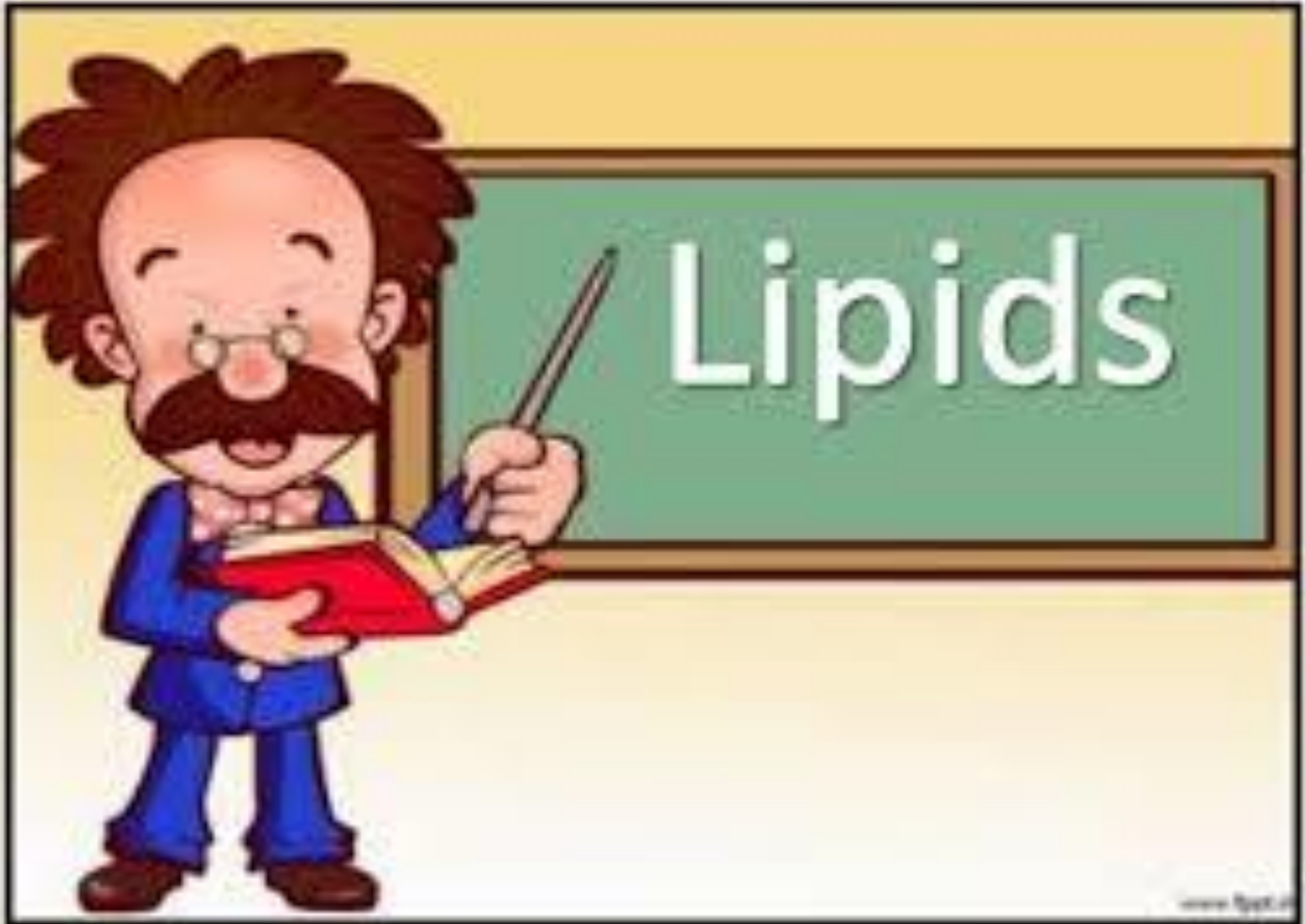


بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ



Classification & Derived Lipids

- Dr.Bela Inayat
- Deptt.of Biochemistry
- KGMC

LAYOUT

- Definition
- Biomedical importance
- Classification of lipids
- Derived Lipids
- Essential fatty acids.



definition

- ***Chemically they are various types of esters of different alcohols. In addition to alcohol and fatty acids some of the lipids may contain phosphoric acid, nitrogenous base and carbohydrates.***



Bloor's Criteria

According to Bloor, lipids are compounds having the following characteristics:

- They are insoluble in water.
- Soluble in one or more organic solvents called “fat solvents” such as ether, chloroform, benzene, acetone etc.
- Some relationship to the fatty acids as esters



lipids include

fats

oils

waxes

An oil is a lipid which is liquid at ordinary temperature.

difference between fats and oils is purely physical one.

Chemically they are all esters of glycerol with higher fatty acids.

BIOMEDICAL IMPORTANCE



- Important dietary constituents and acts as *fuel* in the body.
- Can be stored in the body in almost unlimited amount in contrast to carbohydrates.
- Some deposits may exert an insulating effect in the body, while lipids around internal organs like kidney etc, may provide padding and protect the organs.
- **Building materials:** breakdown products of fats can be used for building biological active materials.
- Lipids supply the so called *essential fatty acids* which can not be synthesized in the body and are essential in the diet for normal health and growth.

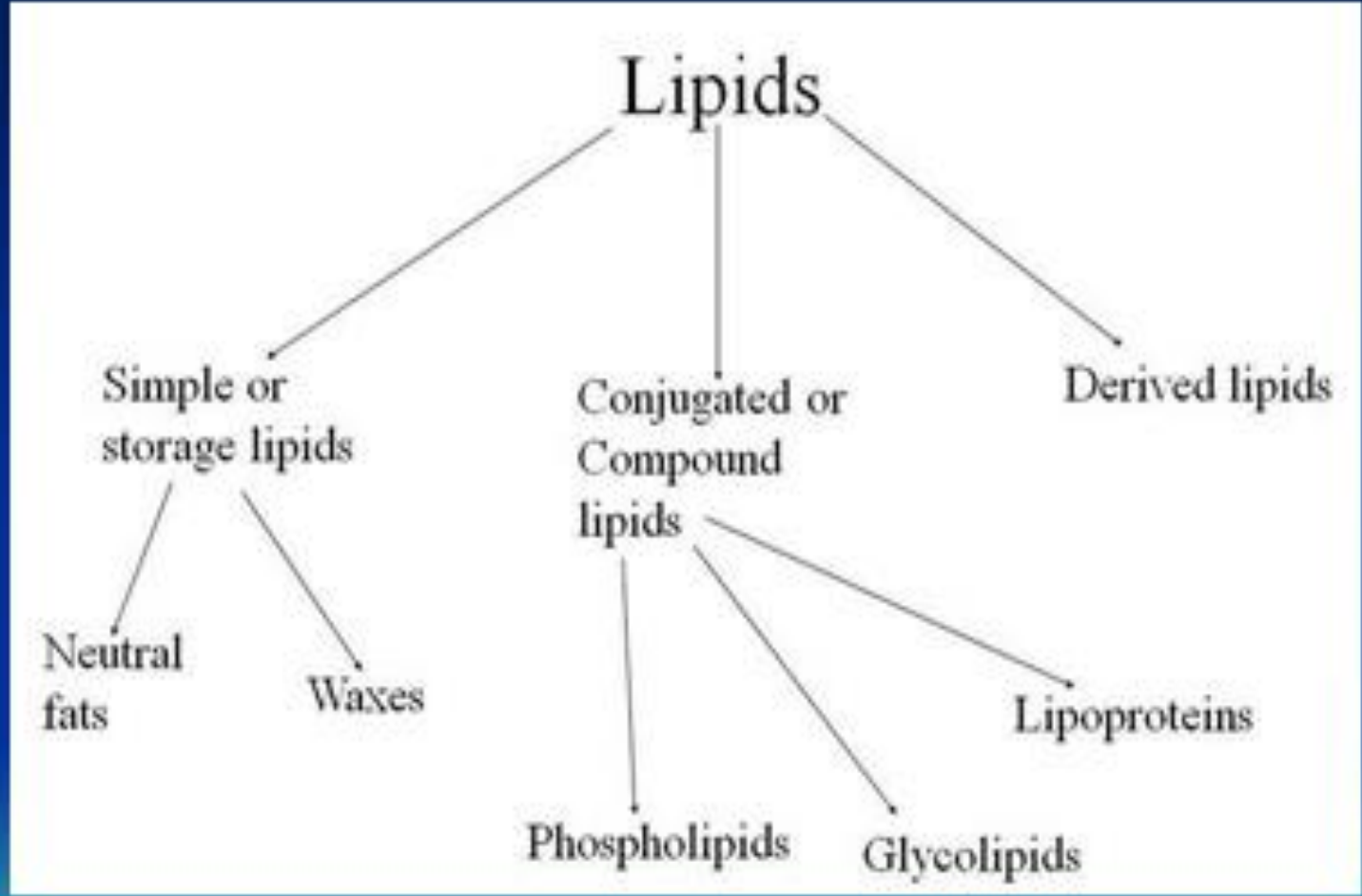


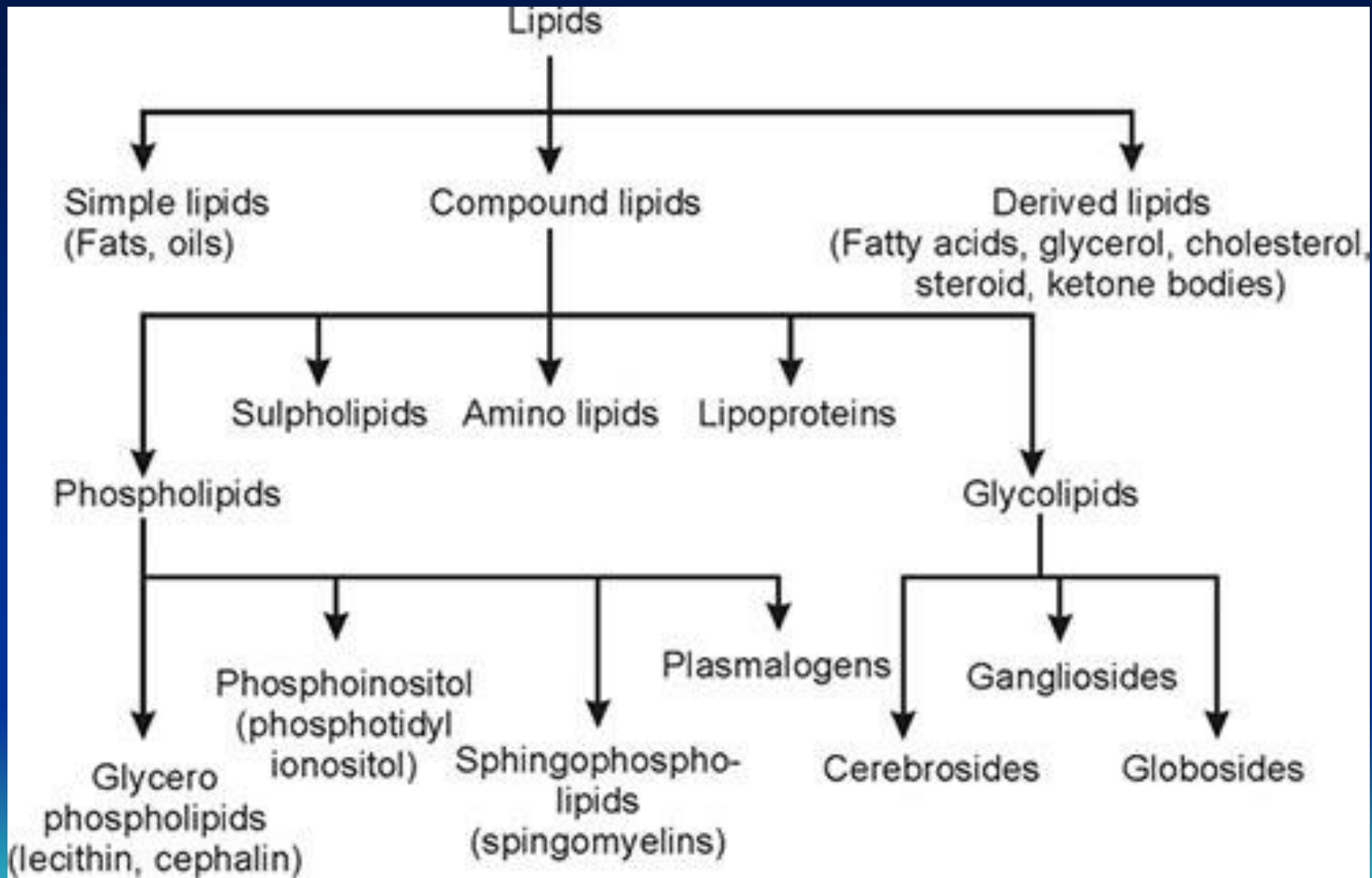
- The nervous system is rich in lipids and they are essential for proper functioning of the nervous system.
- Some vitamins like A,D,E and K are fat soluble therefore lipids are important for these vitamins.
- Lipoproteins and phospholipids are important constituents of many natural membranes such as cell walls and cell organelles like mitochondrion etc.
- Lipoproteins are also “carriers” of triglycerides, cholesterol and phospholipids in the body.



CLASSIFICATION







1) Simple Lipids:

Esters of fatty acids with various - alcohols.

(a) Neutral fats (Triacylglycerol, TG) are triesters of fatty acids with glycerol.





fatty acid

fatty acid

fatty acid

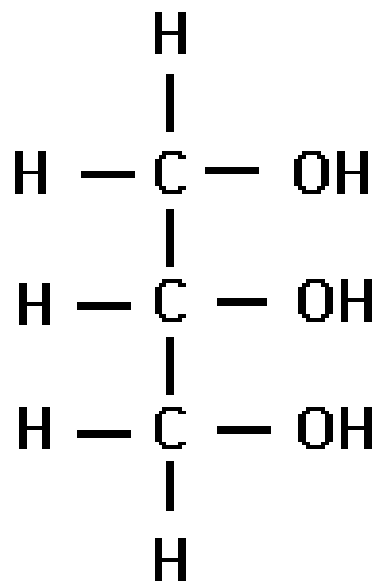
glycerol



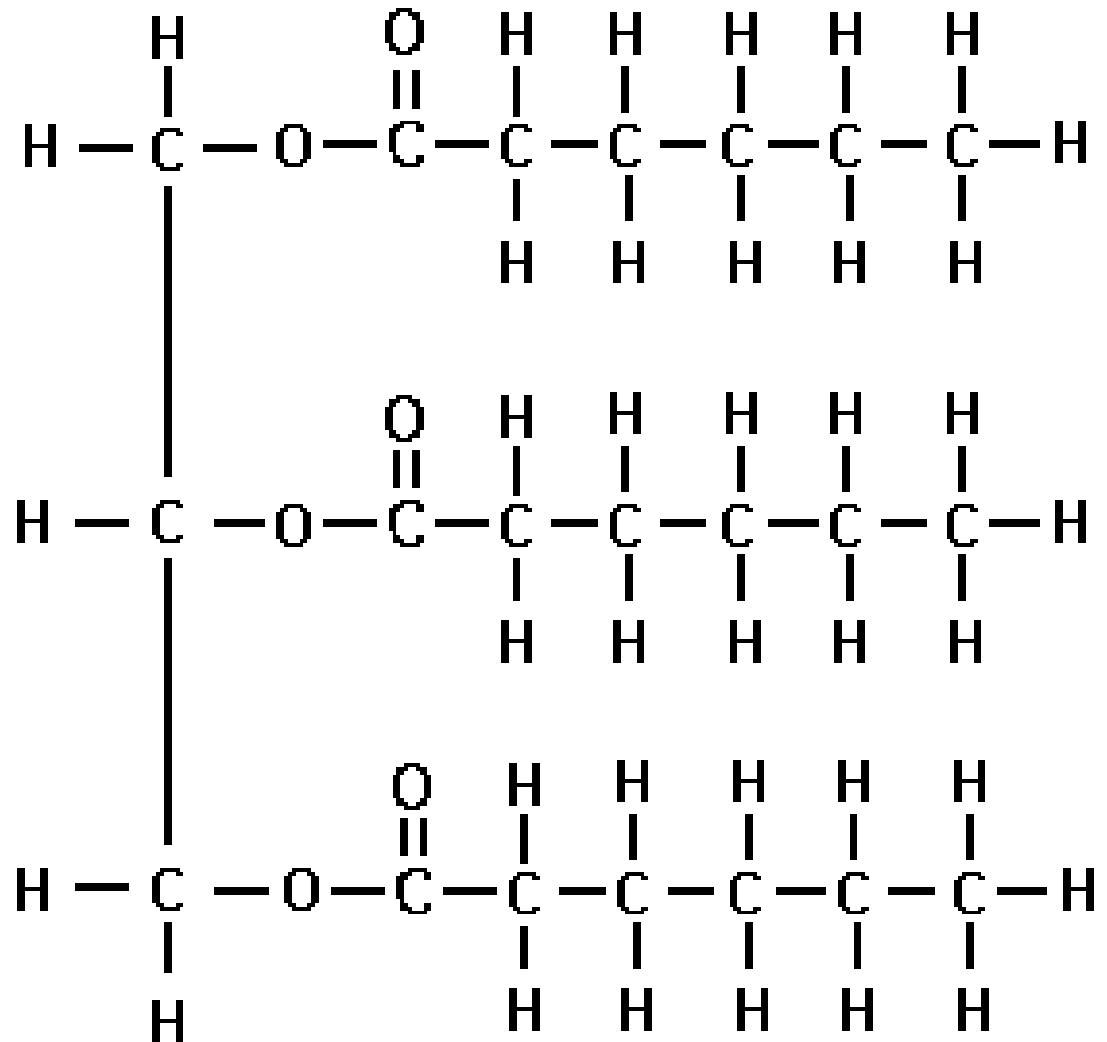
Hydrophobic
part of the
molecule:
repels water

Hydrophilic
part of the
molecule:
attracts water





Glycerol



Triglyceride-Saturated

(b) Waxes are esters of fatty acids with higher mono-hydroxy aliphatic alcohols.

True waxes are esters of higher fatty acids with cetyl alcohol or other higher straight chain alcohols.

1. Simple Lipids

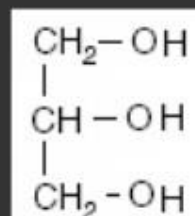
Esters of fatty acids with various alcohols.

a. **Fats** :esters of fatty acids with glycerol.

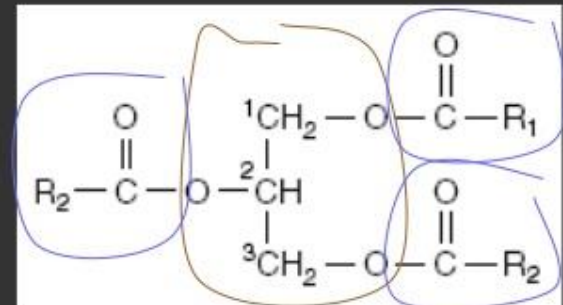
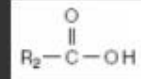
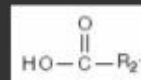
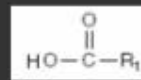
eg: triglycerides.

b. **Waxes**: esters of fatty acids with higher molecular weight monohydric alcohols.

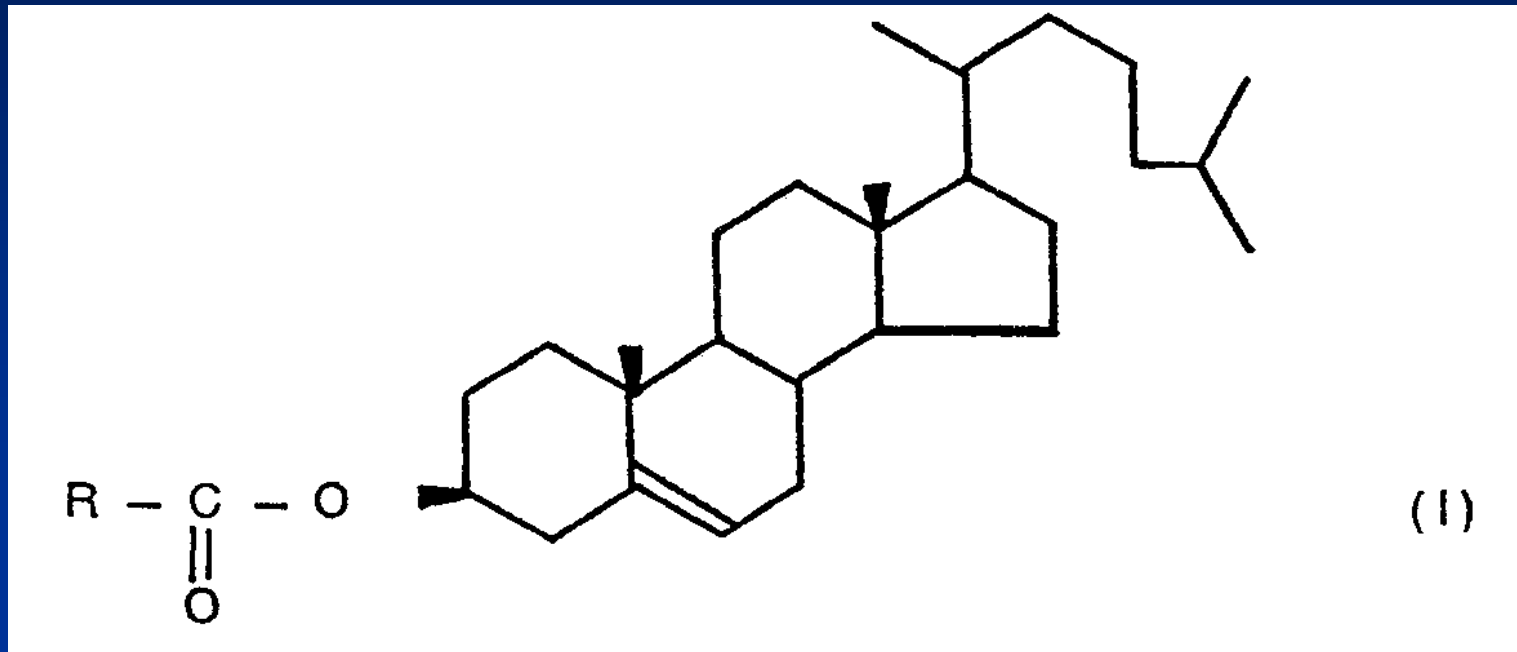
eg: beeswax



Glycerol



Cholesterol esters are esters of fatty acid with cholesterol.



VitA and Vit D esters are palmitic or stearic acids esters of Vit A (Retinol) or Vit D respectively.

II. Compound Lipids:

Esters of fatty acids, containing
an alcohol
fatty acids
and some other group



- Phospholipids
- Glycolipids
- Sulpholipids
- Lipoproteins



(a) phospholipids: They are substituted fats which in addition to fatty acid and glycerol, also contain a phosphoric acid residue, a nitrogenous base and other substituents.



(b) Glycolipids:

Lipids containing carbohydrate mostly are called glycolipids. In addition to fatty acids they contain a special alcohol called sphingosine or sphingol and nitrogenous base

does not contain phosphoric acid or glycerol.



(c) Sulfolipids:

Lipids characterized by possessing sulphate groups.

(d) Lipoproteins:

Lipids as prosthetic group to proteins.

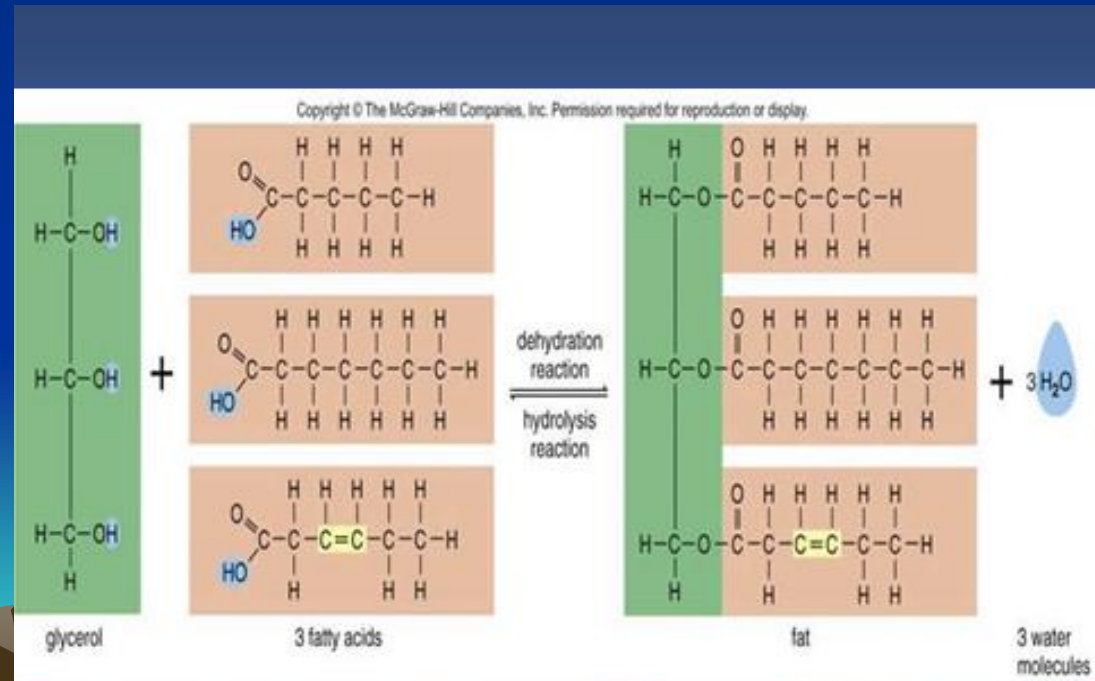


III. Derived Lipids

Derivatives obtained by hydrolysis of those given in group 1 and II

(a) Fatty acids may be

- Saturated
- Unsaturated
- cyclic



(b) Monoglycerides (Monoacylglycerol) and Diglycerides (Di-acylglycerol)

(c) Alcohols:

1. Straight chain alcohols
2. Cholesterol and other steroids including Vit D
3. Alcohols containing β -ionone ring include Vit A and certain carotenoids
4. Glycerol



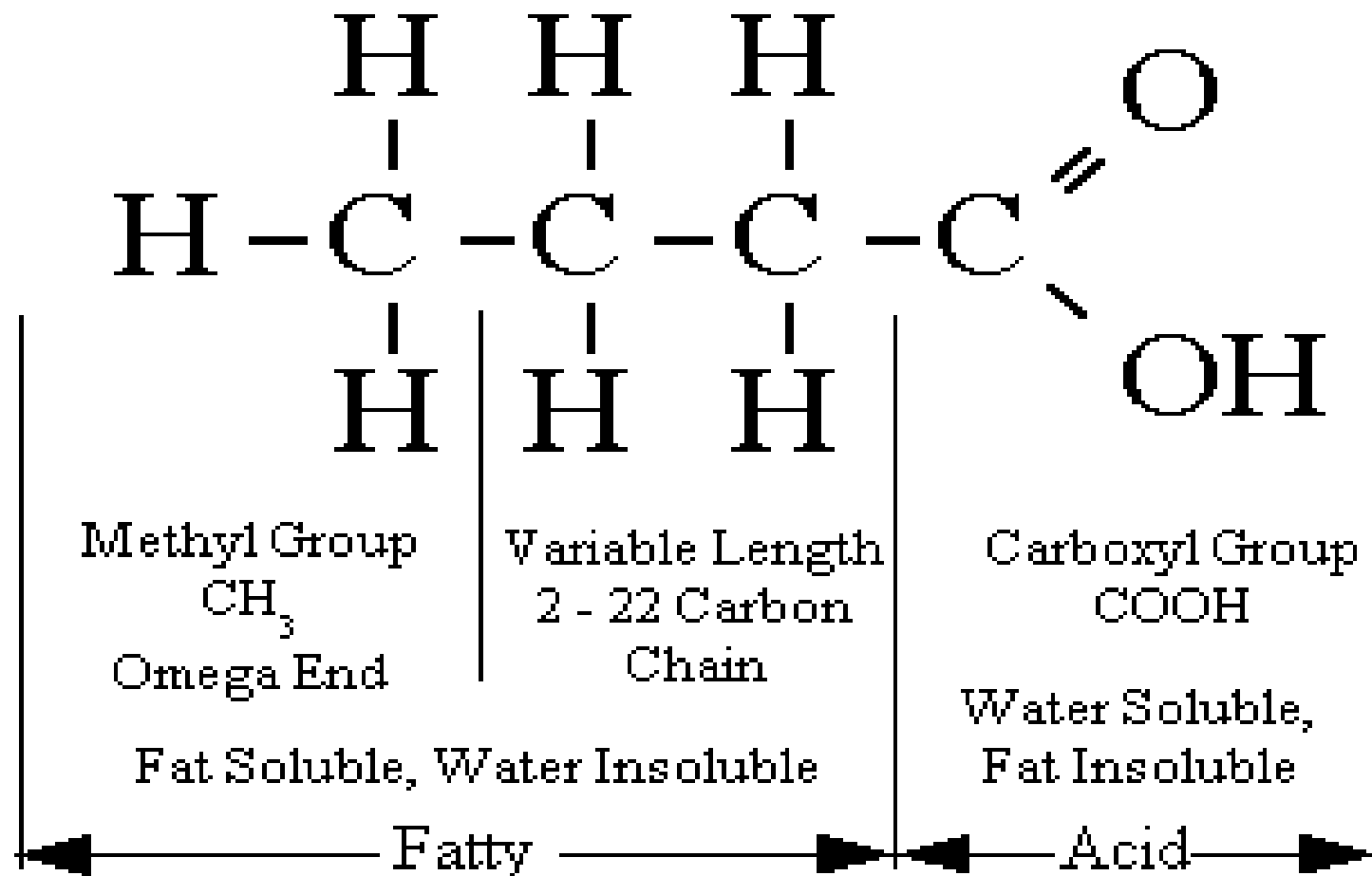
DERIVED LIPIDS

FATTY ACIDS

Definition:

A fatty acid (FA) may be defined as an organic acid that occurs in a natural triglyceride and is a mono-carboxylic acid ranging in chain length from C4 to about 24 carbon atoms. FA are obtained from hydrolysis of fats.



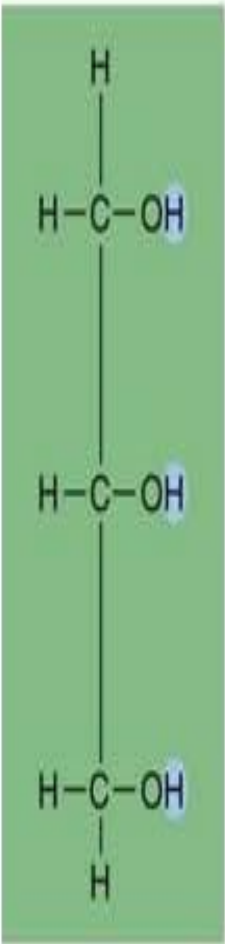


H = Hydrogen Atom C = Carbon Atom O = Oxygen Atom

— = Single bond = = Double bond

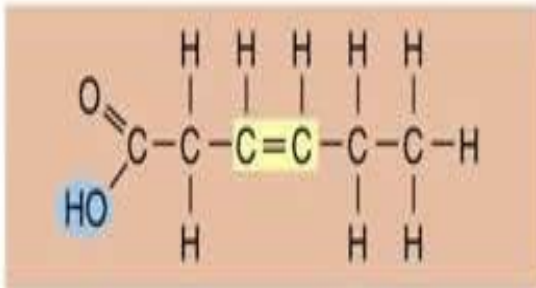
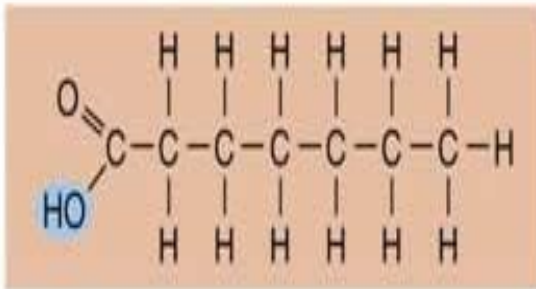
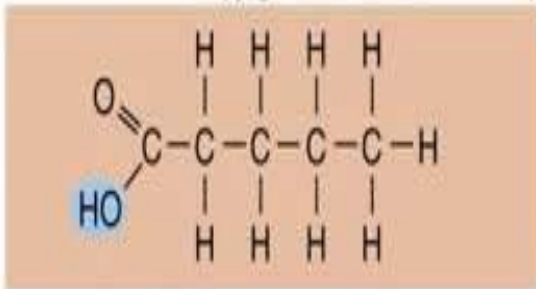
Structure of a saturated fatty acid, butyric acid in butter

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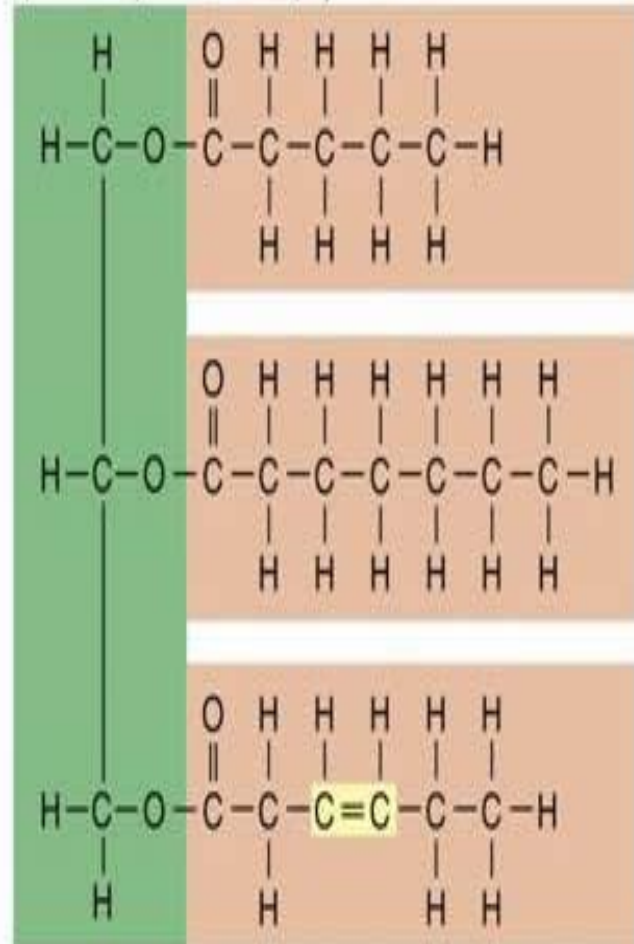
glycerol

+

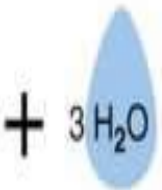


3 fatty acids

dehydration
reaction
⇌
hydrolysis
reaction



fat



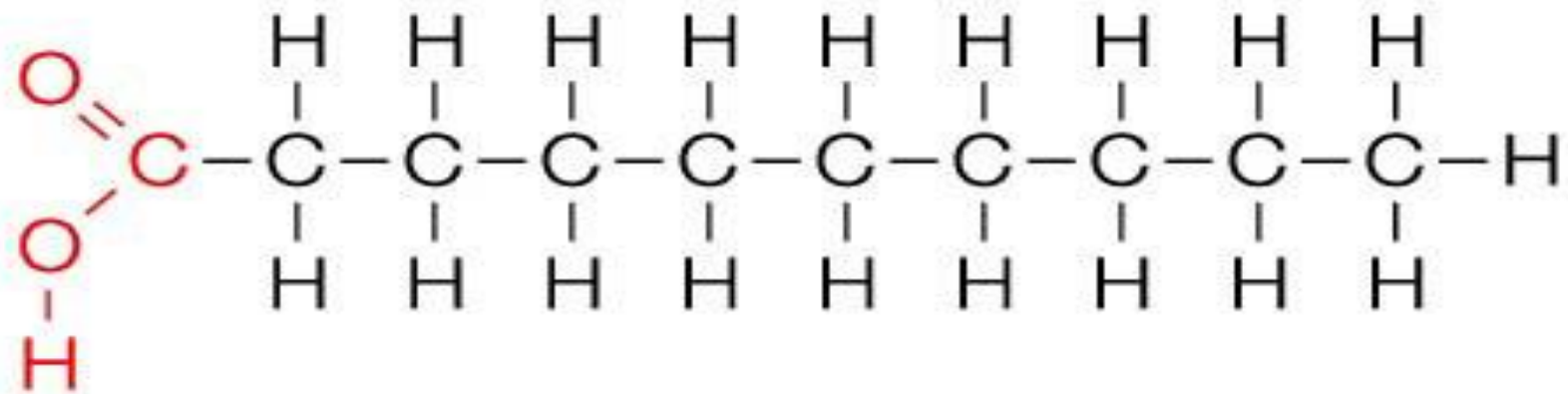
3 water molecules

TYPES OF FATTY ACIDS

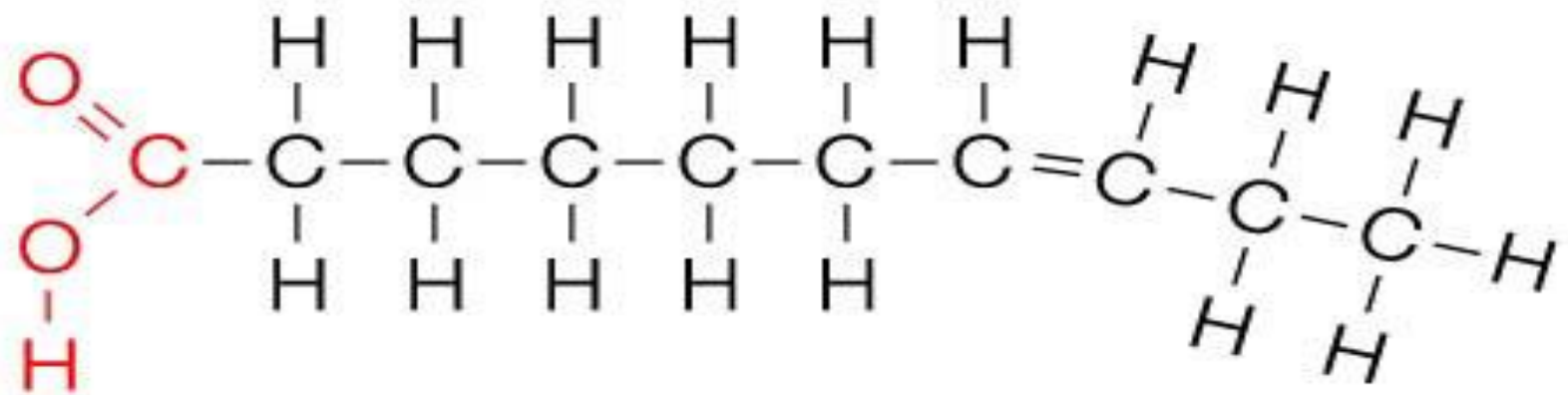
- **Straight Chain FA:** These may be:
- **Saturated FA:** Those which contain no double bonds.
- **Unsaturated FA:** Those which contain one or more double bonds.



Saturated



Unsaturated



a) Saturated FA

Their general formula is $C_nH_{2n+1}COOH$

Examples:

Acetic acid CH_3COOH

Propionic acid C_2H_5COOH

Butyric acid C_3H_7COOH

Caproic acid $C_5H_{11}COOH$

Palmitic acid $C_{15}H_{31}COOH$

Stearic acid $C_{17}H_{35}COOH$ and so on



Saturated fatty acids having 10 carbon or less number of carbon atoms are called as “Lower fatty acids”, e.g. acetic acid, butyric acid, etc. Milk contains significant amount of lower fatty acids.



Saturated fatty acids having more than 10 carbon atoms are called “higher fatty acids”, e.g. palmitic acid, stearic acid, etc.



- **b) Unsaturated FA:**

- They are classified further according to degree of unsaturation.

- **(1) Mono unsaturated fatty acids:** are those which contain one double bond.

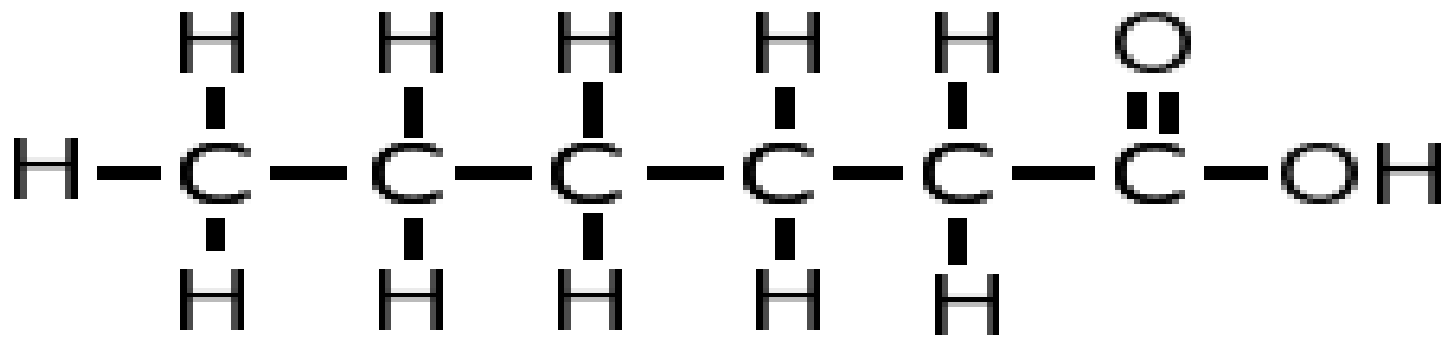
- Example: Oleic acid $C_{17}H_{33}COOH$ is found in nearly all fats (formula 18:1;9).



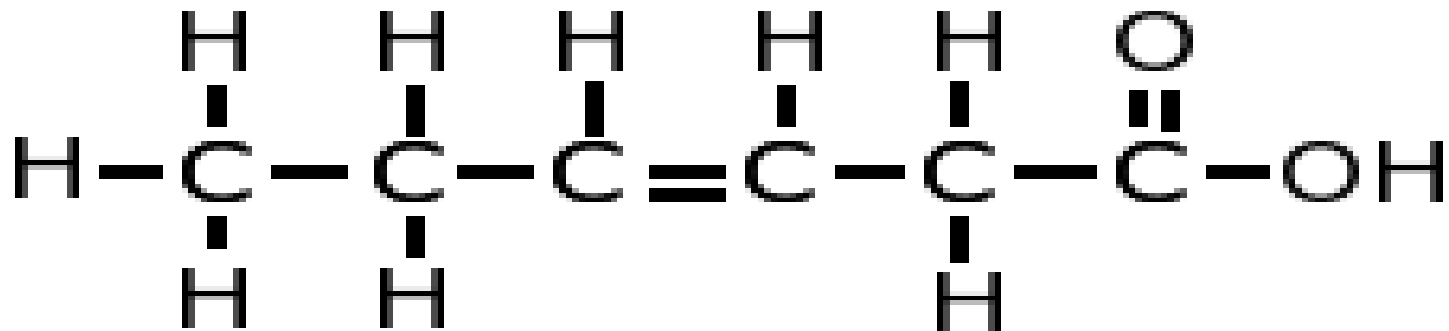
- (2) Polyunsaturated fatty acids:

- -

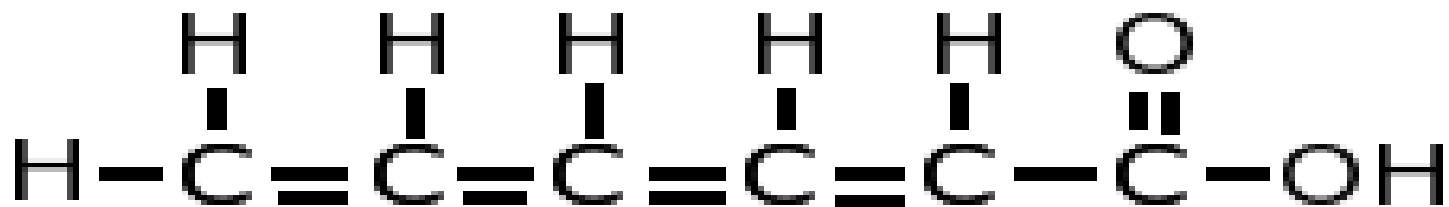




Saturated Fatty Acid



Monounsaturated Fatty Acid



Polyunsaturated Fatty Acid

- There are three polyunsaturated fatty acids of biological importance
- Linolenic acid
- Arachidonic acid
- Linoleic acid



- Note:**

- These three poly unsaturated fatty acids viz. linoleic acid, linolenic acid and arachidonic acid are called as "Essential fatty acids (EFA). They have to be provided in the diet, as they cannot be synthesized in the body.



- (c) **Branched Chain FA**; Odd and even carbon branched chain fatty acids occur in animal and plant lipids, e.g.
- ***Sebaceous glands***: *Sebum* contain branched chain FA
- **Branched chain FA** *is present in certain foods, e.g., pilytanic acid in butter.*



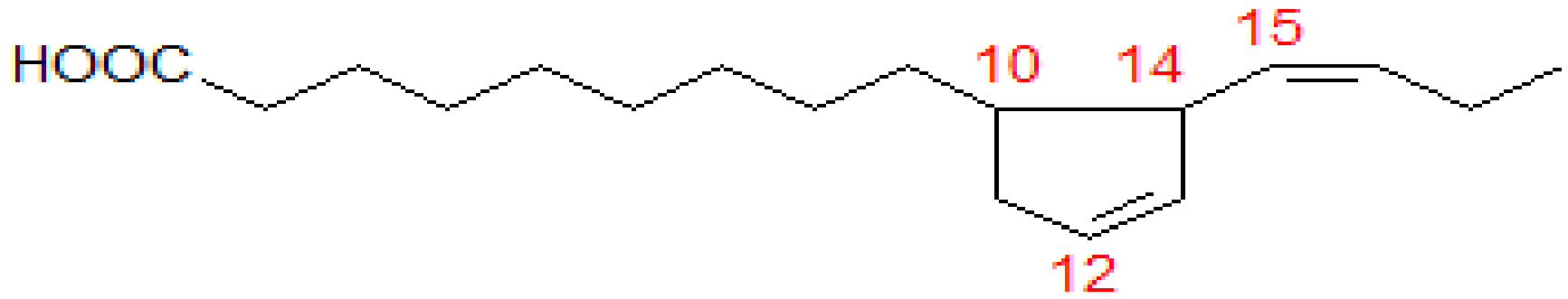
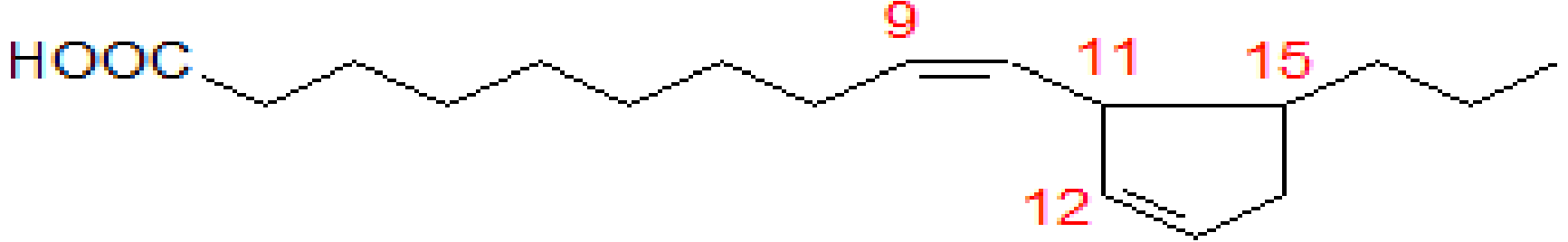
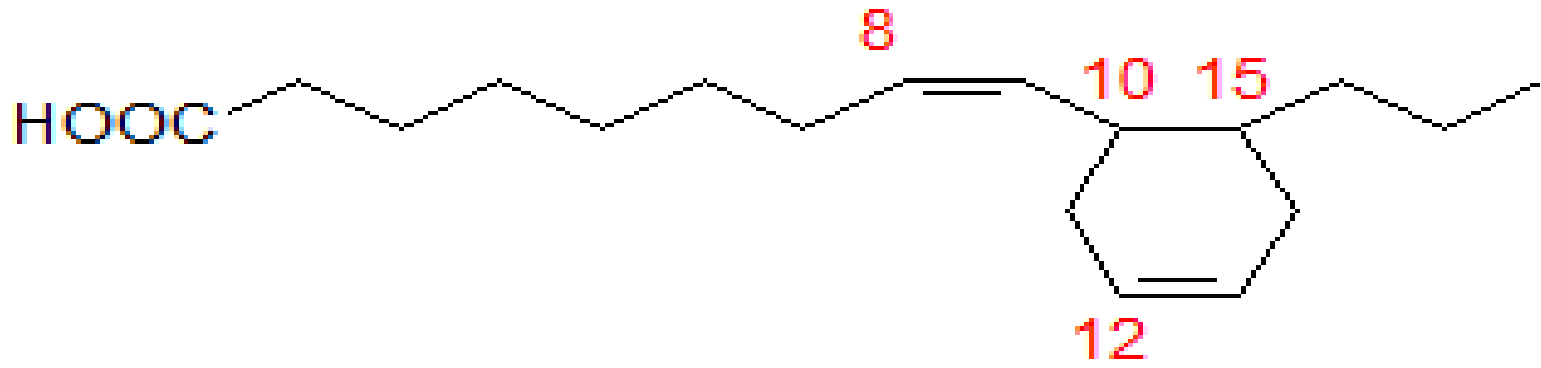
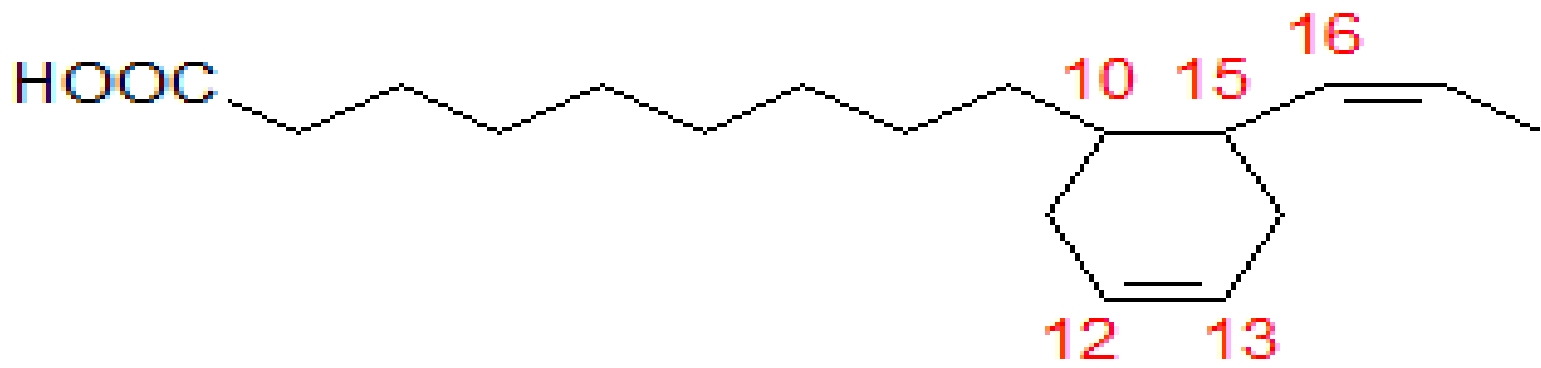
•(d) Substituted Fatty Acids:

•In hydroxy fatty acid and methyl fatty acid, one or more of the hydrogen atoms have been replaced by -OH group or -CH₃ group respectively. Both saturated and unsaturated hydroxy fatty acids, particularly with long chains, are found in nature, e.g., *cerebronic acid* of brain glycolipids, *Ricinoleic acid* in castor oil.



- **(e) Cyclic Fatty Acids:** Fatty acids bearing cyclic groups are present in some seeds, e.g.
 - • *Chaulmoogric acid* obtained from chaulmoogra seeds,
 - • *Hydnocarpic acid*.
- Both of them have been used earlier for long time for treatment of Leprosy.





- (f) Eicosanoids:
- These are derived from eicosapolyenoic FA.



- Eicosanoids are signaling molecules made by oxidation of twenty-carbon essential fatty acids, (EFAs). They exert complex control over many bodily systems, mainly in inflammation or immunity, and as messengers in the central nervous system. The networks of controls that depend upon eicosanoids are among the most complex in the human body.



ISOMERISM

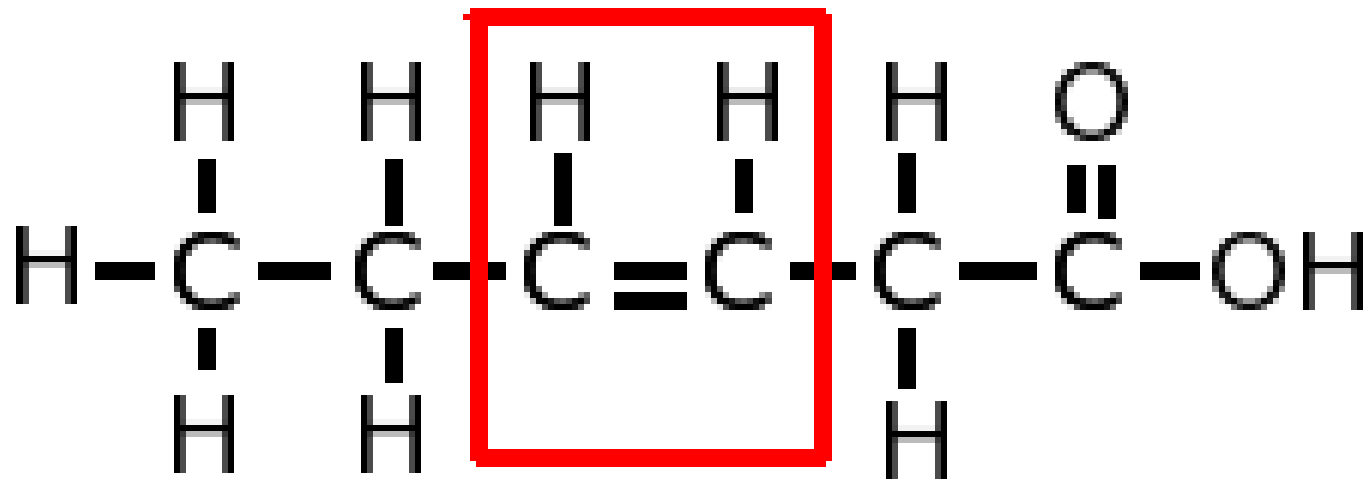


Two types of isomers can occur in an unsaturated fatty acid.

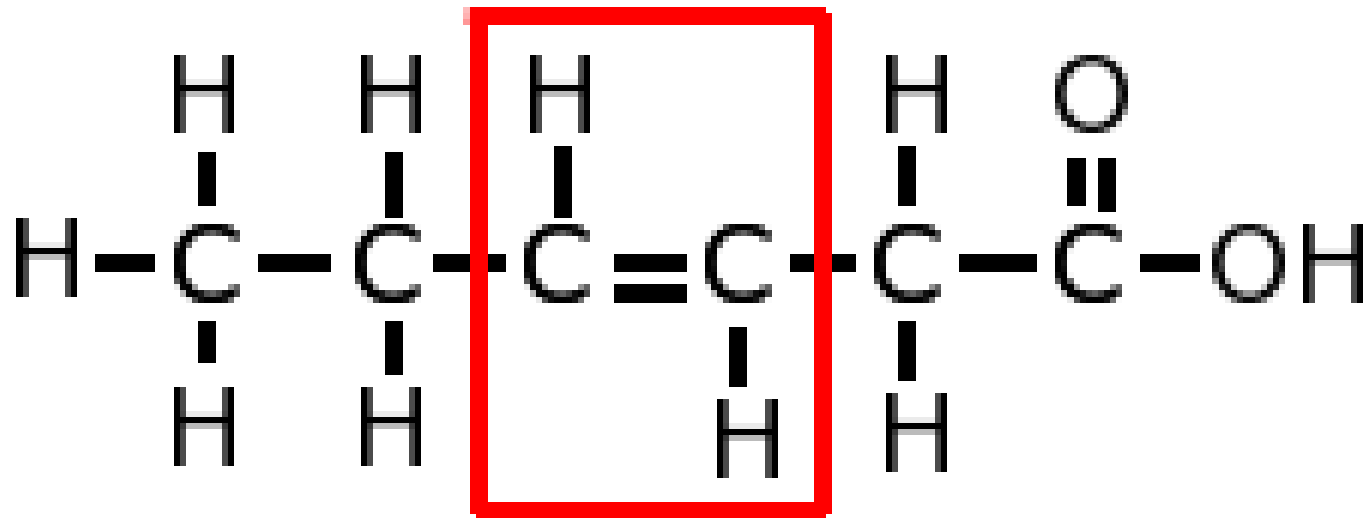
a) Geometric Isomers:

Depend on the orientation of the radicals around the axis of the double bonds. If the radicals are on the same side of the bond, it is called as 'cis' form. If the radicals are on the opposite side, a 'trans' form is produced. 'Cis' form is comparatively unstable and is more reactive.





Cis Fatty Acid



Trans Fatty Acid

b) Positional Isomers:

A variation in the location of the double bonds along the unsaturated fatty acids chain produces isomer of that compound. Thus, oleic acid could have 15 different positional isomers.



Various conventions are used for indicating the number and position of the double bonds, e.g., 9 indicates a double bond between carbon atoms 9 and 10 of the fatty acids, for this sign is used e.g. $\Delta 9$ denotes double bond between 9 and 10 Carbon.



A widely used convention is to express the fatty acids by formula to indicate:

- the number of carbon atoms
- the number of double bonds and
- the positions of the double bonds.

For example Oleic Acid (mol. Formula $C_{17}H_{33}COOH$) has one double bond between C9 and C10, thus:

According to above criteria, it is expressed as 18:1;9, [18 indicates the number of carbon atoms, 1 indicates the number of double bond and 9 indicates the position of the double bond].



ESSENTIAL FATTY ACIDS

Three polyunsaturated fatty acids, Linoleic acid, Linolenic acid and Arachidonic acid are called “essential fatty acids” (EFA). They cannot be synthesized in the body and must be provided in the diet. Lack of EFA in the diet can produce growth retardation and other deficiency manifestation symptoms.

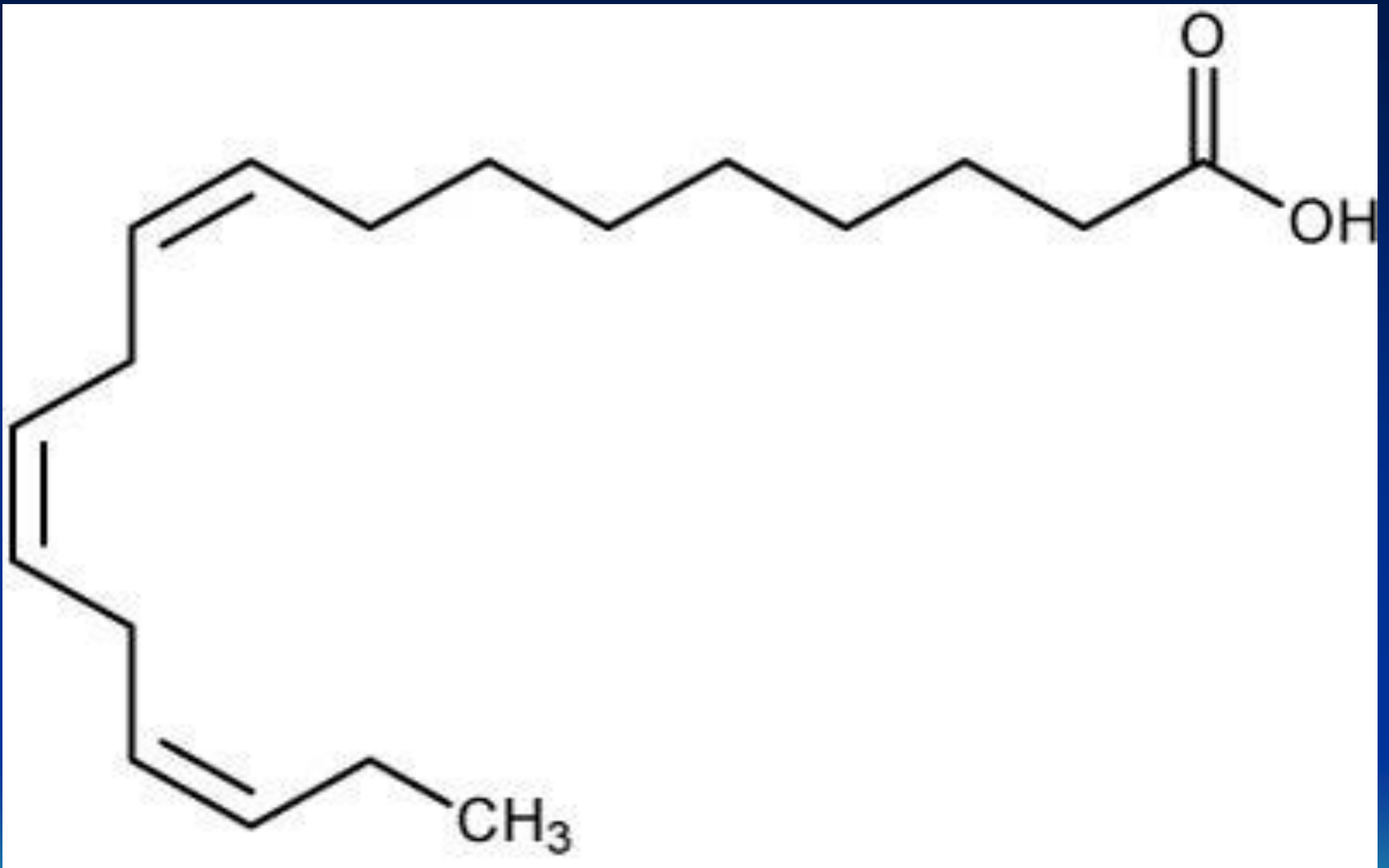


- ***Linolenic acid series (18:3; 9,12,15)***: It contains three double bonds between 9 and 10; 12 and 13; and 15 and 16.

- ***Dietary Source:***

- Found frequently with linoleic acid, but particularly present in linseed oil, soybean oil, fish visceras and liver oil (cod liver oil).





- ***Arachidonic acid ;it contains 4double bonds.***

- ***Dietary Source:***

- Found in small quantity with linoleic and linolenic acid but found particularly in peanut oil.also found in animal fats including liver fats.





- ***Linoleic acid series (18 : 2; 9, 12):*** It contains two double bonds between C9 and C10; and between C12 and C13.

- ***Dietary sources:***

- Linoleic acid is present in sufficient amounts in peanut oil, corn oil, cottonseed oil, soybean .oil and egg yolk.



• **Which EFA is Important?**

• ***Linoleic acid is most important as, arachidonic acid can be synthesized from Linoleic acid by a three stage reaction by addition of Acetyl-C0A. Pyridoxal phosphate is necessary for this conversion.***

Biologically arachidonic acid is very important as it is precursor from which prostaglandins and leukotrienes are synthesized in the body.



Functions of EFA: (Biomedical Importance)

Structural elements of tissues:

Polyunsaturated fatty acids occur in higher concentration in lipids associated with structural elements of tissues.

Structural element of gonads:

Lipids of gonads also contain a high concentration of polyunsaturated fatty acids, which suggests importance of these compounds in reproductive function.



Synthesis of prostaglandins and other compounds:

Prostaglandins & Leukotrienes are synthesized from Arachidonic acid.



Structural element of mitochondrial membrane:

A deficiency of EFA causes swelling of mitochondrial membrane and reduction in efficiency of oxidative phosphorylation. This leads to increased heat production noted in EFA deficient animals.



- **Serum level of cholesterol:**

Fats with high content of polyunsaturated fatty acids tends to lower serum level of cholesterol.

- **Effect on clotting time:**

Prolongation of clotting time is noted in ingestion of fats rich in EFA.

- **Effect on fibrinolytic activity:**

An increase in fibrinolytic activity follows the ingestion of fats rich in EFA.



- **Role of EFA in fatty liver:**
- Deficiency of EFA produces fatty liver.

- **Role in Vision:**
- Docosahexenoic acid is the most abundant polyeneic fatty acids present in retinal photoreceptor membranes.
Docosahexenoic acid is formed from dietary linolenic acid. It enhances the electrical response of the photoreceptors to illumination. **Hence linolenic acid is necessary in the diet for optimal vision.**



- **DEFICIENCY MANIFESTATIONS:**

- A deficiency of EFA has not yet been demonstrated in humans. In weaning animals, symptoms of EFA deficiency are readily produced. They are:



- Cessation of growth.
- Skin lesions: acanthosis (hypertrophy of prickle cells) and hyperkeratosis (hypertrophy of stratum corneum). Skin becomes abnormally permeable to water. Increased loss of water increases BMR.
- Abnormalities of pregnancy and lactation in adult females.
- Fatty liver accompanied by increased rates of fatty acids synthesis, Lessened resistance to stress.
- Kidney damage.



CLINICAL ASPECT

- **Human Deficiency:**
- Some cases of
- Eczema like dermatitis,
- Degenerative changes in arterial wall and
- Fatty liver in man may be due to E.F.A..
deficiency.



There are also some reports that administration of EFA in such cases may produce:

Some improvement of eczema in children kept on skimmed milk,

Prevent fatty liver (some cases) and Lowering of cholesterol levels.

Infants and babies with low fat diet develop typical skin lesions which has shown to be improved with EFA (linoleic acid).



THE END

