FATTY ACIDS .

Types and nomenclature (saturated and unsaturated)

Fatty acids- these are building blocks of lipids. They are monocarboxylic acid having a terminal carboxylate group. Since fatty acid are synthesized from 2C units. They consists of straight chain hydrocarbons with even number of C- atoms (4-30). The chain maybe **saturated** containing only single bond; or they maybe **unsaturated** having 0-6 double bonds mostly in 18-24C acids. Fatty acids are varied and may have acetylinic bond, epoxy, hydroxyl and keto group or cyclopropene and cyclopentene rings.

Saturated fatty acids- are generally solids at room temperature due to large number of carbon atoms. In plants occur in palm oil. They have hydrophobic tail of zig-zag configuration and because of single bond they are free to rotate and are thus more flexible and elongated. They form a fully extended and stable configuration in which the steric hindrances of neighboring atoms is minimized. These molecules can thus pack together tightly to form a nearly crystalline structure. General formula is $C_nH_{2n+1}COOH$.

Lauric acid (12 C) $CH_3(CH_2)_{10}COOH$ – members of Lauracea family

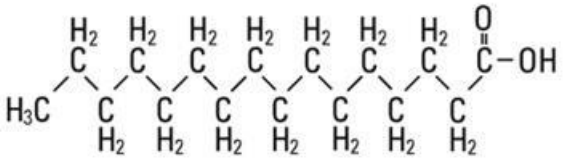
Myristic acid (14 C) $CH_3(CH_2)_{12}COOH$ – members of Myrtaceae family

Palmitic acid (16 C) $CH_3(CH_2)_{14}COOH$ – palm oil

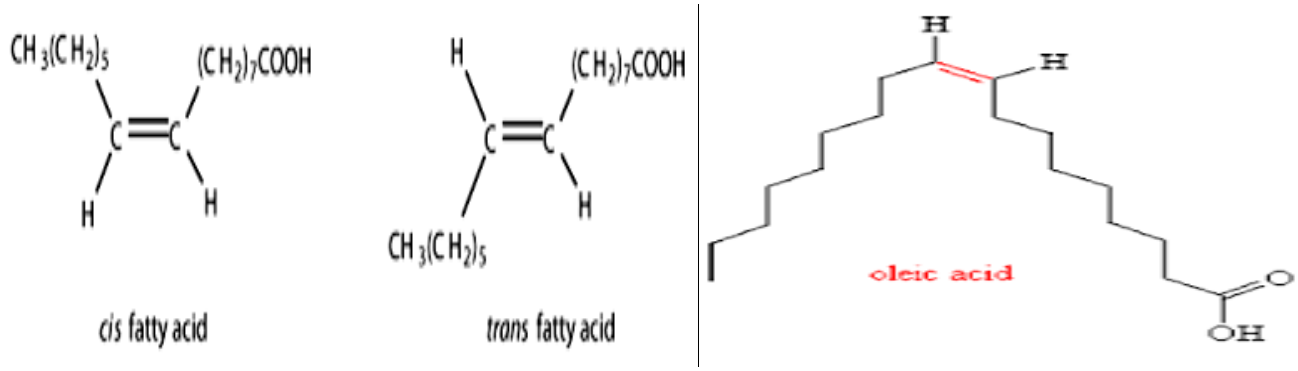
Stearic acid (18 C) $CH_3(CH_2)_{16}COOH$ - palm oil

Arachidinic acid (20 C) $CH_3(CH_2)_{20}COOH$ – peanut oil

Palmitic acid
$C_{16}H_{32}O_2$



Unsaturated fatty acids- presence of double bond. Lowers melting point and therefore lipids with unsaturated acids are mostly oils at room temperature. The number of double bond show the degree of unsaturation. Double bonds produce rigid bends in the HC tail resulting in geometric isomerism. Most common are the less stable 'cis' form rather than 'trans' forms which are more stable.

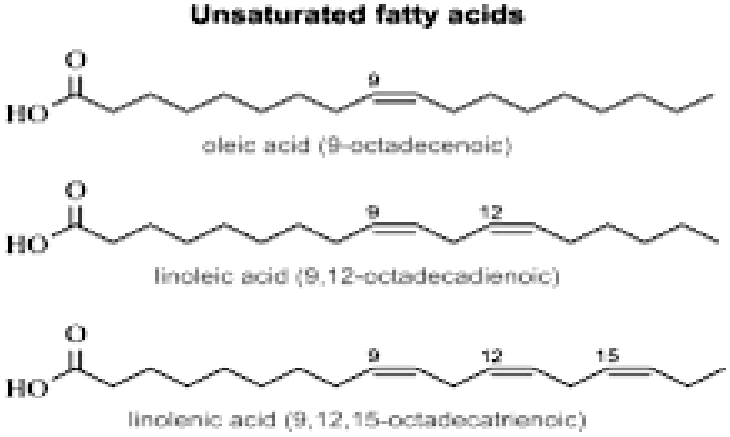


Fatty acids with double bonds have kinks in their structure and therefore cannot pack together like saturated FA and their interaction with each other is poor. These double bonds thus give a large bulky structure to fatty acids and thus require less thermal energy to disorder them resulting in lower melting points and therefore lipids with unsaturated acids are mostly oils at room temperature. Plants and animals contain polyunsaturated acids while bacteria has no polyunsaturated fatty acids except the unsaturated acid vaccenic acid eg. $CH3(CH_2)_5$-CH=CH$(CH_2)_9$-COOH. The double bond system may be

1) **Non- Conjugated double bond system**- where doble bond are interrupted by methylene grop and arrangement is a pentadine structure eg. linoleic acid CH_2-CH=CH-CH_2-CH=CH-CH_2
2) **Conjugated double bond system**- have triene system as in α-elaeostearic acid (….oil……) $CH_3(CH_2)$CH=CHCH=CHCH=CH$(CH_2)_7$COOH.

According to number of double bonds unsaturated acid may be:

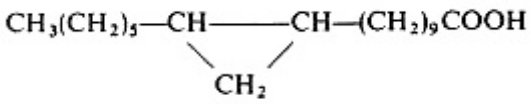
1. **Monoenoic or monoethenoid acid**- C_nH_{2n-1}COOH (18C); oleic acid $CH_3(CH_2)$ CH=CH$(CH_2)_7$COOH- palm oil; erucic acid (20 C) $CH_3(CH_2)_4$CH=CH$(CH_2)_{11}$COOH - mustard oil.
2. **Dienoic or diethenoid acid** - C_nH_{2n-3}COOH (18C); Linoleic acid in cotton seed, linseed and soybean $CH_3(CH_2)_4$CH=CHCH_2CH=CH$(CH_2)_7$COOH
3. **Trienoic or triethenoid** acid - C_nH_{2n-5}COOH (18 C); Linolenic acid in palm and linseed oil $CH_3CH_2CH_{11}$CHCH_2CH=CHCH_2CH=CH$(CH_2)_7$COOH.
4. **Tetraenoic or Tetraethenoid acid** - C_nH_{2n-7}COOH (20); Arachidonic acid in peanut oil. $CH_3(CH_2)_4$CH=CHCH_2CH= CHCH_2CH=CHCH_2CH=CHC$H_2(CH_2)_3$COH.



Unusual fatty acid- hydroxy or oxygenated fatty acid eg. ricinoleic acid (18C) castor oil with OH group on C_{12}.

Ricinoleic acid in castor oil

Cyclic fatty acid – example – lactobacillic acid with a cyclopropyl group and methylene group across the double bond of vaccenic acid.



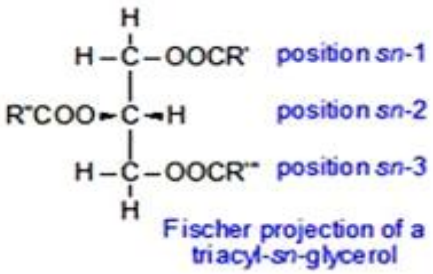
Lactobacillic acid

NOMENCLATURE :

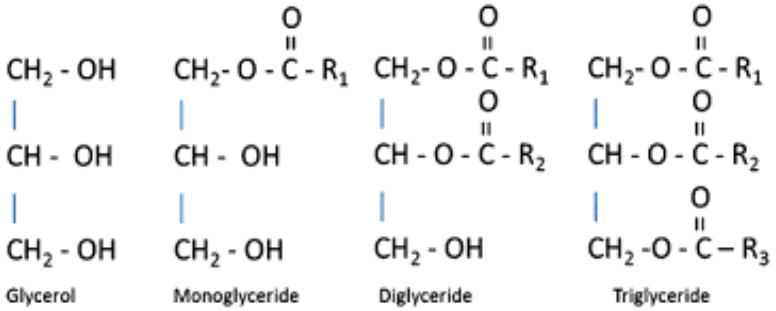
The fatty acids are numbered at the end. First we write no of C atoms then no of double bonds and finally position of first C of double bond counting from carboxylic end. Thus palmitic acid is 16:0 , oleic acid 18:1(9), linoleic acid 18:2 (9,12); linolenic acid 18:3(6+,9+,12); arachidonic acid 20:4 (5,8,11,14).

SIMPLE LIPIDS

These are esters of one or more fatty acids and an alcohol mostly glycerol generically known as **acylglycerols**. Most common are triacylglycerol but mono and diacylglycerol are also common. Because the polar OH group and the polar carboxyl of fatty acid are bound in ester linkage triacylglycerol are non-polar hydrophobic molecules. They have lower specific gravity than water hence they float on it. They are used as fuels more than carbohydrates as carbon atoms in fats are more reduced and therefore oxidation of fats gives more energy. They are present as fsimple ats and oils and complex waxes. When the glycerol is esterified with fatty acid then C-2 becomes asymmetric centre and the 2nd hydroxyl group of glycerol is always show to left of C-2 while C atom above C-2 is called C-1 and below C-2 is C-3. This is stereo specific numbering (SN). Accordingl to the no. of FA esterified to glycerol they may be called mono-,di- or triacylglyceral:



Fischer projection of a triacyl-*sn*-glycerol



Fats and oils- These are the triglycerides or triacylglycerols. They are esters of three fatty acids and glycerol (trihydric alcohol) formed by loss of three H_2O molecules. These are non polar and hydrophobic immiscible in water with general formula $CH_3(CH_2)_nCOOH$ where n= even number. They are most abundant storage form and serve as fuel having high calorie count. forming 95% of dietary lipids. They may exist as either Fats which are solid at room temperature with high proportion of saturated fatty acids resulting in high melting point as in animal triacylglycerols. Oils have low melting point due to presence of unsaturated fatty acid and therefore liquid at room temperature as in plant. Those with single type of fatty acid as simple triacylglycerol eg tristearylglycerol or mixed with two types of fatty acids eg. dietary fat

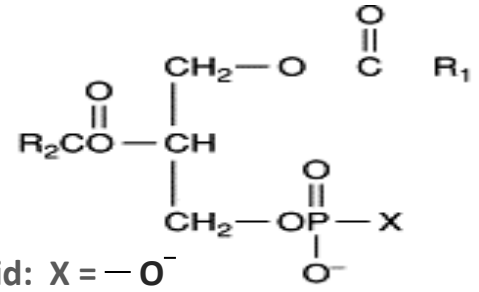
Waxes- occur as protective coating on fruits and leaves or secreted by insects (beewax). These are mixtures of long chain alkanes with odd number of carbon atom C_{25}-C_{35} and oxygenated derivative such as secondary alcohols and ketones. They are insoluble in water and are chemically enert resistant to atmospheric oxygen and therefore protect plants from water loss and abrasive damage. Mostly they are fatty acyl ester of long chain alcohols of long length. The myricyclic alcohol of beewax has 30C ($C_{30}H_{61}OH$-- triacontanol) and is myricyl palmitate RCOOR' R is C_{17}-C_{29} C atoms and R' C_{18} – C_{30} . Sperm whale wax is composed of palmitic acid esterified with hexacoscenol ($C_{26}H_{53}OH$). This was primary wax source for many years but now *Simmondsia chinensis* a desert plant has large oxygen wax esters as storage lipid in its seed. These wax esters act as superior machine lubricants.

COMPOUND LIPIDS

These are esters of fatty acids containing other groups in additional to fatty acids and alcohols:

1. **Phospholipids-** are most abundant membrane stored in large amount lipid being their structural component and never stored in large amounts. These lipids contain a phosphorus atom as phosphoric acid. They differ from triglycerides in having one hydrophilic polar head formed by an ester linkage between 3rd OH group of glycerol and phosphoric acid (to which some other group maybe attached) and 2 hydrophobic non- polar tails of long chain fatty acid. They are thus called polar lipids and sometimes amphipathic lipid and they have negative charge on phosphoric acid at pH 7.0 The group attached to phosphoric acid may also be changed.

   Phosphatidic acid is most simple phospholipid and have two molecules of fatty acid esterified to glycerol with phosphoric acid at terminal end. This polar phosphoryl group generally forms a second ester with some alcohol may be amino alcohol, ethanol amine or its methylated derivative choline, or its carboxylated serine.



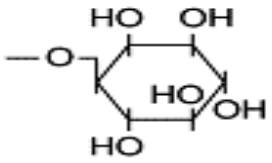
Phosphatidic acid: X = — O^-

Phosphatidylcholine (Lecithin): X = — $OCH_2CH_2\overset{+}{N}(CH_3)_3$

Phosphatidylethanolamine (Cephalin): X = — $OCH_2CH_2\overset{+}{N}H_3$

Phosphatidylserine: X = — $OCH_2CH(\overset{+}{N}H_3)(CO_2^-)$

Phosphatidylinositol: X =



Phosphatidylglycerol: X = — $OCH_2CHOHCH_2OH$

Lecithin – Phosphatidyl choline has methylated derivative of the alcohol, found in soybean and yeast. This is major constituent of all membrane lecithin helps in transport and utilization of lipids accumulation results in fatty liver. It can be broken down by lecithinase resulting in haemolysis of blood (Snake venom). It is yellowship grey soluble in ether alcohol, on exposure it absorbs water and darkens to form a dark greasy wax.

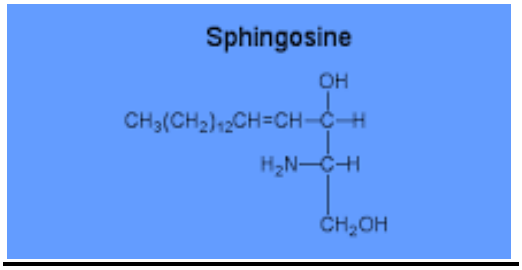
Cephalins – Found in soybean oil is association with lecithin phosphatidyl ethanol amine has the amino alcohol ethanol amine forming ester with phosphoric acids. Positively charged generally R` is palmitic or stearic or poly unsaturated acid.

Phosphatidyl serine – is neutral having amino- and carboxy- groups of serine attached to the amino group of ethanol.

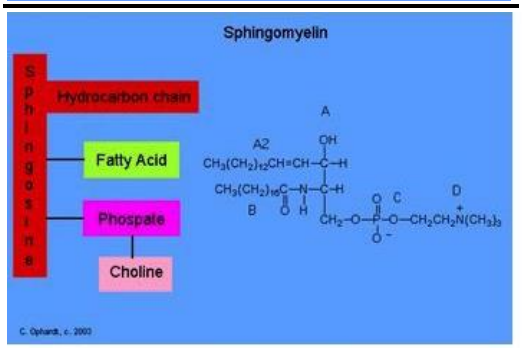
Plasmalgen - not significant in plant but in brain. Here first fatty acid is replaced by unsaturated unsaturated ether. Polar group may be choline and serine

Phosphatidyl inositol - Present in brain and soybean. Important because of the role in transport process of cells. Here cyclic hexahydroxy alcohol called myoinositol replace the base.

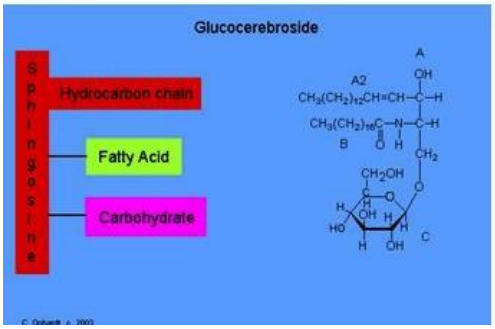
2. **Sphingolipids-** diverse group of complex lipids composed of derivatives of sphingosine now called 4-sphingenine which is a long chain amino alcohol formed from palmityl CoA and serine found in brain nerve and tissue. The sphingosine has a long chain fatty acid attached to it amino acid by amide linkage. This is called ceramide, basic structure and in association with phosphoryl choline it forms sphingomyelin. Glycosphingolipids in which amino alcohol is replaced by sugars. Replacement of phosphoryl choline in sphingomyelin by β-D-galactosyl group. Forms cerebroside.



Sphingosine has three parts, a three carbon chain with two alcohols an amine and a hydrocarbon chain

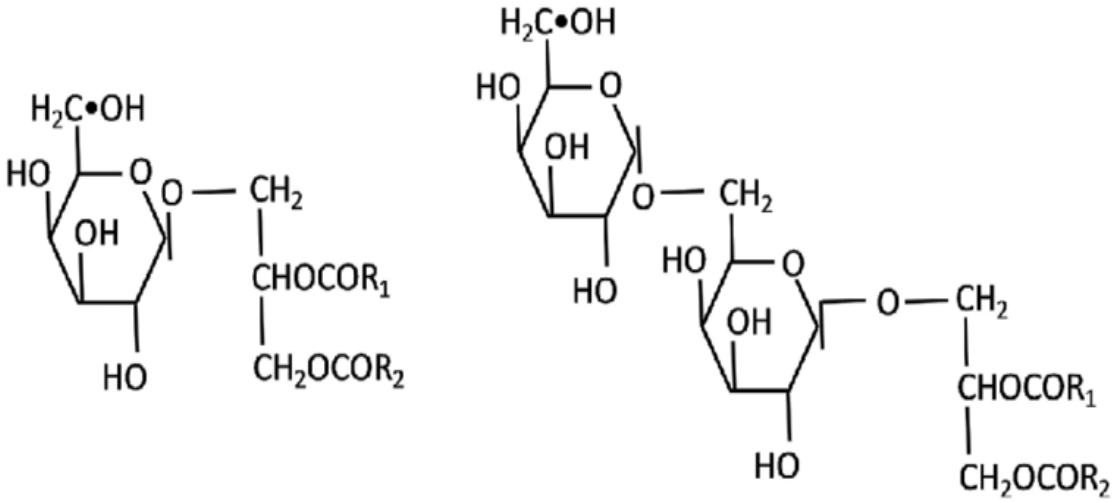


Sphingomyelin has a sphingosine backbone and a fatty acid is attached to the amine through amide bond. Phosphate is attached through a phosphate ester bond, and through a second phosphate ester bond to choline.

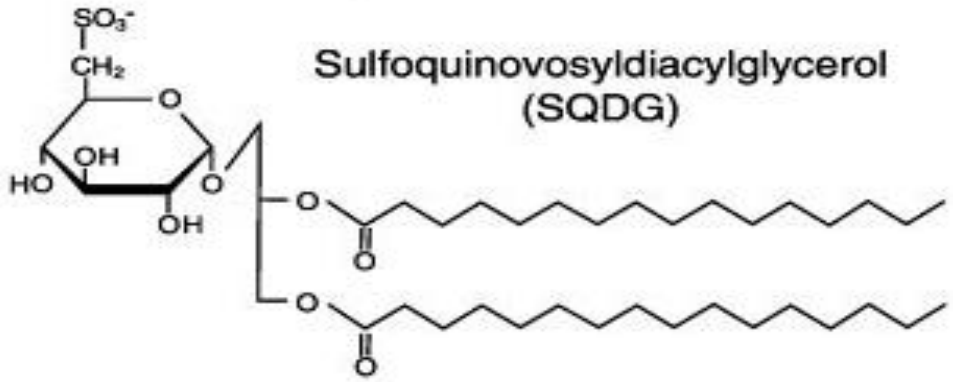


Phosphoryl choline is replaced with a sugar

3. **Glycolipids -** these are primarily amphipathic carbohydrates – glyceride derivatives and do not contain phosphate. These include galactolipids and sulpholipid found primarily in chloroplast membranes



Monogalactosyldiacylglycerol (MGMG) **Digalactosyldiacylglycerol (DGMG)**



Sulfoquinovosyldiacylglycerol (SQDG)

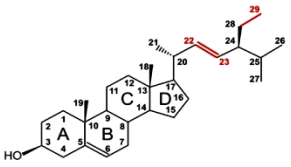
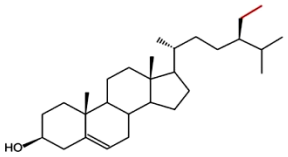
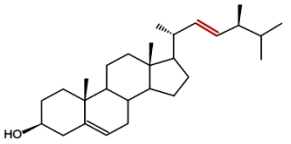
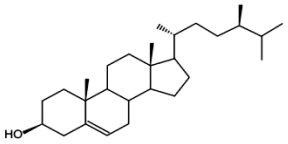
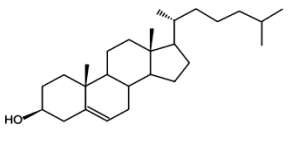
4. **Lipoproteins-** important component of cell membrane of mitochondria, endoplasmic reticulum, nuclei, chloroplast lamellae and play important role in ETS. Lipids maybe triacylglycerol phospholipid or cholesterol ester. The protein is made up of non-polar aminoacids and bonding is due to hyphobic interaction between proteins and lipids. In the plasma the lipids are associated with proteins in the form of lipoproteins. Classified in to 4 types: The lipoprotein of lowest density the chylomicrons are the largest in size and contain the most lipids and smallest percentage of proteins high density lipoproteins (HDL) are smallest in size and have highest percentage of protein and lowest of triacylglycerols.

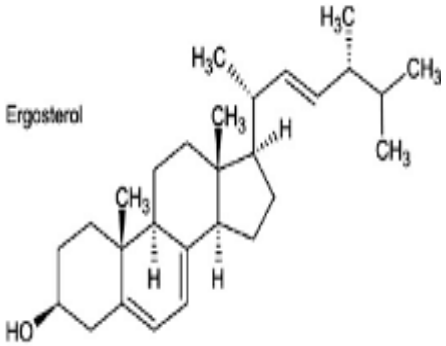
	Chylomicrons	**VLDL**	**LDL**	**HDL**
Diameter (mm)	500-1000	30-70	20-25	10-15
Protein %	1-2	10	25	33
Triacylglycerol	53	50	10	8
Cholesterol and cholesterol ester	8	22	46	30
Phospholipid	7	18	22	29

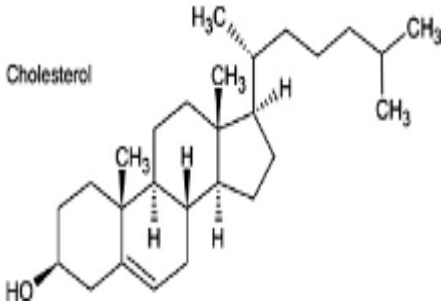
Each has a neutral lipid core of triacylglycerol and cholesterol ester. Around this core is a layer of protein , phospholipid and cholesterol. These lipoprotein serve as mode of transport of triacylglycerol and cholesterol enter from intestine to other tissues in the body. The cholesterol ester is derived from cholesterol and phosphatidycholine on the surface of high density lipoprotein by lecithin cholesterol acyl transferage (LCAT). Cholesterol ester is the storage form of cholesterol in cells and formed by cholesterol and acyl CoA by acyl CoA cholesterol acyl transferase (ACAT).

DERIVED LIPIDS

1. Steroids- polycyclic compound which is unsaponifiable, cannot be hydrolysed. They have a basic structure derived from fully saturated ring system sterane or perhydrocyclopentanephenanthrene which has 3 complex ring fused in a linear or phenanthrene manner and a terminal cyclopentane ring. The presence of C_{8}- C_{10} chain at position 17 and a OH group at 3 characterizes a large number of steroids called sterols. Sterols or steroid alcohol occurring in membrane as transporters of lipids and are soluble in organic solvents. Cholesterol is the best known sterol found in animals. Esterification of one group of cholesterol gives cholesteryl ester which are storage forms. Ultraviolet radiations give rise to Vit D. Deriatyives of cholesterol occur as vitamins such as vitamin E α-tocopherol in wheat germ oil, naphtoquinone/phylloquinone (Vit K). In plants sterols are abundantly present as- stigmasterol- from soybean and wheat germ oil, sitosterol- higher plants, spinasterol- spinach and cabbage.

	Double bond between C22=C23	Single bond between C22-C23
Ethyl-group at C24	 Stigmasterol	 β-Sitosterol
Methyl-group at C24	 Brassicasterol	 Campesterol
Hydrogen at C24		 Cholesterol





2. **Terpenes-** found in plants and made up of repeating unit of isoprene units derived from isopentyl pyrophosphate. Monoterpene consists of 2 isoprene units formed in higher plants. Their oxygenated derivative occur as essential oils e.g myrcene (oil of bay), geranoil (rose oil), limonene (lemon oil), menthol (peppermint oil). Diterpenes, triterpenes and tetraterpenes include important compounds like gierellins, phytol ring structure, carotenoids, xanthophylls, flavonoids,plant pigments, chalcone and stilbenes.