LIPIDS

Introduction

Lipids cannot be defined based on the chemical nature of the members since they differ widely in structure and possess different chemical groups. But they are commonly soluble in certain non polar organic solvents. Based on this, lipids have been defined as compounds soluble in ether, chloroform and benzene. Moreover almost of the lipids are soluble in petroleum ether. Lipids are greasy substances present in both plants and animals and constitute as main components of foods along with proteins and carbohydrates.

Classification

Different authors adopt different systems for classification of lipids. We are narrating a system of classification consisting of four classes such as **simple lipids, compound lipids, derived lipids** and **lipids complexedto other compounds**.

Structures of different lipids and some related narration

Before we are discussing about the structures of higher lipids, we need to know the structures of fatty acids which are derived lipids. Fatty acids are carboxylic acids which take part in the formation of lipidous substances of organisms. Depending on the number of carbon atoms they have, they may be even carbon and odd carbon acids. Even carbon acids are generally found in natural fats. However, certain plants and animals fats have odd carbon acids. Short chain, medium chain and long chain fatty acids have 2-6, 8-14 and 16-24 carbon atoms respectively. Very long chain fatty acids have more than 24 carbon atoms. Moreover based on the nature of hydrocarbon chain, they may be saturated, unsaturated, branched and hydroxyl derivatives.

Numbering of carbon atoms of fatty acids can be done starting from carboxyl group carbon or from terminal methyl group carbon atom denoting it as ω-1, next carbon atom as ω-2 and so on. In the former case, the position of double bond is indicated by prefixing number in the systematic name. In the latter case if the fatty acid is referred to as ω-3, then it indicates this fatty acid has a double bond between ω-3 and ω-4 carbon atoms as one nearest to ω-1 carbon atom.

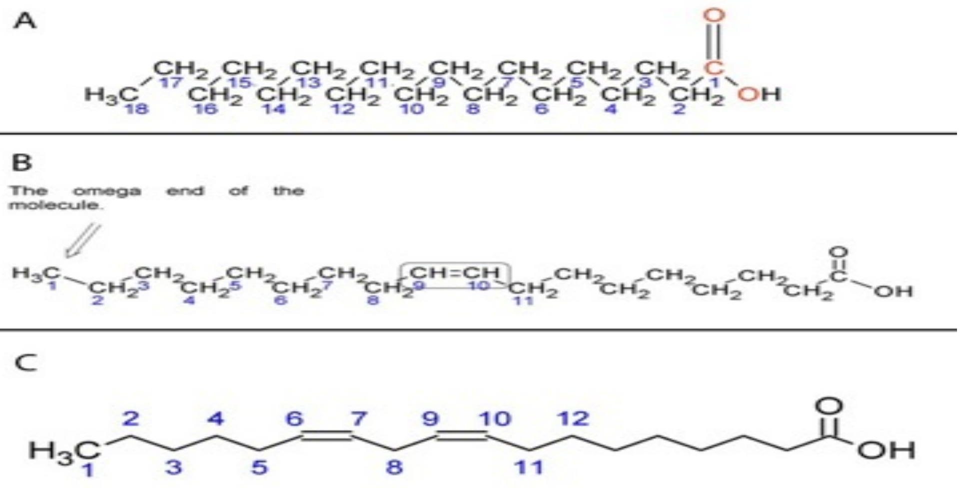


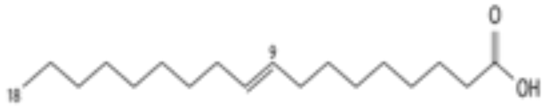
Table 1.Saturated fatty acids.

Common name	Systematic name	Formula	I (lacks last set)	Occurrence
Acetic acid	n-Ethanoic	CH	2:0	Triacetin (artificial)
Butyric acid	n-Butanoic	CH H	4:0	Milk fats
Caproic acid	n-Hexanoic	CH H	6:0	Plant fats
Caprylic acid	n-Octanoic	CH H	8:0	Coconut oil
Caproic acid	n-Decanoic	CH H	10:0	Plant fats
Lauric acid	n-Dodecanoic	CH H	12:0	Laurel oil

Myristic acid	n - Tetradecanoic	CH H	14:0	Nutmeg
Palmitic acid	n - Hexadecanoic	CH H	16:0	Palm oil
Stearic acid	n - Octadecanoic	CH H	18:0	Animal and plant fats
Arachidic acid	n-Eicosanoic	CH H	20:0	Groundnut
Bohenic acid	n-Docosanoic	CH H	22:0	Groundnut
Lignoseric acid	n - Tetracosanoic	CH H	24:0	Groundnut & rapeseed
Cerotic acid	n - Hexacosanoic	CH H	26:0	Wool fat

Examples of saturated fatty acids are given in table 1. Their general formula is $C_nH_{2n+1}COOH$. Their common names, systematic names, formulae and occurrence have been displayed in the table.

Since the freedom of rotation of groups and atoms about the double bond is prevented, the unsaturated fatty acids exhibit a type of stereoisomerism known as geometrical isomerism. The basis is the different arrangement of groups and atoms about the double bond. Two isomeric forms cis and trans are produced when like groups and atoms are on the same side and opposite sides of the double bond respectively. Illustration is given with the isomers of of the formula $C_{17}H_{33}COOH$. The cis isomer is oleic acid and trans isomer is elaidic acid. They have different melting points and other physical constants. In this case oleic acid is fatty acid.



Oleic acid (cis), m.p. 13ºC Elaidic acid (trans), m.p. 45ºC

In table 2, example of dienoic fatty acid is given with linoleic acid. Its prefixing numbers are 9 and 12. These double bonds have cis arrangement of groups and atoms. This table further shows that trienoic fatty acids such as ɑ-linolenic acid and ϒ-linolenic acid differ only in the position of double bonds. Table 2 further displays the positions of double bonds of polyenoic fatty acids. Again this table shows that ɑ-linolenic acid, timnodonic acid and cervonic acid are ω-3 fatty acids. It is very interesting that ω-3 fatty acids reduce blood cholesterol , triglycerides and blood pressure of human .

Table-2.Unsaturated fatty acids

a. Monoenoic (having only one double bond)
COOH

Common name	**Systematic name**	**Formula**	**I**	**Omega family**
Myristoleic acid	cis-9-Tetradecenoic	C_{13} H	14:1(	w-5
Palmitoleic acid	cis-9-Hexadecenoic	C_{15} H	16:1(	w-7
Oleic acid	cis-9-Octadecenoic	C_{17} H	18:1(	w-9
Vaccenic acid	cis-11-Octadecenoic	C_{17} H	18:1(	w-7
Nervonic acid	cis-15-Tetraeicosenoic	C_{23} H	24:1(	w-9

b. Dienoic (having two double bonds).

Linoleic acid	all cis-9,12-Octadecadienoic	C_{17} H	18:2(	w-6

c. Trienoic (having three double bonds).

α-Linolenic acid	all cis-9,12,15-Octadecatrienoic	C_{17} H	16:3(	w-3
γ-Linolenic acid	all cis-6,9,12-Octadecatrienoic	C_{17} H	16:3(	w-6

d. Polyenoic fatty acids (having more than three double bonds).
General formula: $C_nH_{2(n-x)}O_2$ where x = no. of double bonds.

Arachidonic acid	all cis-5,8,11,14-Eicosatetraenoic	C_{20}	20:4(Δ	w-6
Timnodonic acid	all cis-5,8,11,14,17-Eicosapentaenoic	C_{20}	20:5(Δ	w-3
Cervonic acid	all cis-4,7,10,13,16,19-Docosahexanoic	C_{22}	22:6(Δ ^{9})	w-3

I: Distinguishing three sets of number. These sets such as 18:3($\Delta^{9,12,15}$) and 20:5($\Delta^{5,8,11,14,17}$) can be alternatively written as 18:3;9,12,15 and 20:5;5,8,11,14,17 respectively.

Moreover tables 1&2 indicate that fatty acids have been distinguished by three sets of number. The first set indicates the total number of carbon atoms. The second number separated from the first number by colon indicates the number of double bond. Then delta follows it. Superscripts on delta indicate the numbers of carbon atoms preceding double bonds. Alternatively, instead of delta semicolon is used. It is then followed by preceding numbers of double bonds.

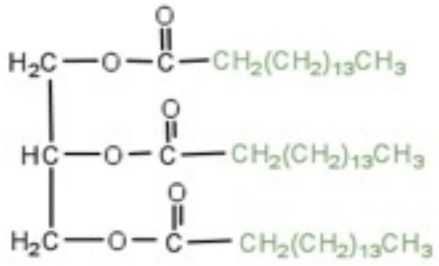
Saturated fatty acids are solid at room temperature. This is due to parallel arrangement of their alipathic chains. However cis double bonds disturb this regular packing and thus unsaturated fatty acids are liquids at room temperature. Melting point of fatty acids lowers with increasing degree of unsaturation.

Linoleic acid and linolenic acid are essential fatty acids. Arachidonic acid becomes essential when its precursor linoleic acid is not sufficiently obtained from the diets.

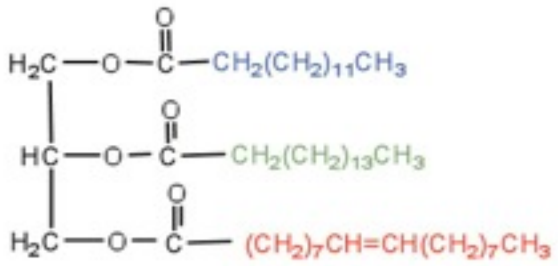
Simple lipids

They are esters of alcohols and fatty acids. If alcohol is glycerol, and it is esterified by three fatty acid molecules, they are triglycerides. Fats and oils are triglycerides. On the other hand, esters formed by long chain alcohols comprising 16 to 30 carbon atoms and long chain saturated and unsaturated fatty acids comprising 14 to 36 carbon atoms are waxes. Examples of waxes are beeswax, lanolin of lamb's wool and spermaceti oil of whales etc. Waxes are used in the preparation of candles, cosmetics, lubricants, ointments, polishes .

Triglycerides are simple when they formed with identical fatty acid molecules. Example is tristearin present in beef fat. Mixed triglyceride is formed with at least two different fatty acid molecules.



Tristearin
a simple triglyceride

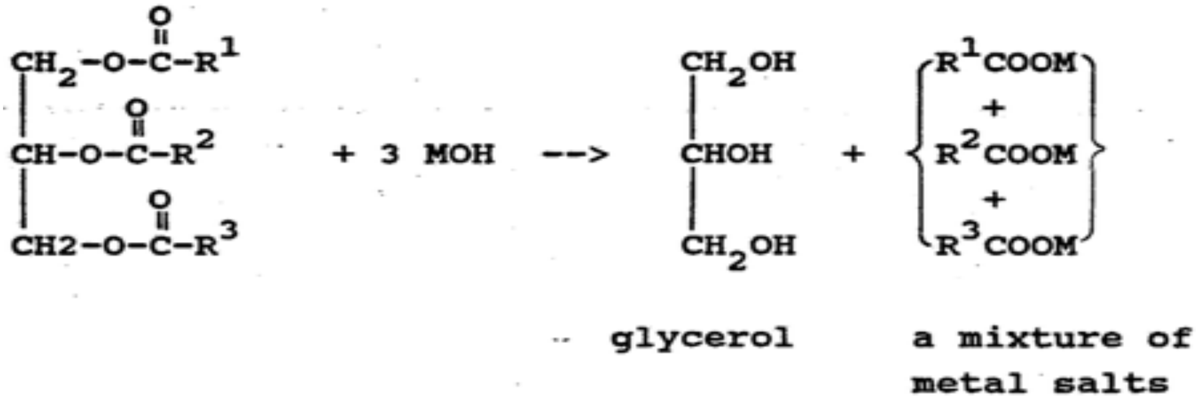


a mixed triglyceride

Triglycerides with higher composition of unsaturated fatty acids exist as liquid at room temperature and therefore they are oils. The terms fats and oils cannot be implied for distinct triglycerides since a triglyceride may be solid ei fat at low temperature and liquid ei oil higher temperature. For example ghee is solid at room temperature and oil at higher temperature.

Saponification number

Previously it has discussed that fatty acids composed in fats vary widely in chain length. Thus the molecular weights of different fats are to vary. We can have an idea on this by determining their saponification number. Saponification number is defined as the amount KOH in milligram required to saponify 1 g of fat. We know that a molecule of fat is saponified by three molecules of KOH. Since a gram of fat composed by low molecular weight fatty acids has more of its molecules, requires more amount of KOH for complete saponification. Thus saponification number is an index of average molecular size of fatty acids of fat. It can be experimentally found out.



Iodine number

Halogens can be added to the double bonds of unsaturated fatty acids of fats. Iodine number expresses the amount of iodine in g added to 100g of fat. This can be experimentally found out. It expresses the degree of unsaturation of fats.

$$\textbf{-CH=HC-} \quad + \quad \mathbf{I_2} \rightarrow \textbf{-CIH-HIC-}$$

Rancidity of fats

During storage in presence of lipases, fats undergo slow hydrolysis with the liberation of free fatty acids. Short chain fatty acids have bad smell. Such development of unpleasant taste and odour is known as rancidity and fat is said to be rancid. Another cause of rancidity is the reaction between unsaturated fatty acids of fat and atmospheric oxygen. As done by free unsaturated fatty acids, unsaturated fatty acids of fats combine with oxygen to form peroxides. The peroxides then undergo scission to form aldehydes of objectionable odour. Addition of antioxidants such as vitamin E prevents oxidation by atmospheric oxygen.

Acid number

It expresses the amount of KOH in mg required to neutralize the free fatty acids present in 1 g of fat. It indicates the degree of rancidity of fat.

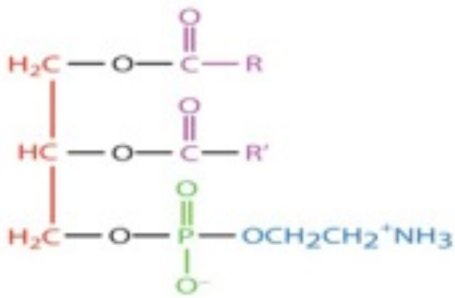
Compound lipids

Compound lipids occur in phosphorylated and non phosphorylated forms. Phosphorylated lipids or phospholipids are the derivatives of glycerol phosphate and sphingosine phosphate.

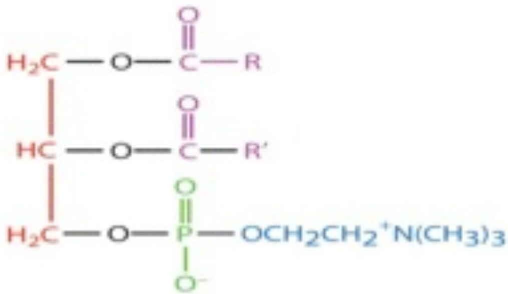
Glycerol phosphate derivatives

Glycerol phosphate derivatives are lecithins which are chemically phosphatidyl choline, cephalins which are chemically phosphatidyl ethanolamine and phosphatidyl serine. Other examples are phophatidyl inositol and phosphatidyl inositol phosphate etc. All these are derivatives of L-α-phosphatadic acid in which two hydroxyl groups of α^{I} and β carbon atoms of glycerol are esterified to two fatty acid molecules while hydroxyl group of α carbon atom is esterified to phosphoric acid. Its β carbon atom is assymmetric and it exists in L-form. Therefore it is known as L-α-phosphatidic acid.

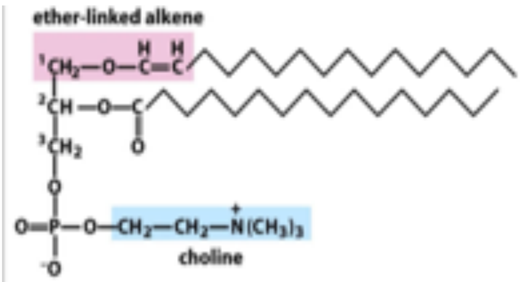
In case of plasmalogens α^{I} carbon atom is ether linked with long chain aliphatic aldehyde. Aliphatic aldehyde changes to its enol form before formation of ether bond.



Phosphatidylethanolamine
(cephalin)



Phosphatidycholine
(lecithin)



PlasmalogenEnol form of aliphatic aldehyde

Sphingosine phosphate derivatives

They are known as phosphosphingosides or sphingomyelins. One molecule of sphingomyelin is composed by one molecule for each of sphingosine or dihydrosphingosine, phosphoric acid, choline and fatty acid. They are found in nerve tissues.

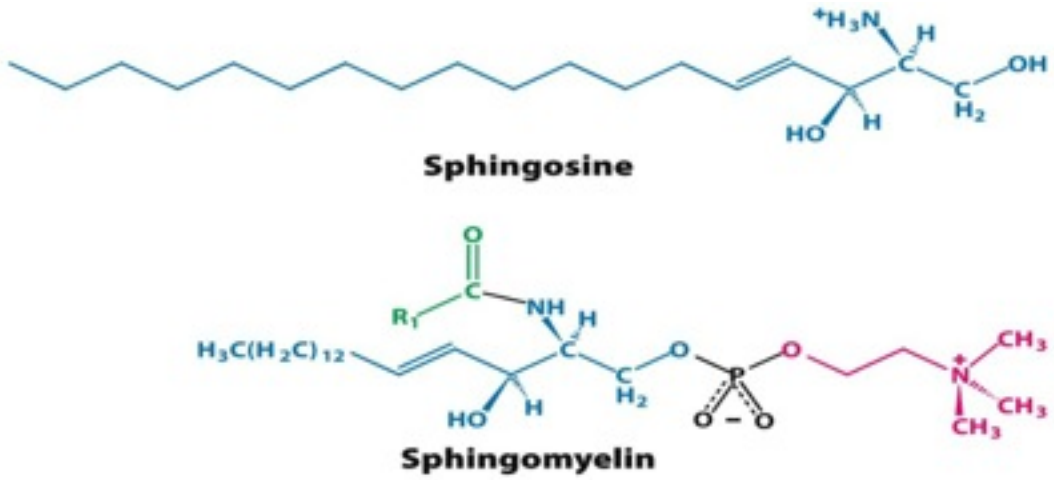


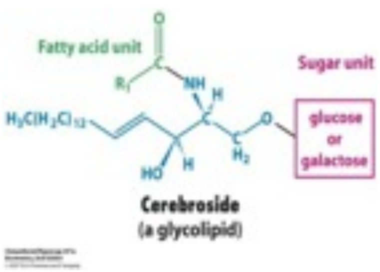
Figure 12.6
Biochemistry, Seventh Edition

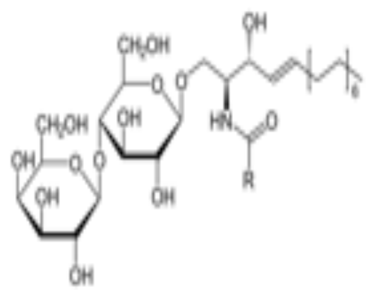
Non phosphorylated derivatives

Non phosphorylated lipids include glycolipids and sulpholipids

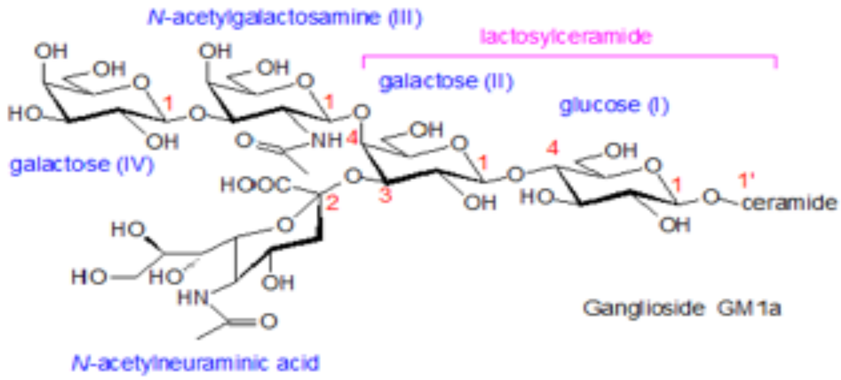
Glycolipids

Glycolipids are also known as glycosphingolipids. Cerebrosides, globosides and gangliosides belong to glycolipids. One molecule of cerebroside is composed by one molecule for each of sphingosine, fatty acid, glucose or galactose. Its sphingosine and fatty acid portion is known as ceramide. Globosides are ceramide oligosaccharides. Their oligosaccharides are made up of glucose and galactose and other combinations of hexoses and hexoseamine. Gangliosides are derived forms of globosides with attachment of N-acetyl neuraminic acid. Cerebrosides and gangliosides are found in brain.



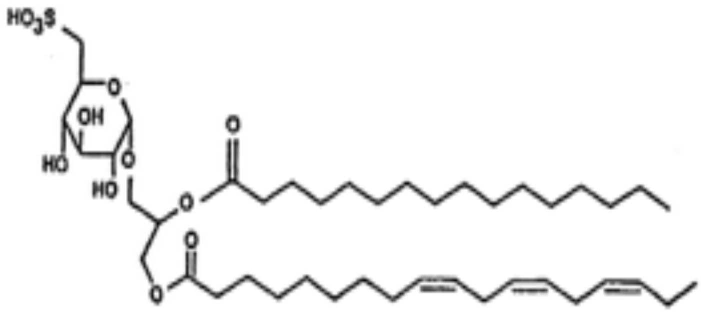


Globoside



Sulpholipids

Lipids having sulphate groups are known as sulpholipids or sulphatides.



Sulfolipid

Derived lipids

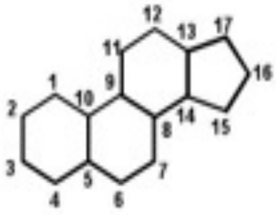
Fatty acids

Fatty acids are examples of derived lipids because they can be obtained from other lipids. Their structures, certain physical and chemical properties have been discussed preiviosly.

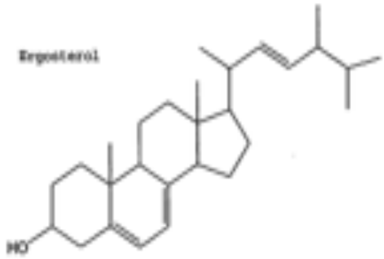
Steroids

They are compounds derived from basic structure of four fused rings- three of cyclohexane and one of cyclopentane. Such fused ring system is known as perhydrocyclophentanophenanthrene. If such structure has one hydroxyl group at carbon atom no. 3 and a chain of 8-10 carbon atoms at carbon atom no. 17, then it is known as sterol. Examples of sterols are lanosterol, ergosterol, cholesterol, 7-

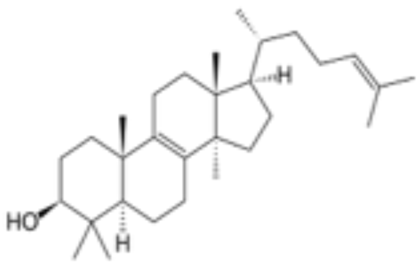
dehydrocholesterol etc. Other forms of steroids are bile acids, sex hormones, adrenocorticoids and insect hormone etc.

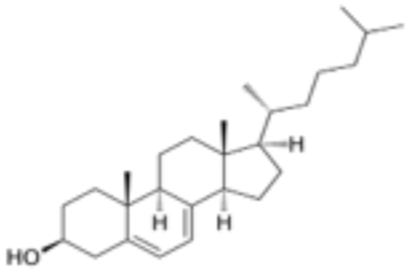


Perhydrocyclopentanophenanthrene

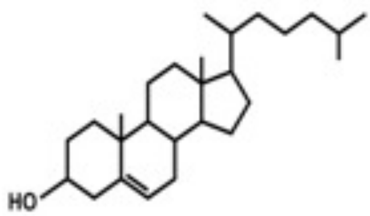


Ergosterol





Lanosterol 7-Dehydrocholesterol



Cholesterol

Vitamin D is formed by cleaving ring B of ergosterol upon irradiation with UV. Hence it is member of the class derived lipids.

Terpenes

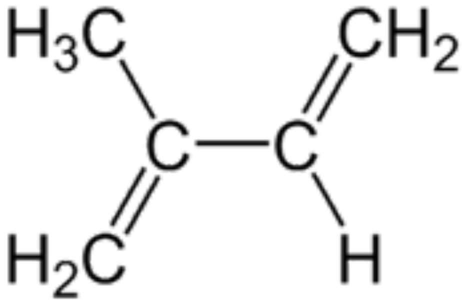
Terpenes are hydrocarbons formed by polymerisation of repeating unit of isoprene. An isoprene has five carbon atoms and eight hydrogen atoms. Some authors use the word terpenoids for terpenes whose methyl groups are eliminated, moved or containing oxygen. However, organic chemists use both words interchangeably. A monoterpene is composed by two isoprene units and it has ten carbon atoms. Examples are geraniol, limonene, menthol. A sesquiterpene has three isoprene units and thus it has 15 carbon atoms. Example is farnesol. Diterpenes, triterpenes and tetraterpenes are composed by 4,6 and 8 isoprene units respectively.

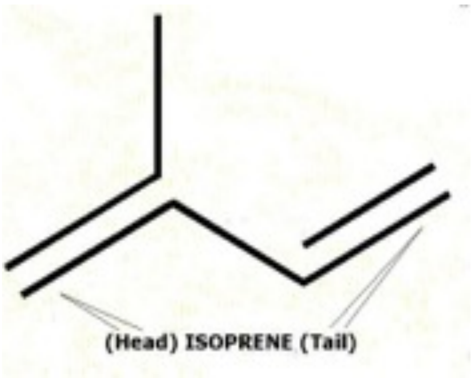
Table 3 displays their numbers of carbon atoms and examples. The table also shows that rubber is a polyterpene composed by 500-5000 isoprene units.

Table 3.Terpenes

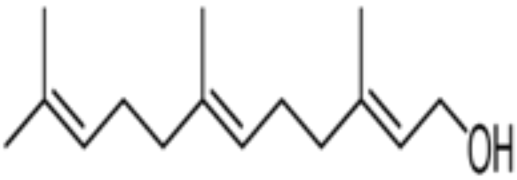
Terpenes	No. of repeating units	No. of carbon atoms	Terpenoids
Monoterpenes	2	10	Geraniol, limonene, menthol
Sesquiterpenes	3	15	Farnesol
Diterpenes	4	20	Abietic acid, sapeitic acid
Triterpenes	6	30	Lanosterol
Tetraterpenes	8	40	Carotenoids
Polyterpenes	500-5000	2500 - 2500	Rubber

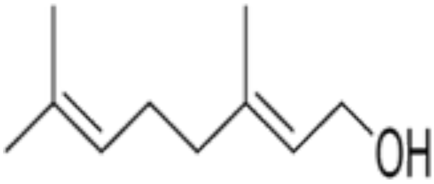
Isoprene units combine to form terpenes following special rule. In accordance to this rule, isoprene units combine with the formation of head to tail linkage. No. 1 and no. 4 carbon atoms of isoprene are known as head and tail respectively. However, this rule is not always followed. For example cryptone has nine carbon atoms instead of ten carbon atoms. Moreover isoprene units are not head to tail linked in lavandulol. Again in carotenoids two isoprene units in the centre of the chain are tail to tail linked.



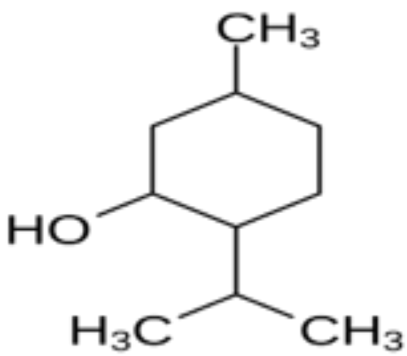


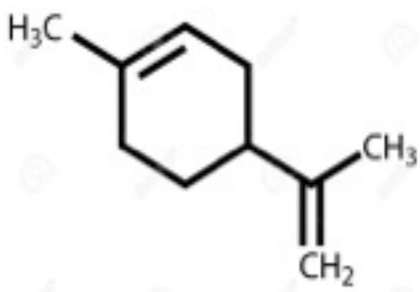
Isoprene





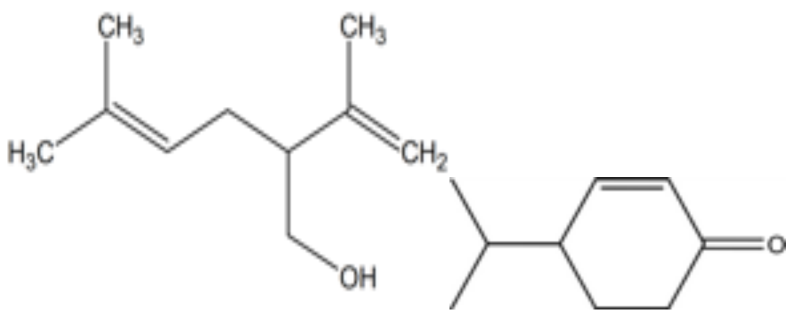
FarnesolGeraniol





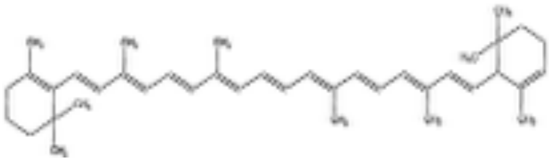
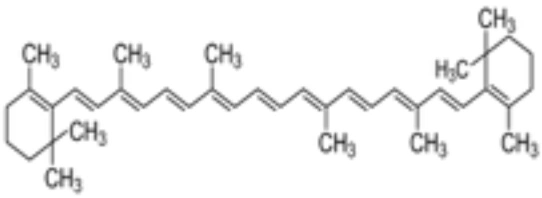
Menthol

Limonene

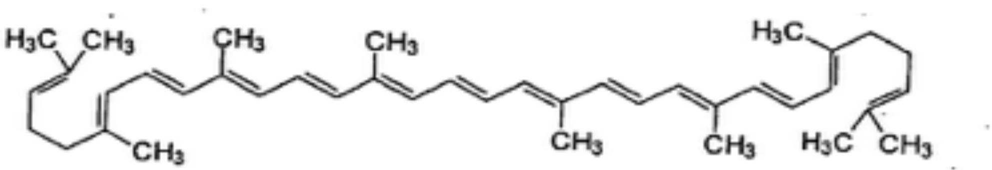


LavandulolCryptone

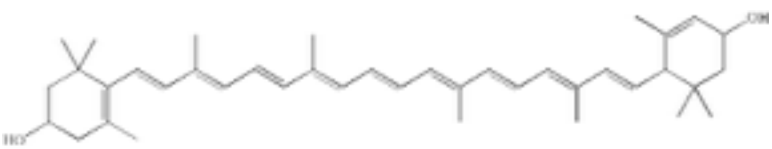
It has ascertained from table 3 that carotenoids are tetraterpenes. Members of carotenoids are more than 600 and they are divided into carotenes and xanthophylls. Carotenes are hydrocarbons and they are in the subclass of unsaturated hydrocarbons. Examples are α-carotene and β carotene and lycopene. Xanthophylls are oxygen containing carotenoids. Examples are lutein and zeaxanthin.

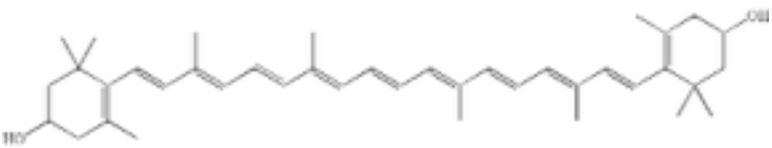
α-carotene β-carotene



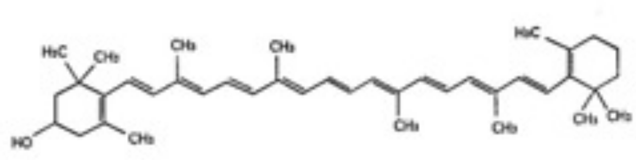
Lycopene



Lutein



Zeaxanthin

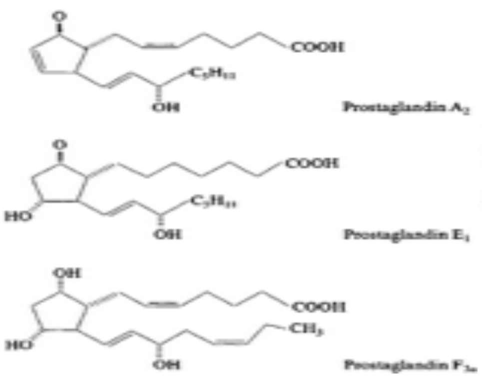


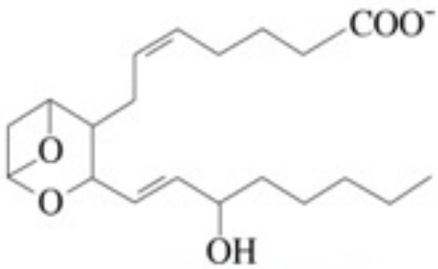
β-cryptoxanthin

α- Carotene, β- carotene and β- cryptoxanthin serve as precursors of vitamin A for human. Therefore vitamin A is regarded as lipid under the class derived lipids. On the other hand, vitamins E and K have isoprenoids side chain. Therefore they are also members of the class derived lipids.

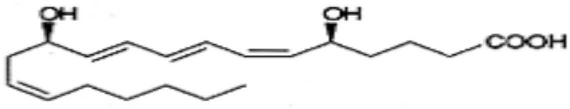
Eicosanoids

Arachidonic acid is the dominant precursor of eicosanoids. It can be noted that all eiconoids have twenty carbon atoms. Eicosanoids include prostaglandins, thromboxanes, leukotrienes and lipoxins etc. In our body prostaglandins function as local hormones, Leukotrienes bring about contraction of smooth muscles. Thromboxanes participate in the formation of blood clot. Lipoxins exert immunoregulatory function.

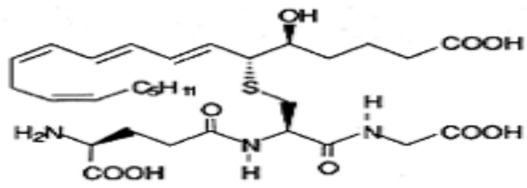




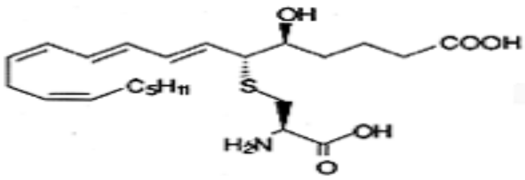
Thromboxane A_2
(TxA_2)



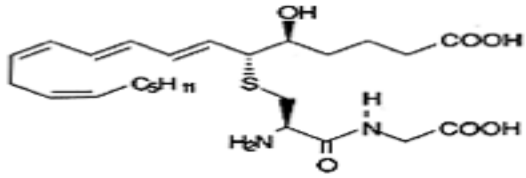
LEUKOTRIENE B_4



LEUKOTRIENE C_4



LEUKOTRIENE E_4



LEUKOTRIENE D_4

Lipids complexed to other compounds

Lipoproteins

Certain lipoproteins occur in blood as transport form of lipids. They are complexes of proteins, phospholipids, triglycerides and cholesterol. Based on fraction migration in density gradient separation, they are classified into very low density lipoproteins (VLDL), low density lipoproteins (LDL), high density lipoproteins (HDL). VLDL is mainly synthesized in liver, but in intestine it is also synthesized in small amount with absorbed lipids. LDL is largely derived from VLDL. HDL is the transport form of cholesterol from peripheral cells to liver where it is excreted in bile as bile acids. These lipoproteins have different half life periods.

Proteolipids

They are complexes of protein, phosphoglycerides and cerebrosides, and occur in brain tissue.

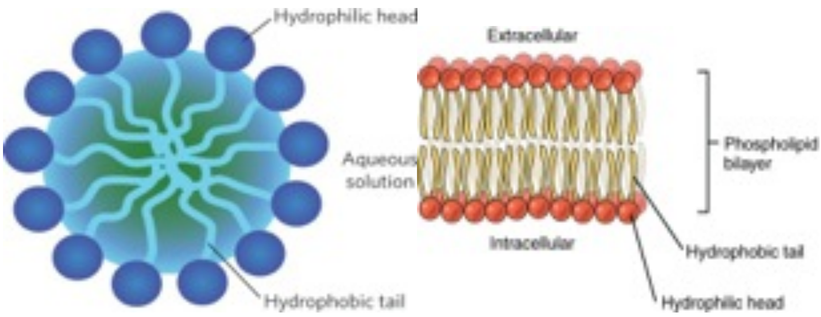
Lipopolysaccharides

These lipids occur in the outer layer of the cell wall of gram negative bacteria. Permeability barrier exhibited by outer layer is due to presence of these lipids.

Polar and non polar lipids

Lipids such as phophatidyl choline, phosphatidyl ethanolamine etc. have charged groups. Such polar groups are hydrophilic. But their hydrocarbon chains are hydrophobic. Therefore they are amphipathic molecules. Other lipids such as monoglyceride, diglyceride and sterols have polar hydroxyl groups and they are also amphipathic molecules. The hydrophilic and hydrophobic parts of such amphipathic molecules are known as head and acyl chain respectively.

When cross sectional area of the head is larger than that of acyl chain, amphipathic molecules form micelles when mixed with water. Examples are soap molecules. A micelle has few dozen to few thousand of molecules. In a micelle hydrophobic side chains aggregate inside excluding water while their hydrophilic heads are in contact with water. On the other hand when their head and acyl chain have equal cross sectional



Micelle Lipid bilayer

area, they organise into lipid bilayer when mixed with water. In lipid bilayer, acyl chains of each monolayer occupy inner portion due to their hydrophobic interaction and Van der Waals' force and thus they exclude water. The hydrophilic heads of each monolayer interact with water molecules forming hydrogen bonds. Examples are phosphatidyl choline, phosphatidyl ethanolamine etc.

Biological importance

Biological roles of lipids in plants and animals are several and some important biological roles are discussing below.

Fats serve as chief energy reservoir of plants and animals.

Fats prevent loss of heat from the body. They also support and protect internal organs by serving as padding substance.

Glycolipids, phospholipids, cholesterol and other steroids are the major structural components of mitochondrial and other cellular membranes.

Lipoproteins are the transport forms of lipids in blood. They involve in the absorption of free fatty acids from intestine.

Glycolipids, phospholipids and steroids play essential roles in the functions of mitochondria.

Cerebrosides, gangliosides and sulpholipids play specific roles in the brain functions.

Cholesterol gives rise to bile acids.

Cholesterol insulates impulse generating and transmitting units of brain and nerve.

Waxes of animals’ skins and furs serve as protective lipids. Plant waxes protect leaves and fruits. Ear wax is also an example of protective lipid.

Vitamins A,E,D and K are also members of lipids. These vitamins play magnificent roles in the vital processes.

Eicosanoids such as protaglandins serve as local hormones. Functions of other eicosanoids are causing contraction of smooth muscles, formation of blood clot and regulation of blood pressure etc.

Conclusion

From the above narration, it can be concluded that many organic molecules widely differed in structure and function include as members of lipids. The structure of a lipid may be as simple as that of acetic acid and complex one as that of a lipoprotein. Fats and oils are neutral lipids whereas phospholipids are polar lipids. The functions of lipids are diversified as fats and oils are storage lipids of plants and animals; phospholipids, glycolipids and steroids serve as structural components of cell membranes; fats prevent loss of heat the body as well as serve as padding substance of tissues and organs; some other lipids serve as vitamins ei vitamins A,E,D,K and moreover lipoproteins serve as transport form of cholesterol etc.Ceretain lipids such as prostaglandins serve as local hormones. In foods lipids present as one of the main components. The essential fatty acids such as linoleic acid and linolenicacid are to be regularly obtained from the lipids of diets with their required amounts. Arachidonic acid becomes essential when its precursor linoleic acid is not sufficiently obtained from the diets.