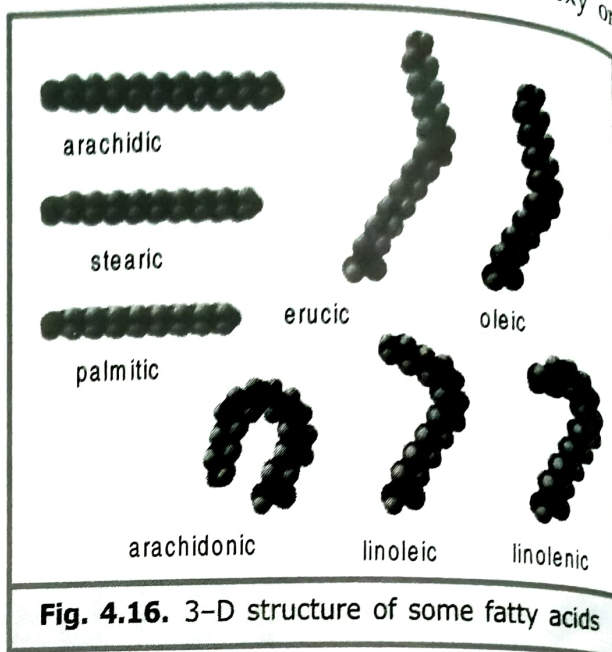
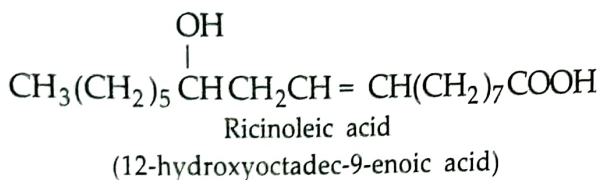
(B) Simplified structure of oleic acid having one double bond (Unsaturated fatty acid)

Fig. 4.15. Simplified structure of Stearic acid (A) and Oleic acid (B)

Example : Linolenic acid and linolic acids found in linseed oil, others found to accumulate in the cellular organelles, oleic acid having one double bond (Fig. 4.15).

Apart from the saturated and unsaturated fatty acids, fatty acid may be hydroxy or oxygenated fatty acids and cyclic fatty acids as follows :

(a) **Hydroxy (or oxygenated) fatty acids:** In these fatty acids hydroxyl (-OH) group is present on the carbon atom instead of only H atom. Thus it is oxygenated means one oxygen atom is added to normal H atom making it OH group. Example is **ricinoleic acid** present in castor oil (87%). It is a fatty acid with carbon no. 18 and one double bond at C₉ and an OH group on C₁₂.



Other examples of hydroxy fatty acids are :

(i) Cerebronic acid (with an OH group on C₂) present in animal lipid, (ii) 9,10-dihydroxystearic acid, with OH group on C₉ and 10 present in plants and bacteria, (iii) 9,10-epoxystearic acid present in rust spore lipid (20%).

(b) **Cyclic fatty acids :** These fatty acids have cyclic structure opposite to the carboxyl (-COOH) end, for example, **Chaulmoogra oil** which contains 2 such fatty acids : **hydnocarpic** and **chaulmoogric acid**, both have cyclopentenyl ring in its 16- and 18-carbon structure respectively. Chaulmoogra oil is used for the treatment of leprosy.

C. Essential Fatty Acids (EPAs)

Human body can not convert saturated fatty acids into unsaturated fatty acid e.g. stearic acid to oleic acid. For normal cell functioning especially of skin tissues, one of three unsaturated fatty acid e.g. *linoleic acid*, *linolenic acid* and *arachidonic acid* is required. Since they cannot be synthesized by the cells, they must be obtained from diet. Due to this important physiological role, these three unsaturated fatty acids are called *essential fatty acids*. (EFAs).

The term 'essential fatty acid' refers to fatty acids required for biological processes but does not include the fats that only act as fuel. Essential fatty acids should not be confused with essential oils, as 'essential' is in the sense of being a concentrated essence. Linolenic acid is an **omega-3 fatty acid** (having 3 double bonds) while linoleic acid (having 2 double bonds) is an **omega-6 fatty acid**. The EPAs were discovered in 1923 and initially designated as vitamin F. However in 1929, research on rats showed that the EPAs are fatty acids rather than vitamins.

What are omega (ω)-3 and (ω)-6 fatty acids ? : Fatty acids are straight chain hydrocarbons having carboxyl (COOH) group at one end and methyl (CH₃) group at the other end. The carbon next to the carboxylate end is alpha (α), the next carbon beta (β) and so forth. Since biological fatty acids are of different length, the last position (i.e. methyl carbon) is termed as omega (ω), the last letter of the Greek alphabet. Since the physiological properties of unsaturated fatty acids depend mainly on the position of the first unsaturation relative to the end position, hence ω -3 means the first double bond that exists at the third carbon-carbon bond from the terminal end (ω) of the carbon chain.

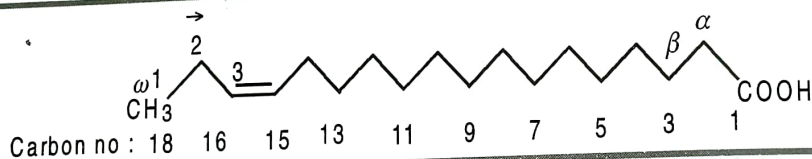


Fig. 4.18. Structure of a typical omega-3 fatty acid.

Likewise in case of ω -6 fatty acid the first double bond is present at the sixth carbon-carbon bond from the terminal end as follows.

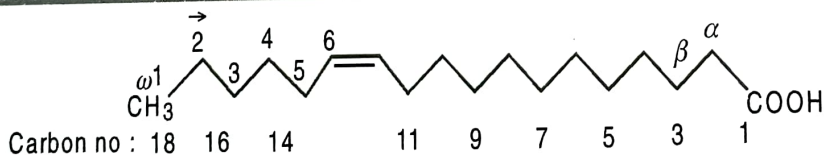


Fig. 4.19. Structure of a typical omega-6 fatty acid

Linoleic acid and linolenic acid are not synthesized by human cell, because humans lack the enzyme '**desaturase**' required for their production. These two fatty acids are actually the essential fatty acids as the third one i.e. arachidonic acid can be synthesized from linoleic acid by alternative desaturation and chain elongation. Thus, if linoleic acid is not available in the human cell then arachidonic acid can not be synthesized. Hence **arachidonic acid is not an absolute essential fatty acid**. Omega-3 and ω -6 fatty acids are present in fish, shellfish, linseed, hemp seed, soya oil, canola (rapeseed)oil, pumpkin seeds, sun flower seeds, leafy vegetables and walnuts.

EPAs play important role in many metabolic processes. Low level of EPAs or the wrong balance of these types among the essential fatty acids may be a factor in a number of illness.

including osteoporosis. EPAs play an important role in the life and death of cardiac cells. Deficiency of EPAs results in dermatitis similar to that seen in zinc or biotin deficiency.

III. Triacylglycerols (TG) or Triacylglycerides (TAG)

Triacylglycerols or triacylglycerides are the simple lipids, the fats and oils which are discussed under 'Simple lipids' previously. They are commonly known as **triglycerides**.

A. Structure : Triacylglycerol has three fatty acids ester linked to a molecule of glycerol as in **Tripalmitin**.

In triglycerides, the hydroxyl groups of the glycerol join the carboxyl groups of the fatty acids to form ester bonds.

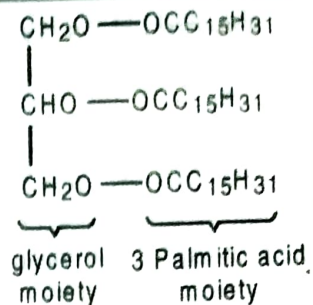


Fig. 4.20. Structure of Tripalmitin, a saturated triacylglycerol

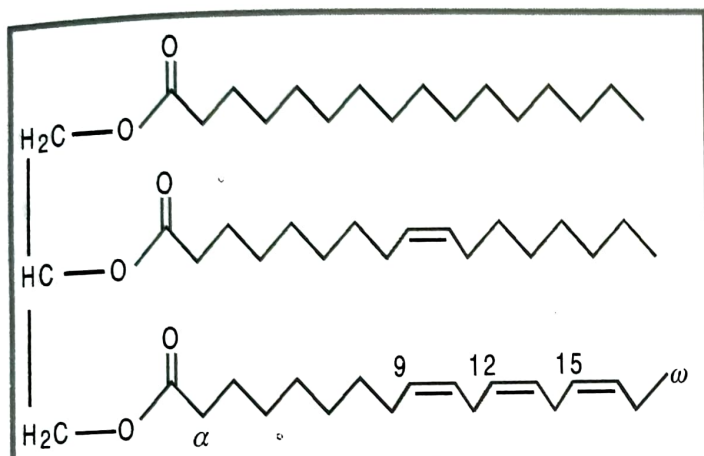


Fig. 4.21. Typical structure of an unsaturated triglyceride. Left part: glycerol, right part from top to bottom : palmitic acid, oleic acid, alpha-linolenic acid. Chemical formula : $\text{C}_{55}\text{H}_{98}\text{O}_6$.

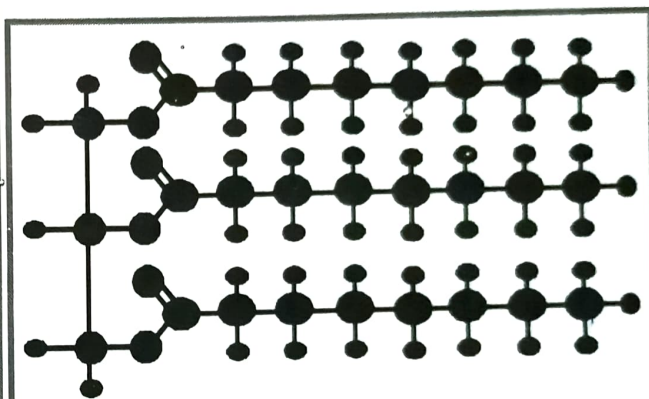


Fig. 4.22. Three-D structure of a triglyceride.

B. Functions :

1. There are many **triglycerides** depending upon the oil source, some are highly unsaturated and some are less so. The unsaturated triglycerides are good for health. The **vegetable oils** contain typically more unsaturated and the animal fats contain more saturated fatty acids. Hence the vegetable oils like flax seed oil, soybean oil, linseed oil, olive oil etc. contain more unsaturated fatty acids. Triglyceride is a **major component of human skin oil**.
2. Triglycerides upon hydrolysis yield fatty acids and glycerol. The fatty acids by universally occurring β -oxidation and respiratory process release **energy in the form of ATP**, the energy currency of the cell. ATP is required for different works and growth & development of the plants and animals containing triglycerides.
3. Different kinds of oils are used in **cooking and preparation** of fast foods.
4. Triglycerides, a major component of very-low-density lipoprotein (VLDL) play an important role in metabolism as energy sources and transporters of dietary fat. As pointed earlier **triglycerides contain more than twice as much energy as carbohydrates**.
5. In human body high levels of triglycerides in the bloodstream have been linked to **atherosclerosis** and by extension, the risk of **heart diseases and stroke**. The level of

triglycerides in the blood is normal below 150 mg/dl and above this value risk comes. The higher the level above this value, the higher the risk factor. The American Heart Association recommends an optimal triglyceride level of 100 mg/dl. (1.1 mmol/L) or lower to improve heart health.

6. Linseed oil and related oils are important components of useful products used in **oil paints and related coatings**.
7. Triglycerides are also used in the manufacture of **biodiesel**, where these split into fatty acids, esters that can be used as fuel in diesel engines.
8. **Glycerol**, a component of triglyceride is used in manufacture of food and in the production of pharmaceuticals.
9. Triglycerides are also used in **staining industry**.
10. Triglyceride, as a blood lipid, helps the bidirectional transference of adipose fat and blood glucose from the liver.
11. **High density lipoprotein cholesterol (HDL-C)** is better for health than **low density lipoprotein cholesterol (LDL-C)**. High level of the latter causes heart diseases.
12. Many **vitamins** like vit-A,D,E and K are fat soluble.

C. Properties: The saturated triglycerides have no double bonds as all the carbon atoms are fully saturated with hydrogen atom. On the other hand, unsaturated triglycerides have one or more than one double bonds at specific carbon sites.

Each triglyceride is an ester of a molecule of glycerol and 3 molecules of fatty acids (may be saturated or unsaturated).

I. Physical properties

1. Triglycerides are generally colourless, odourless and possess bland taste, but they are capable of absorbing a variety of odours and flavour during storage. This property is used in essence making from flowers.

2. Triglycerides are sparingly soluble in water i.e. they are **hydrophobic**, but freely soluble in organic solvents like chloroform, ether, acetone and benzene.

3. Depending on the chain length of the fatty acids and the degree of unsaturation, the melting point of triglycerides vary. Triglycerides with saturated fatty acids with C_4 to C_8 are liquid at room temperature, but with C_{10} or more carbons are solid. Thus, the melting point increases with increase in chain length. Further greater the degree of unsaturation (i.e. higher the no. of double bonds), the lower the melting point of the triglycerides, for example, oleic acid with one double bond and linoleic acid with 2 double bonds and arachidonic acid with 4 double bonds have 13.4°C , -5°C and -50°C melting points respectively. Thus, all the unsaturated triglycerides are liquid at room temperature.

4. **Specific gravity** : The triglycerides or simple fats have less specific gravity than water i.e. about 0.86 as water has specific gravity of 1.0. Hence simple fats float on water surface. Solid fats are lighter than the liquid fats.

5. **Geometric isomerism** : Presence of double bonds in the unsaturated fatty acid part of the simple fat molecule produces geometric isomerism i.e. *cis*- and *trans*-forms. Example of *cis* form of fatty acids is oleic acid, while the *trans* form is elaidic acid. Most of the unsaturated fatty acids are present as the unstable *cis*-isomer rather than as the more stable *trans*-isomer. In *cis*-isomer the two H atoms on two carbon atoms of a double bond are present towards

one sides, while in a *trans*-form, they are present on opposite side (Fig. 4.23).

6. Insulation : Triglycerides have high insulating power *i.e.* bad conductor of heat, for example the fat layer of whales, a warm blooded animal (homoiotherms) serves as a blanket in the cold waters.

7. Emulsification : Triglycerides and other lipids are converted into a number of small liquid droplets with water or with emulsifying agents like soaps, gums, proteins etc. This property is of great metabolic significance. Different fat molecules have to be emulsified before they can be absorbed by the intestinal walls and this work is done by the bile juice secreted from the liver.

8. Surface tension : Liquid triglycerides uniformly spread over the surface of water in the form of a unimolecular layer and reduces the surface tension of water.

II. Chemical properties

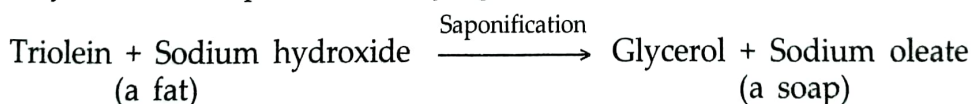
1. Hydrolysis : By the action of the enzyme lipases triglycerides and other fats are hydrolyzed (at pH 7.5 – 8.5) into three molecules of fatty acids and one molecule of glycerol in three steps (Fig. 4.22). In the intestine of humans, mono-, di- and tri-glycerides are absorbed rapidly and hence very little free glycerol is formed.

- (a) Triglycerides + H₂O → Diglyceride + Fatty acid (R₃.COOH)
 (b) Diglyceride + H₂O → Monoglyceride + Fatty acid (R₂.COOH)
 (c) Monoglyceride + H₂O → Glycerol + Fatty acid (R₁.COOH)

Fig. 4.23 Hydrolysis of a triglyceride to glycerol and 3 molecules of fatty acids. Here radicals R₁, R₂ R₃ may be similar or dissimilar.

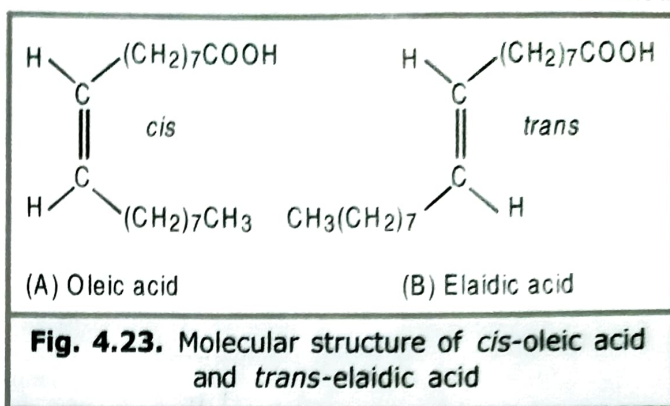
2. Saponification : Saponification is the phenomenon of hydrolysis of fats by alkali which leads to the formation of glycerol and salts of fatty acids, known as soaps. Thus **salt of a fatty acid is the commercial soap**. Soaps may be (i) *hard soaps* : the common bar soaps which are sodium salts of higher fatty acids (ii) *soft soaps* : the bathing soaps which are potassium salts of higher fatty acids and these are semisolids or pastes.

Calcium soaps are used as lubricating greases, while zinc soaps are used in the manufacture of talcum powder and other cosmetics. Lead and magnesium soaps are employed in paint industry as they hasten the process of drying.



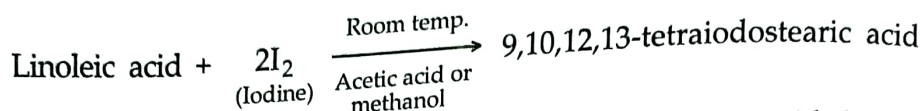
The cleaning property of soaps is due to their emulsifying action.

3. Hydrolytic and oxidative rancidity : If fats like butter or ghee are kept or stored for longer period, they become rancid *i.e.* an unpleasant odour and flavour is generated so that they are not palatable. This rancidity occurs due to growth of micro-organisms in the fats which liberate the enzyme lipases that breakdown fats into glycerol and free fatty acids. These fatty acids impart the rancid flavour. Rancidity can be overcome by keeping the ghee or butter in refrigerator.



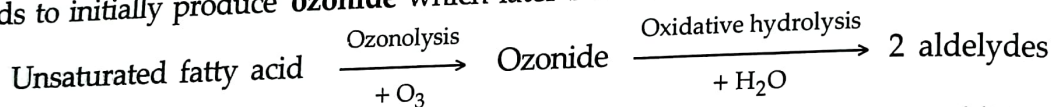
Likewise oxidative rancidity may occur if the butter or ghee is kept open so that the atmospheric oxygen causes oxidative rancidity of the fats at room temperature by **autoxidation** to short chain fatty acids and aldehydes that give the rancid odour and taste to the fats. Oxidative rancidity is observed more frequently in animal fats than in vegetable fats, because the latter contain natural antioxidants.

4. Halogenation : The unsaturated fatty acids can be halogenated with halogens like iodine and bromine at the double bonds at room temperature in a solution of methanol or acetic acid. For example, linoleic acid is halogenated with iodine to produce *tetraiodostearic acid* as follows.



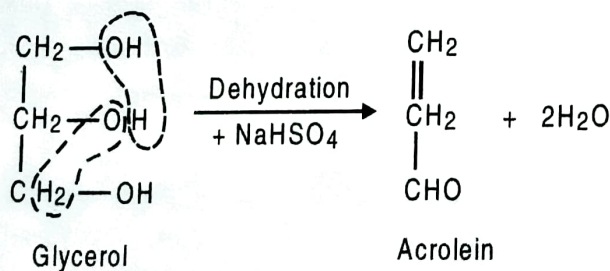
5. Hydrogenation : Unsaturated fatty acids in free or bound state with lipids by reaction with hydrogen produce saturated fatty acids, catalyzed by nickel, palladium or platinum. The hydrogen atoms are added at the carbon-carbon double bond(s). This reaction has great importance from commercial view point as the inexpensive vegetable unsaturated oils are converted into solid fats that are used in different confectionaries and manufacture of candles, and oleomargarine. For example, oleic acid, an unsaturated fatty acid is converted to stearic acid, a saturated fatty acid by hydrogenation.

6. Ozonolysis : With ozone (O_3), the unsaturated fatty acids are oxidized at their double bonds to initially produce **ozonide** which later breaks down to 2 molecules of aldehydic groups.



7. Oxidative reactions : Different oxidation reactions are used for establishing the position of double bond or bonds in the unsaturated fatty acid chain. This also helps in establishing the fat or lipid structure.

8. Dehydration : Triglycerides or fats when dehydrated by heating in presence of dehydrating agents like NaHSO_4 or KHSO_4 , an unsaturated aldehyde called **acrolein** is formed from the glycerol moiety. Acrolein has a pungent odour so that it can be easily recognized. This is also known as '**acrolein test**' used for knowing the presence of glycerol in an unknown lipid molecule.



IV. Phosphoglycerides

Phosphoglycerides or glycero-phospholipids or simply phospholipids are glycerol-based phospholipids. They are the main component of **biological membranes**. These are compound or structural lipids described in brief under classification of lipids. Some more information on phospho-glycerides are described below.

A. Structure: The term phospho-glyceride or glycerophospholipid signifies any derivative of glycerophosphoric acid that contains at least one O-acyl, or O-alkyl, or O-alk-1'-enyl residue attached to the glycerol moiety.

The alcohol here is **glycerol**, to which two fatty acids and a phosphoric acid are attached as esters. The two fatty acid chains attached to the molecule of glycerol are nonpolar hence **hydrophobic** while the polar heads which mainly consists of the phosphate group attached to the third carbon of the glycerol molecule is **hydrophilic**. As has been discussed earlier, this dual characteristic leads to the **amphipathic nature** of phosphoglycerides. They are usually organized into a bilayer in membranes with the polar **hydrophilic heads** sticking outwards to the cytoplasmic side and the non-polar **hydrophobic tails** pointing inwards. Phosphoglycerides consists of various diverse species which usually differ slightly in structure. The most basic structure is a **phosphatidate**. This species is an important intermediate in the synthesis of many phosphoglycerides. The presence of an additional group attached to the phosphate allows for many different phosphoglycerides.

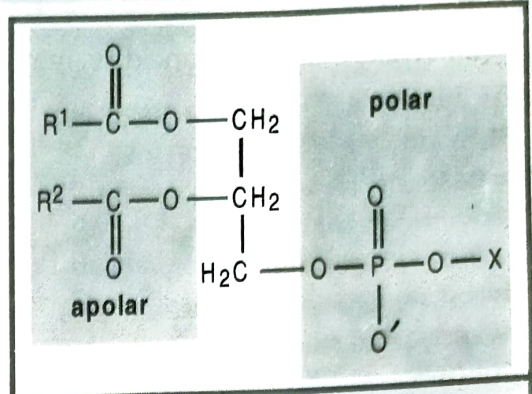


Fig. 4.24. Phosphoglyceride : a schematic diagram R¹ : usually a saturated fatty acid, R² : usually an unsaturated fatty acid and X : some other small molecule.

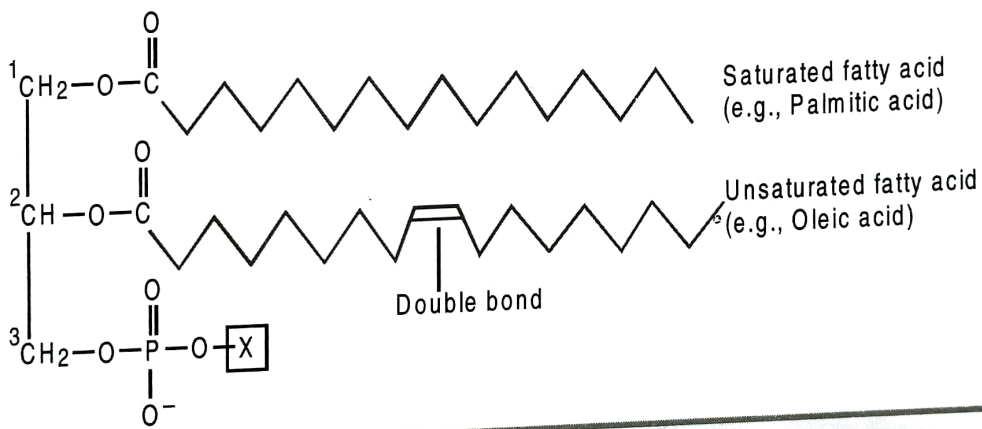


Fig. 4.25. General Structure of glycerophospholipid. X : a small molecule

By convention, structures of these compounds show the 3 glycerol carbon atoms vertically with the phosphate attached to carbon atom number three (at the bottom). **Plasmalogens, phosphatidates and others** are common examples, discussed below :

1. Plasmalogens: Plasmalogens are a type of phosphoglyceride. The first carbon of glycerol has a hydrocarbon chain attached via an **ether, (not ester) linkage**. The linkages are more resistant to chemical attack than ester linkages. The second (central) carbon atom has a **fatty acid** linked by an ester. The third carbon links to an **ethanolamine** or **choline** by means of a phosphate ester. These compounds are key components of the membranes of muscles and nerves.

2. Phosphatidates: Phosphatidates are lipids in which the first two carbon atoms of the glycerol are fatty acid esters, and the third carbon is a phosphate ester. The phosphate serves as a link to another alcohol-usually ethanolamine, choline, serine, or a carbohydrate. The

identity of the alcohol determines the subcategory of the phosphatidate. There is a negative charge on the phosphate and, in the case of choline or serine, a positive quaternary ammonium ion. (Serine also has a negative carboxylate group.) The presence of charges give a "head" with an overall charge. The phosphate ester portion ("head") is hydrophilic, whereas the remainder of the molecule, the fatty acid "tail", is hydrophobic. These are important components for the formation of lipid bilayers.

Phosphatidylethanoamines, phosphatidylcholines, and other phospholipids are examples of phosphatidates.

Phosphatidylcholines (Lecithins): Phosphatidylcholines are lecithins. Choline is the alcohol, with a positively charged quaternary ammonium, bound to the phosphate, with a negative charge. Lecithins are present in all living organisms. An egg yolk has a high concentration of lecithins which are commercially important

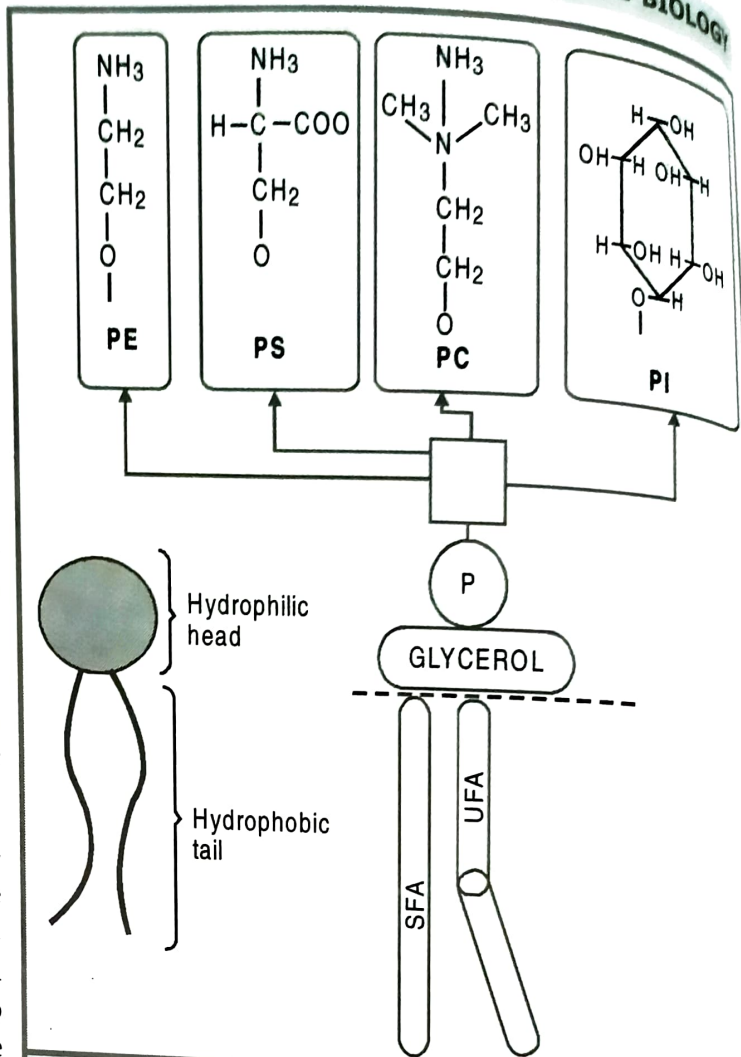


Fig. 4.26. A model of Phosphoglyceride with different head groups PE : Ethanamine group, PS : Serine group, PC : Choline group, PI : Inositol group, SFA : Saturated Fatty Acid, UFA : Unsaturated Fatty Acid

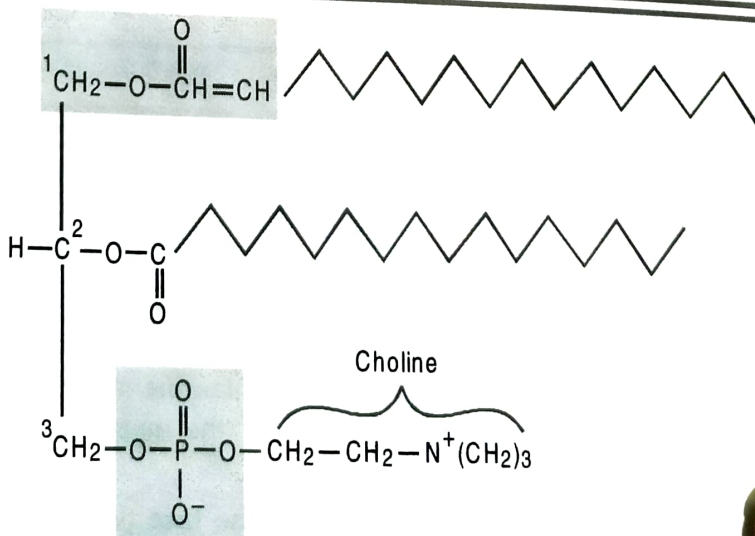


Fig. 4.27. General Structure of a plasmalogen

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as an emulsifying agent in products such as **mayonnaise**. Lecithins are also present in **brain** and **nerve tissue**. Lecithin is also present by 1–3% in **soybean oil**.

Other phospholipids: There are many other phospholipids, some of which are glycolipids. The glycolipids include phosphatidyl sugars where the alcohol functional group is part of a carbohydrate. Phosphatidyl sugars are present in plants and certain microorganisms. A carbohydrate is very hydrophilic due to the presence of large number of hydroxyl groups present.

B. Functions:

- (1) One of the main functions of phosphoglycerides is to serve as a structural component of **biological membranes**. Their amphipathic nature drives the formation of the lipid bilayer structure of membranes. The cell membrane seen under the electron microscope consists of two identifiable layers, or "leaflets", each of which is made up of an ordered row of glycerophospholipid molecules. The composition of each layer can vary widely depending on the type of cell. Each glycerophospholipid molecule consists of a small polar head group and two long hydrophobic chains. In the cell membrane, the two layers of phospholipids are arranged as follows:
 - (i) the hydrophobic tails point to each other and form a fatty, hydrophobic center
 - (ii) the ionic head groups are placed at the inner and outer surfaces of the cell membrane

This is a stable structure because the ionic hydrophilic head groups interact with the aqueous media inside and outside the cell, whereas the hydrophobic tails maximize hydrophobic interactions with each other and are kept away from the aqueous environments. The overall result of this structure is to construct a fatty barrier between the cell's interior and its surroundings.

- (2) Phosphoglycerides function in other cellular processes such as **signal induction** and **transport**. In regards to signalling, they provide the precursors for prostaglandins and other leukotrienes. It is their specific distribution and catabolism that enables them carry out the biological response processes listed above.
- (3) Their roles as **storage centers for secondary messengers** in the membrane is also a contributing factor to their ability to act as transporters.
- (4) They also **influence protein function**. For example, they are important constituents of lipoproteins (soluble proteins that transport fat in the blood) and hence affect their metabolism and function
- (5) Natural membrane phospholipids are also involved in **apoptosis**, modulation of activities of transporters, and membrane bound enzymes.

C. Uses: Phosphoglycerides can also act as an emulsifying agent to promote dispersal of one substance into another. This is sometimes used in candy making and ice-cream making. Lecithin is used as an emulsifying agent in textiles, leathers, cosmetics, paints, concrete release agent and insecticides, The global market for lecithin is estimated to be in the range of 1,30,000 metric tonnes per year.

D. Synthesis: The synthesis of phosphoglycerides is different in eukaryotes and prokaryotes. Synthesis in prokaryotes involves the synthesis of phosphoglycerides, phosphatidic acid and polar head groups. **Phosphatidic acid synthesis** in eukaryotes is different, There are two routes, one and the other toward phosphatidylcholine and phosphatidylethanolamine. Phosphoglycerides are generally metabolized in several steps with different intermediates. The

very first step in this metabolism involves the addition or transfer of the fatty acid chains to the glycerol backbone to form the first intermediate, **lysophosphatidic acid (LPA)**. LPA then becomes acylated to form the next intermediate **phosphatidic acid (PA)**. PA can be dephosphorylated leading to the formation of **diacylglycerol** which is essential in the synthesis of **phosphatidylcholine (PC)**. PC is one of the many species of glycerophospholipids. In a pathway called the **Kennedy pathway**, the polar heads are added to complete the formation of the entire structure consisting of the polar head regions, the two fatty acid chains and the phosphate group attached to the glycerol backbone. In this Kennedy pathway, Choline is converted to **CDP-Choline** which drives the transfer of the polar head groups to complete the formation of PC. PC can then be further converted to other species of glycerophospholipids such as **phosphatidylserine (PS)** and **phosphatidylethanolamine (PE)**.