Biochemistry of lipids

1. Classification of lipids and their biochemical functions MUSHTAQ

2. Structure and biochemical function of phospholipids. glycolpids and sphingolipids MUSHTAQ

3.Classification of fatty acids and their biochemical functions MUSHTAQ

4.Functions of essential fatty acids LIPPINCOTT (NUTRION) MUSHTAQ vol II

5. Eioosanoides and their function in health and disease

LIPPINCOTT

6. Steroids and their biochemical role MUSHTAQ

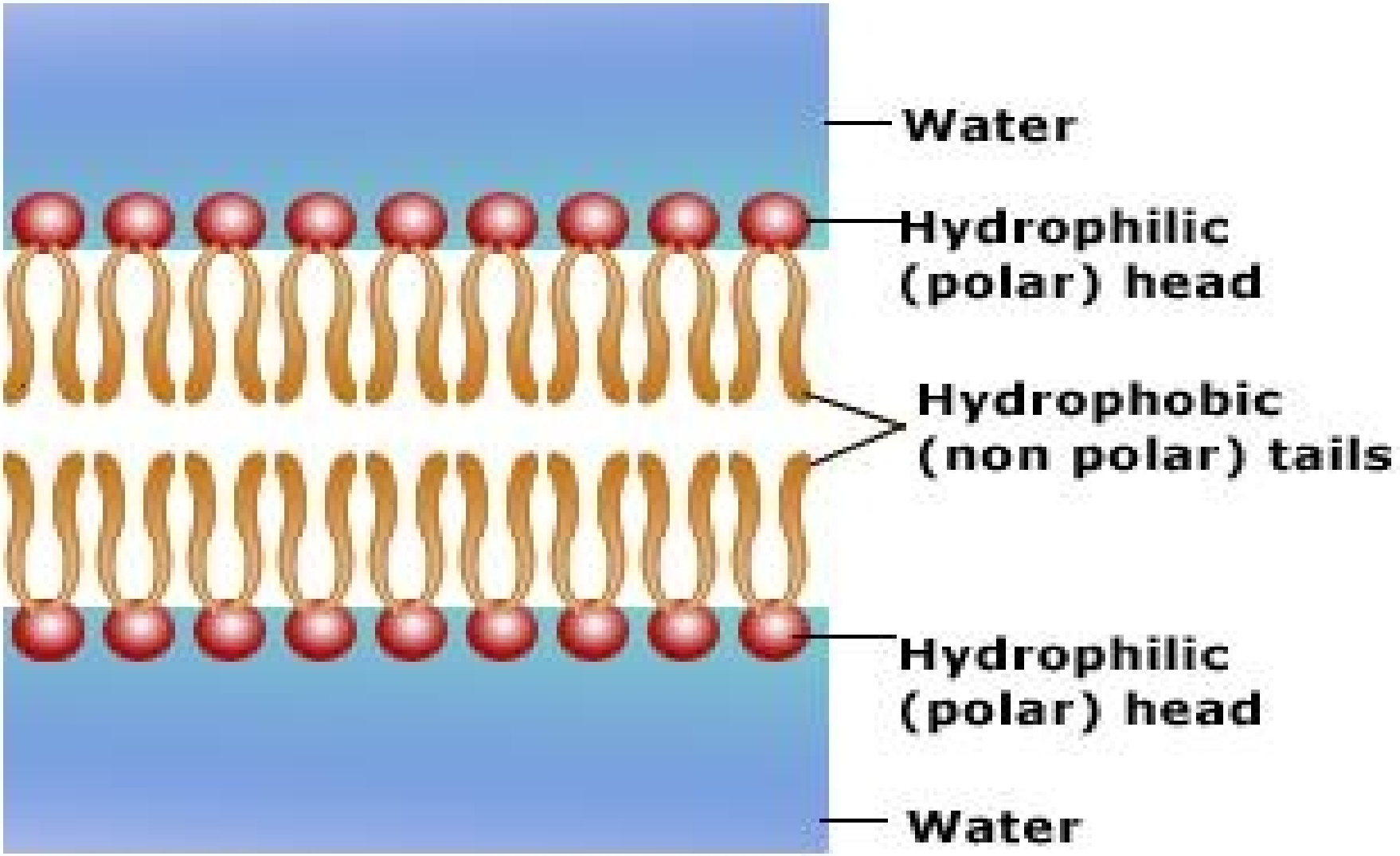
7.Cholesterol. its structure chemistry and function. MUSHTAQ

8.Lipid peroxidation and its significance. HARPER'S


Mazola
Crisco
Crisco
Soap Galore
Lipids
Cholesterol

Obesity

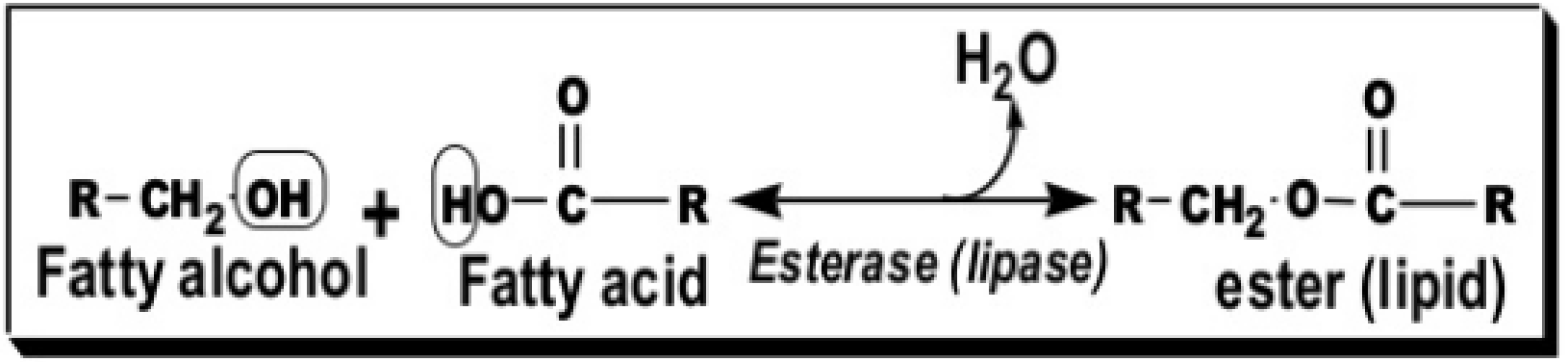
Diabetes Mellitus


Water
Hydrophilic
(polar) head
Hydrophobic
(non polar) tails
Hydrophilic
(polar) head
Water

Chemistry of Lipids

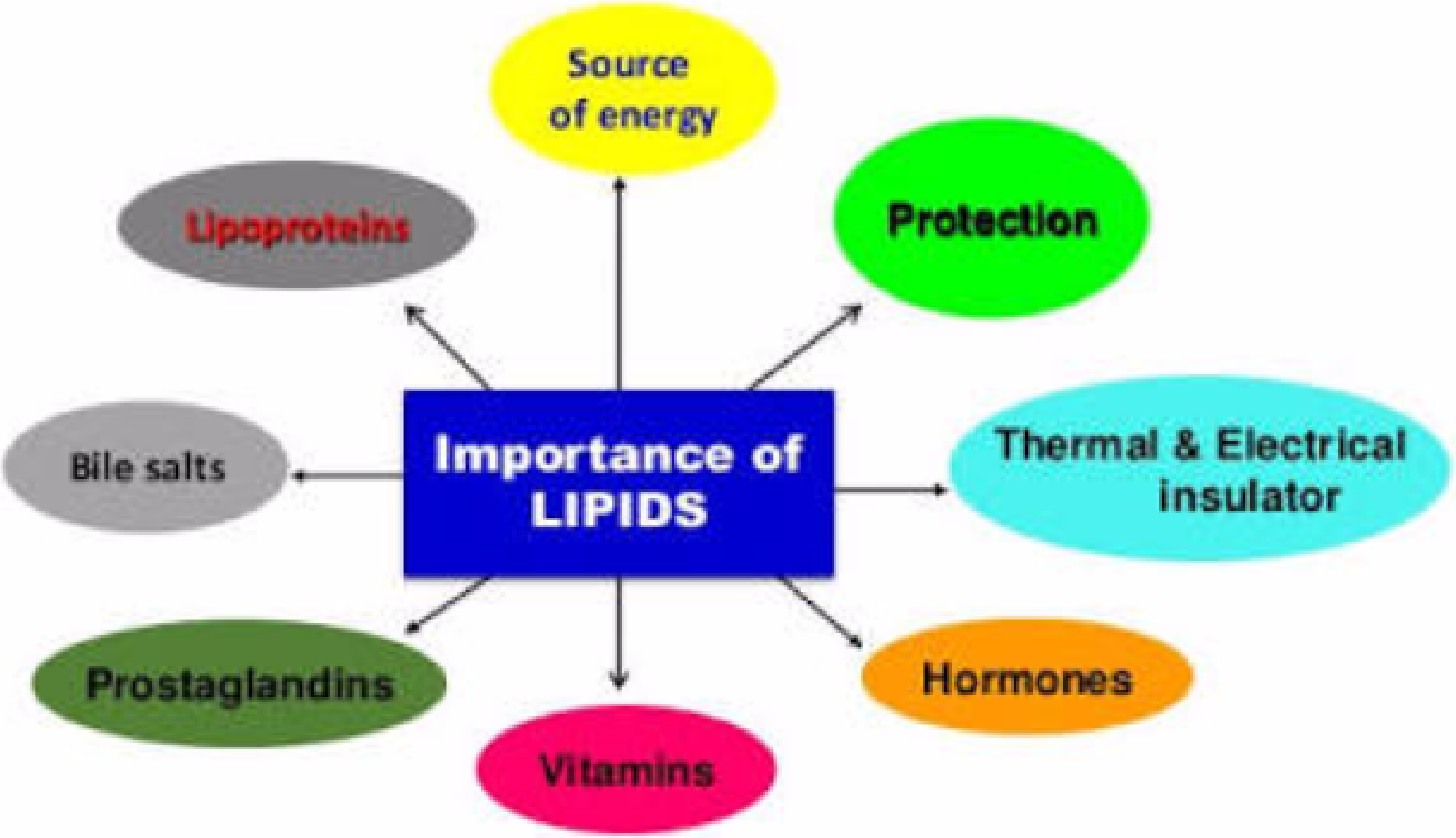
Definition:

- - Lipids are organic compounds formed mainly from alcohol and fatty acids combined together by ester linkage.



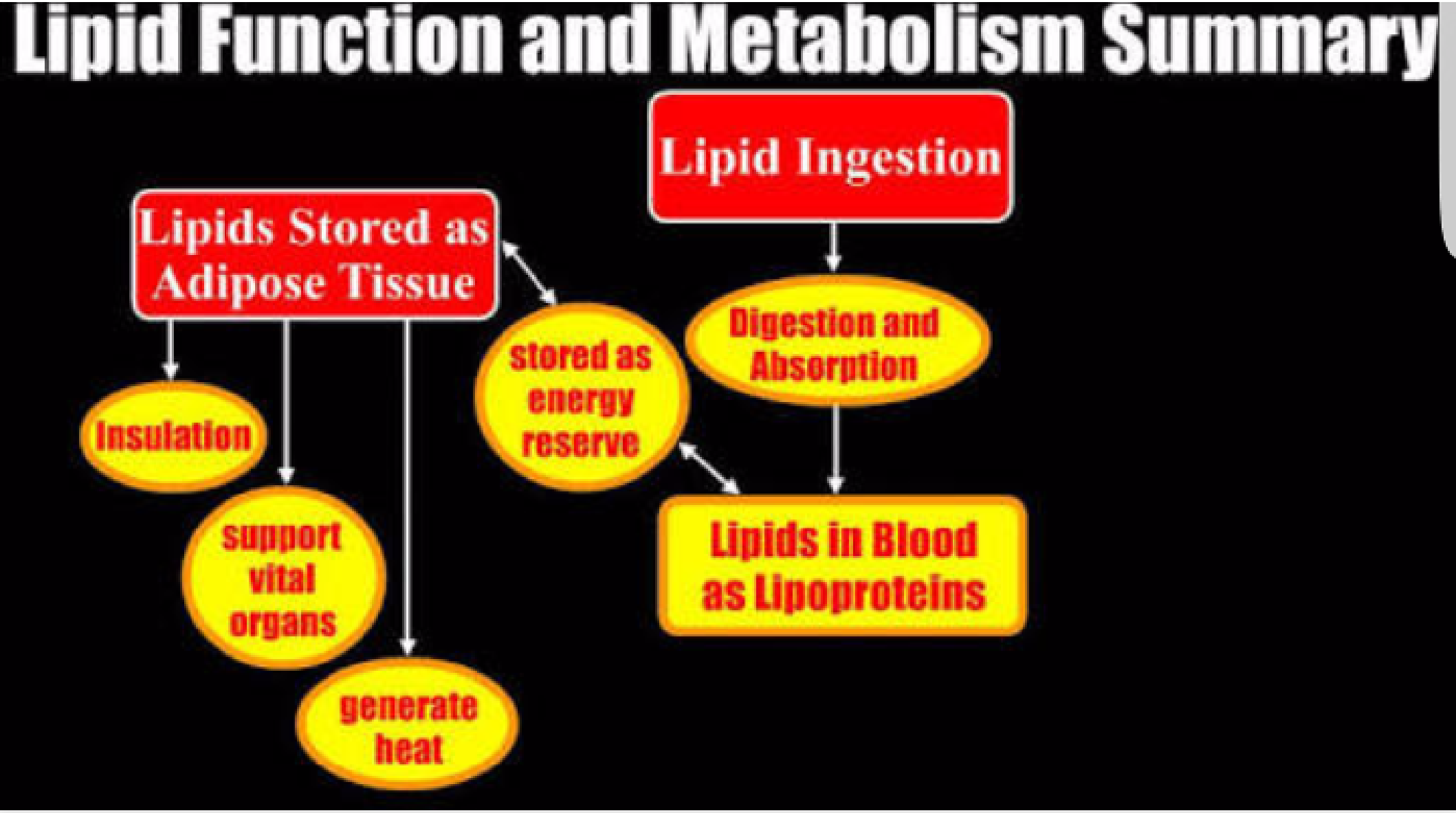
- Lipids are insoluble in water, but soluble in fat or organic solvents (ether, chloroform, benzene, acetone).
- – Lipids include fats, oils, waxes and related compounds.
- They are widely distributed in nature both in plants and in animals.

Biomedical Importance of Lipids



Biological Importance of Lipids:

1. They are more palatable and storable to unlimited amount compared to carbohydrates.
2. They have a high-energy value (25% of body needs) and they provide more energy per gram than carbohydrates and proteins but carbohydrates are the preferable source of energy.
3. Supply the essential fatty acids that cannot be synthesized by the body.
4. Supply the body with fat-soluble vitamins (A, D, E and K).
5. They are important constituents of the nervous system.
6. Tissue fat is an essential constituent of cell membrane and nervous system. It is mainly phospholipids in nature that are not affected by starvation.


Lipid Function and Metabolism Summary
Lipid Ingestion
Lipids Stored as Adipose Tissue
Digestion and Absorption
stored as energy reserve
Insulation
support vital organs
generate heat
Lipids in Blood as Lipoproteins

7-Stored lipids "depot fat" is stored in all human cells acts as:

- A store of energy.
- A pad for the internal organs to protect them from outside shocks.
- A subcutaneous thermal insulator against loss of body heat.

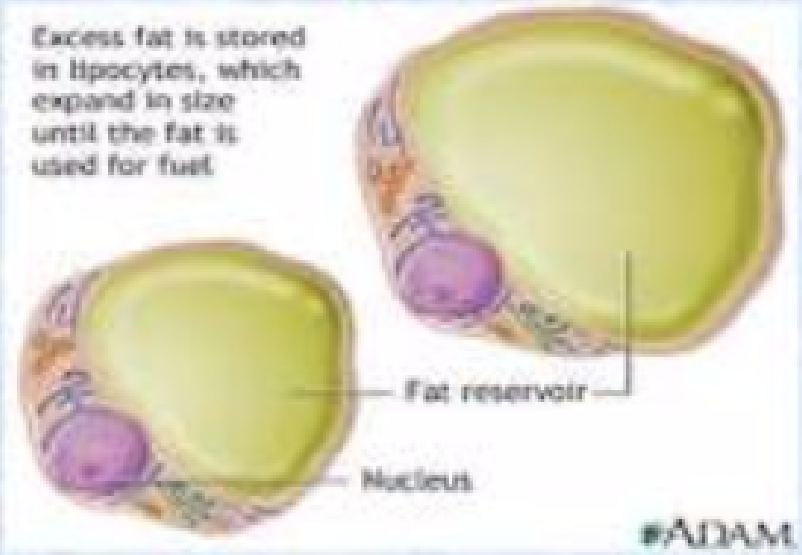
8-Lipoproteins, which are complex of lipids and proteins, are important cellular constituents that present both in the cellular and subcellular membranes.

9-Cholesterol enters in membrane structure and is used for synthesis of adrenal cortical hormones, vitamin D3 and bile acids.

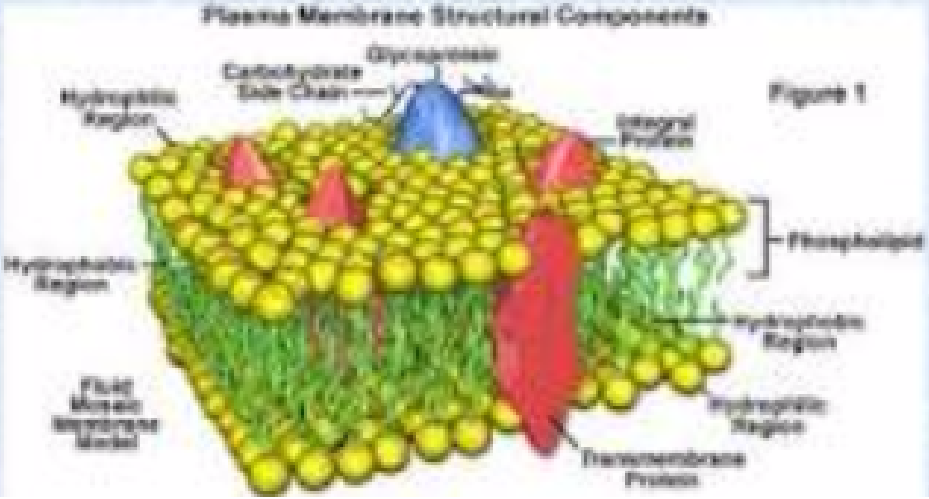
10- Lipids provide bases for dealing with diseases such as obesity, atherosclerosis, lipid-storage diseases, essential fatty acid deficiency, respiratory distress syndrome,

The Functions of Lipids

- 2 major functions of lipids
- store energy

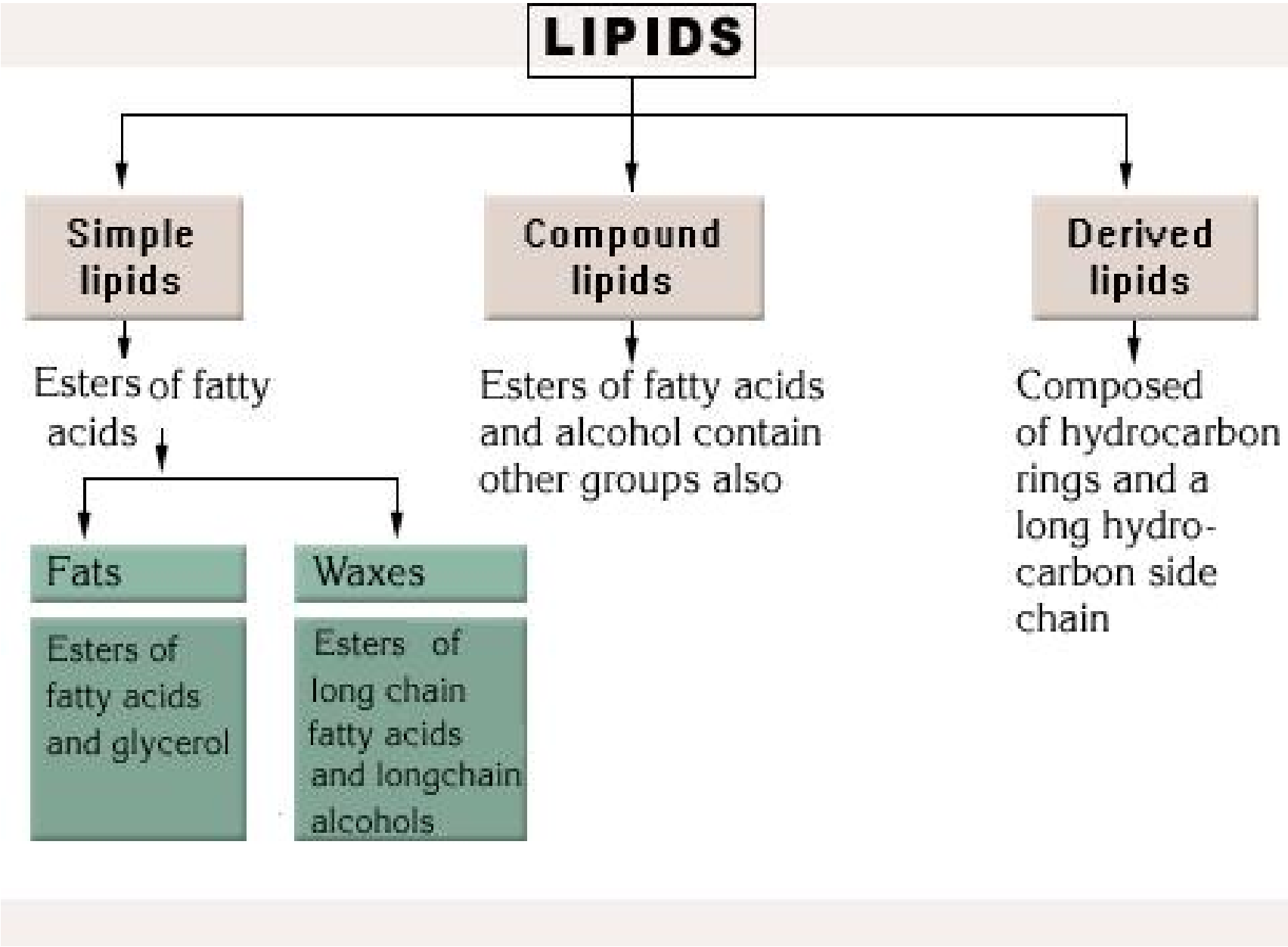


- Form cell membranes



Classification of Lipids

1. Simple lipids (Fats & Waxes)
2. Compound or conjugated lipids
3. Derived Lipids
4. Lipid-associating substances

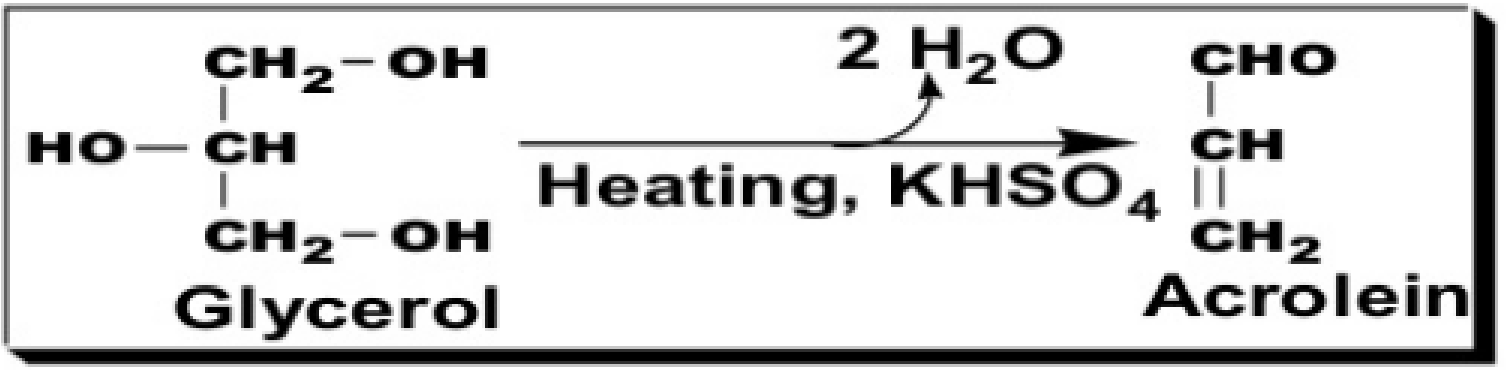

LIPIDS
Simple lipids
Compound lipids
Derived lipids
Esters of fatty acids
Esters of fatty acids and alcohol contain other groups also
Composed of hydrocarbon rings and a long hydro-carbon side chain
Fats
Waxes
Esters of fatty acids and glycerol
Esters of long chain fatty acids and longchain alcohols

Fatty alcohols

1-Glycerol:

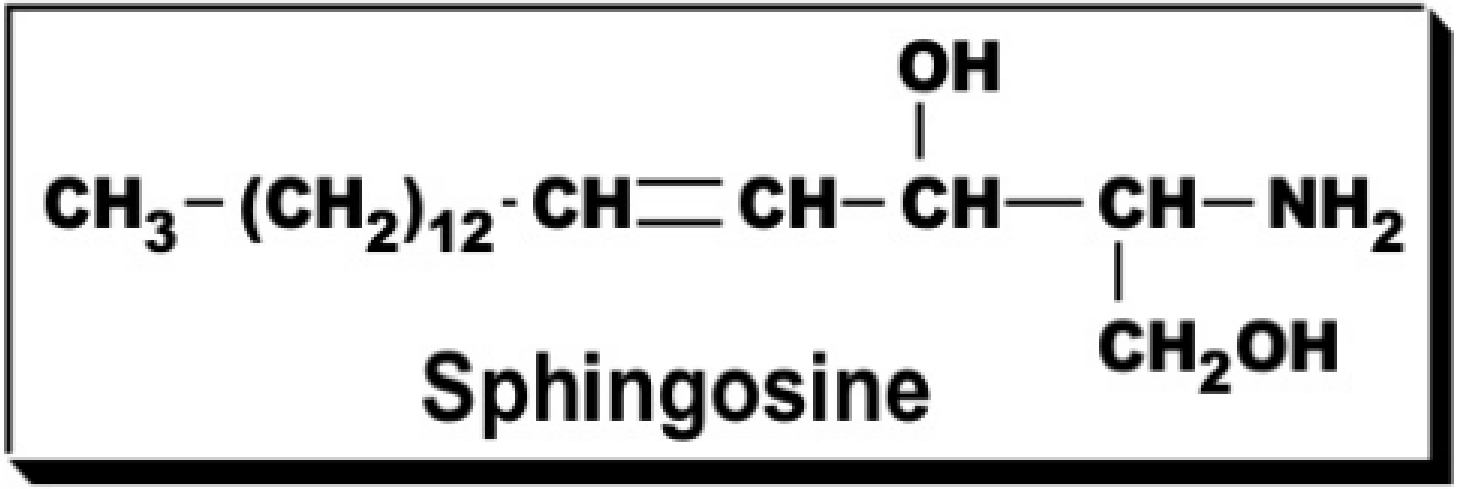
- It is a trihydric alcohol (i.e., containing three OH groups) and has the popular name glycerin.
- It is synthesized in the body from glucose.
- It has the following properties:

1. Colorless viscous oily liquid with sweet taste.
2. On heating with sulfuric acid or KHSO4 (dehydration) it gives acrolein that has a bad odor. This reaction is used for detection of free glycerol or any compound containing glycerol.



2-Sphingosine:

- - It is the alcohol(monohydric) present in sphingolipids.
- - It is synthesized in the body from serine and palmitic acid.
- It is not positive with acrolein test.



Fatty Acids

Definition:

- Fatty acids are aliphatic mono-carboxylic acids that are mostly obtained from the hydrolysis of natural fats and oils.
- Have the general formula $R\text{-}(CH_2)_n\text{-}COOH$ and mostly have straight chain (a few exceptions have branched and heterocyclic chains). In this formula "n" is mostly an even number of carbon atoms (2-34) with a few exceptions that have an odd number.
- Fatty acids are classified according to several bases as follows:

Fatty acids

- Simplest form of lipids
- Aliphatic monocarboxylic organic acids with hydrocarbon side chain
- FA are included in the group of derived lipids
- Most common component of lipids in the body
- Free FA are formed only during metabolism
- General formula R-COOH.
- R → Alkyl / hydrocarbon chain

  COOH→ Carboxyl end
- Occurs mainly as ESTERS in natural fats and oils.

General Structure of a Fatty Acid

-Fatty acids are amphipathic molecules composed of a hydrophilic (polar, ionized) head (formed by the carboxyl group) and a hydrophobic (non-polar, non-ionized) tail (formed by the hydrocarbon chain).

-The degree of solubility of a fatty acid depends on the length of the hydrocarbon chain.

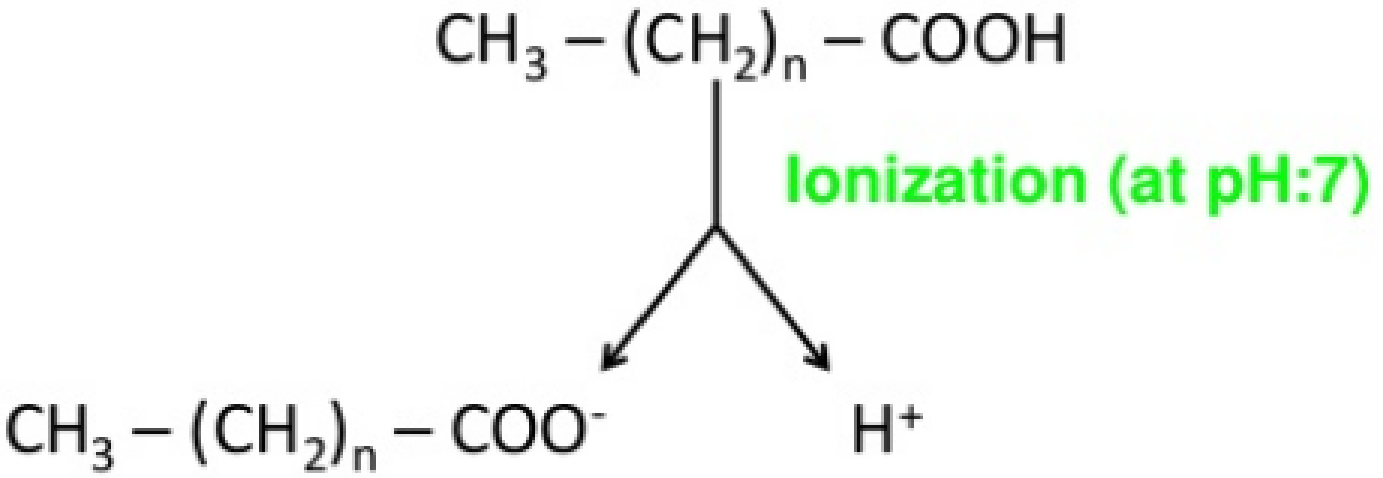
Non-polar

polar

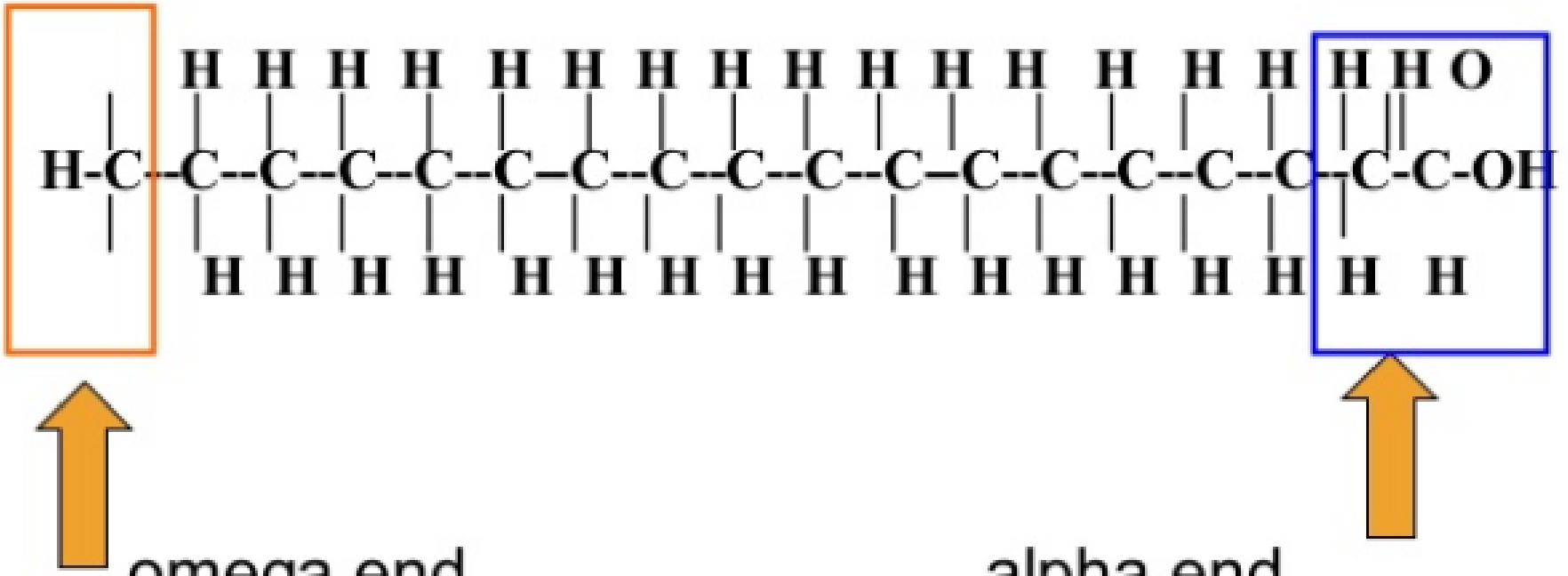
H_2O-insoluble

H_2O-soluble

General Formula of Fatty Acids



Fatty Acid Structure



Even and Odd carbon fatty acids

- Fatty acids that occur in natural lipids are of even carbons (usually 14C – 20C)
- This is due to biosynthesis of fatty acids mainly occurs with the sequential addition of 2 carbon units.
- Palmitic acid (16C) and Stearic acid (18C) are most common.
- Propionic acid (3C) and valeric acid (5C) are common odd chain fatty acids.

Nomenclature

- Systematic name
- It is based on hydrocarbon from which it is derived.
- After the name of the parent hydrocarbon
- With suffix – anoic acid for saturated fatty acid,
- – enoic acid for unsaturated fatty acid.

8 7 6 5 4 3 2 1

CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-COOH

Hydrocarbon chain Carboxyl group

Octane + acid = Octanoic acid

- Common name – Caprylic acid

Numbering

- The Carbon atoms are numbered from COOH group as 1.
- The carbons adjacent to this are 2,3,4 etc or α, β, γ
- Carboxyl group carbon is C_1, next carbon atom is C_2 / α-carbon, next is β and so on,
- Last carbon atom or CH_3 group, ω / n carbon.

Numbering of fatty acids

ω

$CH_3 - CH_2 - CH_2 - COOH$ Butyric acid

4 3 2 1 *(Arabic numbers)*

γ β α *(Greek alphabetical numbers)*

1 2 3 4 *(Omega numbers)*

Classification of Fatty Acids

1. According to chain length

   short, medium and long

2. According to degree of saturation

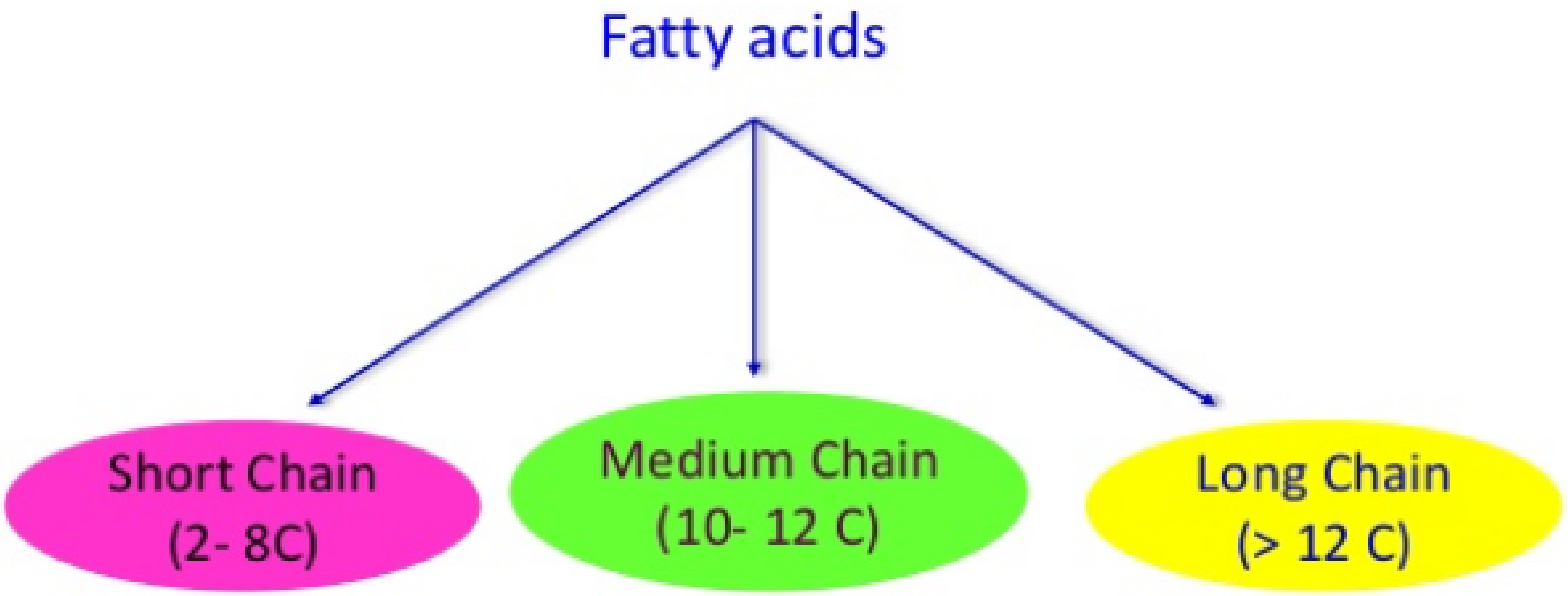
   saturated & unsaturated

3. According to Biological value

   essential & non-essential

4. Aliphatic, branched and cyclic

According to Chain Length



Saturated fatty acids (no double)

A-Short chain Saturated F.A. (2-10 carbon).

a-Short chain Saturated volatile F.A.(2-6 carbon).

b- Short chain Saturated non volatile F.A.(7-10 carbon).

B-Long chain Saturated F.A.(more the10 carbon)

a-Volatile short-chain fatty acids:

- They are liquid in nature and contain (1-6) carbon atoms.
- water-soluble and volatile at room temperature, e.g., acetic, butyric, and caproic acids.
- **Acetic F.A. (2C)** CH_3-COOH.
- **Butyric F.A. (4C)** CH_3-$(CH_2)_2$-COOH.
- **Caproic F.A. (6C)** CH_3-$(CH_2)_4$-COOH.

b-Non-volatile short-chain fatty acids:

- They are solids at room temperature and contain **7-10** carbon atoms.
- They are water-soluble and non-volatile at room temperature include caprylic and capric F.A.

- **caprylic (8 C)** $CH_3-(CH_2)_6-COOH$.
- **Capric (10 C)** $CH_3-(CH_2)_8-COOH$.

B-Long-chain fatty acids:

- They contain more than 10 carbon atoms.
- They occur in hydrogenated oils, animal fats, butter and coconut and palm oils.
- They are non-volatile and water-insoluble
- Include palmitic, stearic, and lignoceric F.A.

- palmitic(16C) $CH_3-(CH_2)_{14}-COOH$
- stearic (18 C) $CH_3-(CH_2)_{16}-COOH$
- lignoceric (24C) $CH_3-(CH_2)_{22}-COOH$

B-Unsaturated Fatty Acids

They contain double bond

- **monounsaturated**

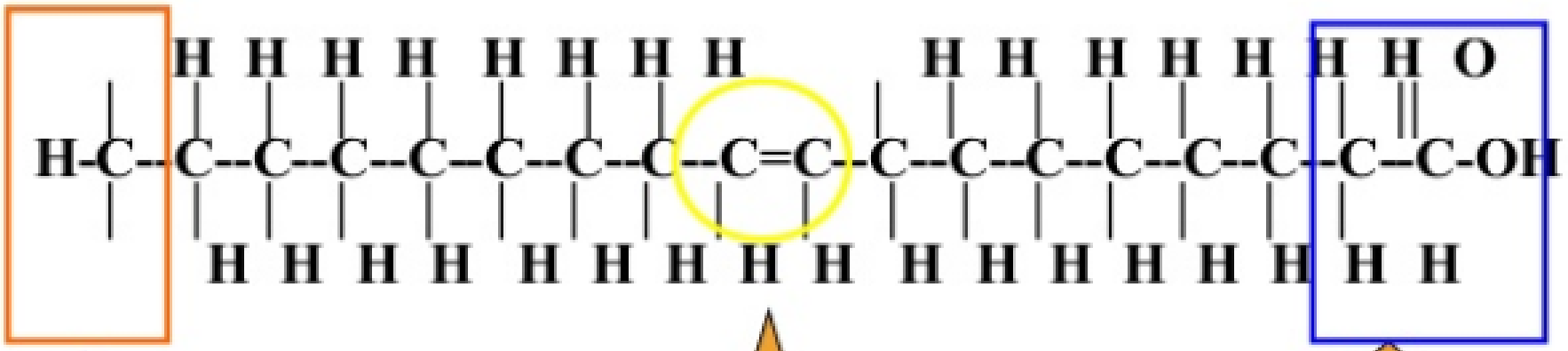
they contain one double bonds .

(C_nH_{2n-1} COOH)

- **polyunsaturated**

they contain more the one double bond ($C_nH_{2n-\text{more than 1}}$ COOH).

Monounsaturated Fatty Acid Structure

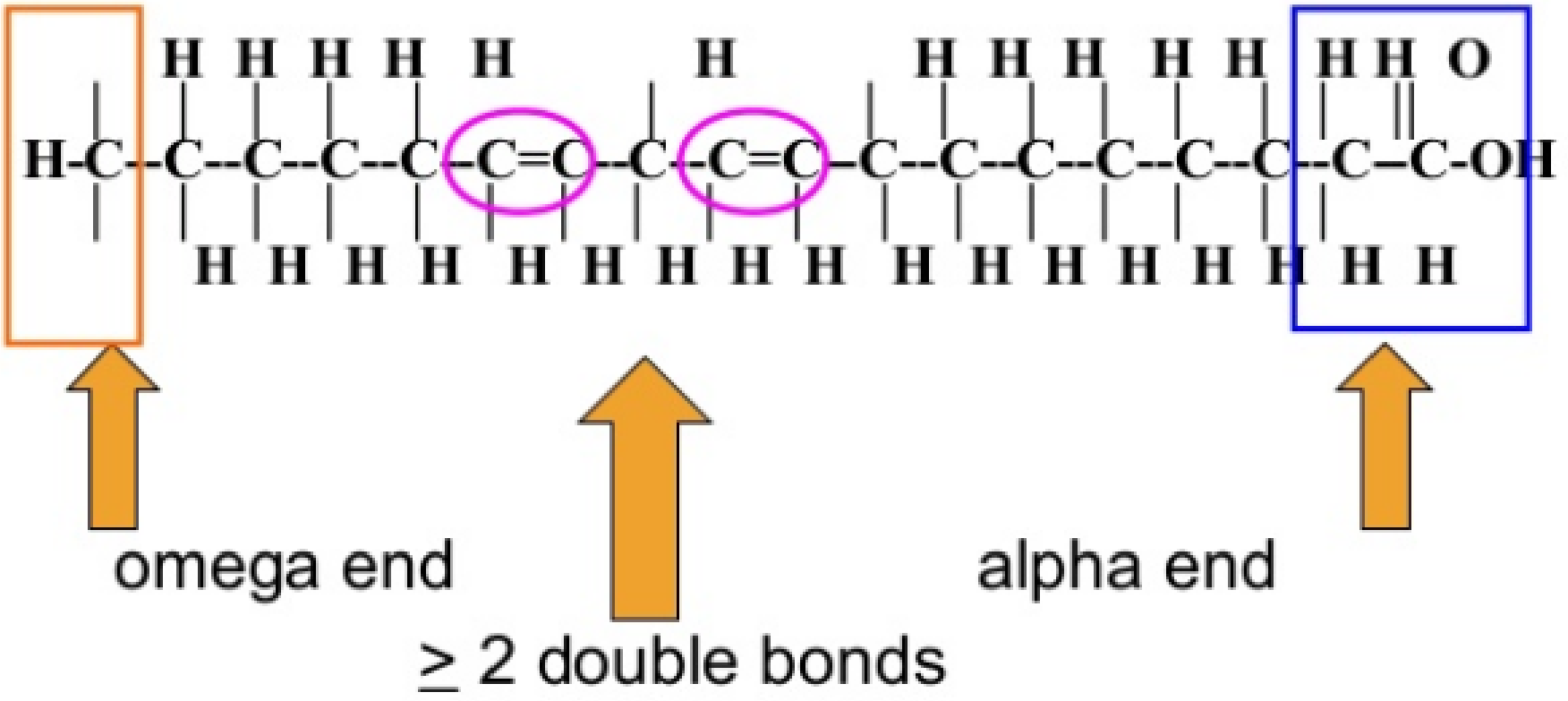


omega end

One double bond

alpha end

Polyunsaturated Fatty Acid Structure



1-Monounsaturated fatty acids:

1-Palmitoleic acid :

- It is found in all fats.
- It is C16:1Δ9, i.e., has 16 carbons and one double bond located at carbon number 9 and involving carbon 10.

$$CH_3-(CH_2)_5CH = CH-(CH_2)_7-COOH$$

2-Oleic acid

- Is the most common fatty acid in natural fats.
- It is **C18:1Δ9**, i.e., has 18 carbons and one double bond located at carbon number 9 and involving carbon 10.

$$CH_3\text{-}(CH_2)_7\text{-}CH{=}CH-(CH_2)_7\text{-}COOH$$

3-Nervonic acid

(Unsaturated lignoceric acid).

- **It is found in cerebrosides.**
- **It is C24:1Δ15, i.e., has 24 carbons and one double bond located at carbon number 15 and involving carbon 16.**

$$CH_3 - (CH_2)_7\ CH = CH - (CH_2)_{13} - COOH$$

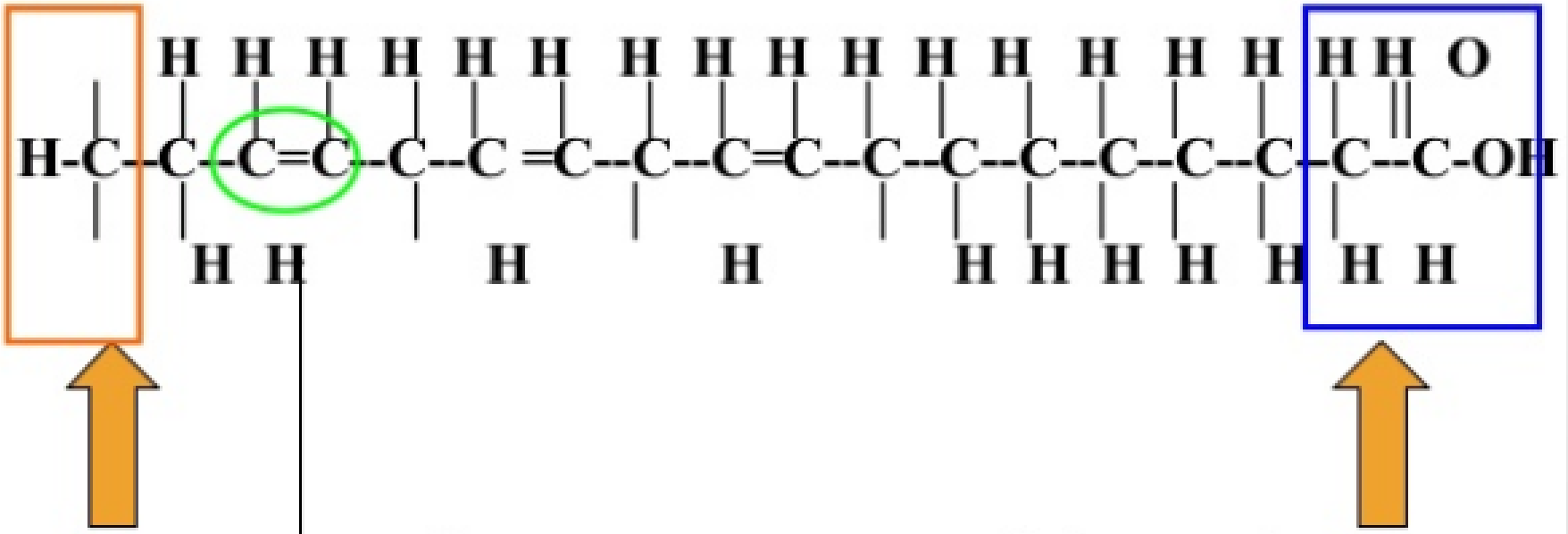
2-Polyunsaturated fatty acids :

(Essential fatty acids):

- Definition:
- They are essential fatty acids that can not be synthesized in the human body and must be taken in adequate amounts in the diet.
- They are required for normal growth and metabolism

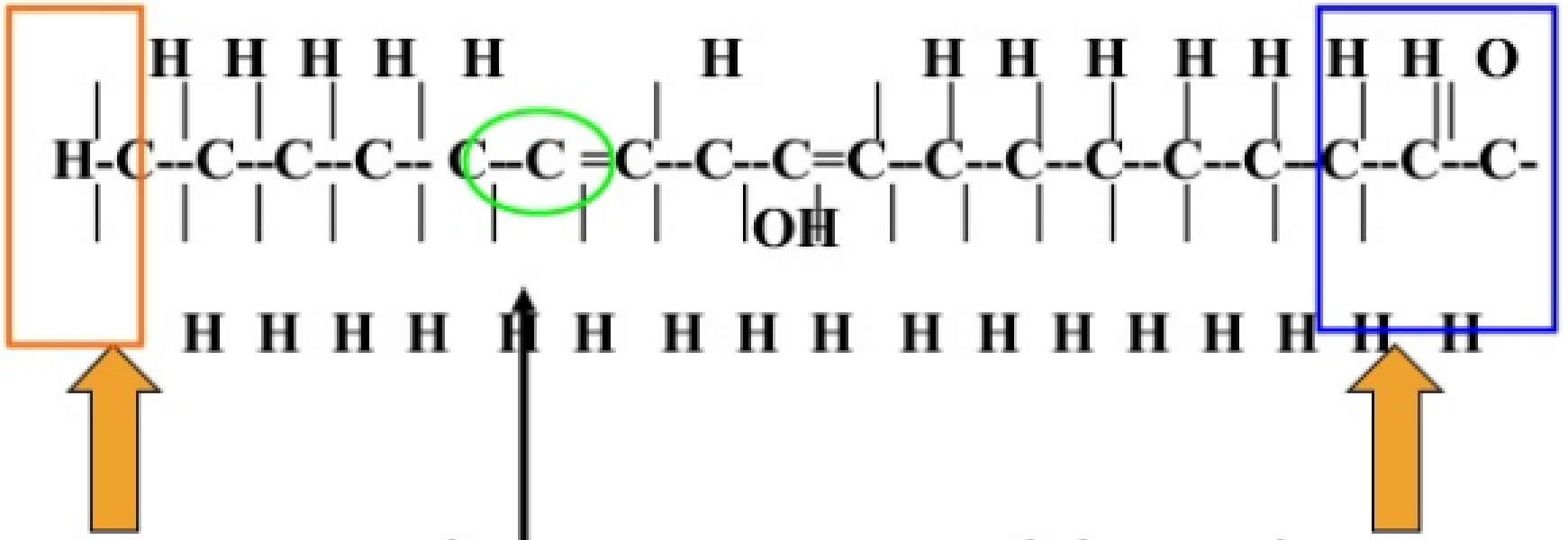
- **Source:** vegetable oils such as corn oil, linseed oil, peanut oil, olive oil, cottonseed oil, soybean oil and many other plant oils, cod liver oil and animal fats.
- **Deficiency:** Their deficiency in the diet leads to nutrition deficiency disease.
- Its symptoms include: poor growth and health with susceptibility to infections, dermatitis, decreased capacity to reproduce, impaired transport of lipids, fatty liver, and lowered resistance to stress.

Essential Fatty Acid- Omega-3 (alpha-linolenic acid)



1st double bond is located on the 3rd carbon from the omega end

Essential Fatty Acid- Omega-6 (linoleic acid)



1st double bond is located on the 6th carbon from the omega end

1-Linoleic:

- C18:2Δ9, 12.
- It is the most important since other essential fatty acids can be synthesized from it in the body.

$$CH_3-(CH_2)_4-CH = CH-CH_2-CH=CH-(CH_2)_7-COOH$$

2-Linolenic acid:

- C18:3Δ9, 12, 15,
- in corn, linseed, peanut, olive, cottonseed and soybean oils.

$$CH_3\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}(CH_2)_7\text{-}COOH$$

3-Arachidonic acid:

- C20:4Δ5, 8, 11, 14.
- It is an important component of phospholipids in animal and in peanut oil from which prostaglandins are synthesized.

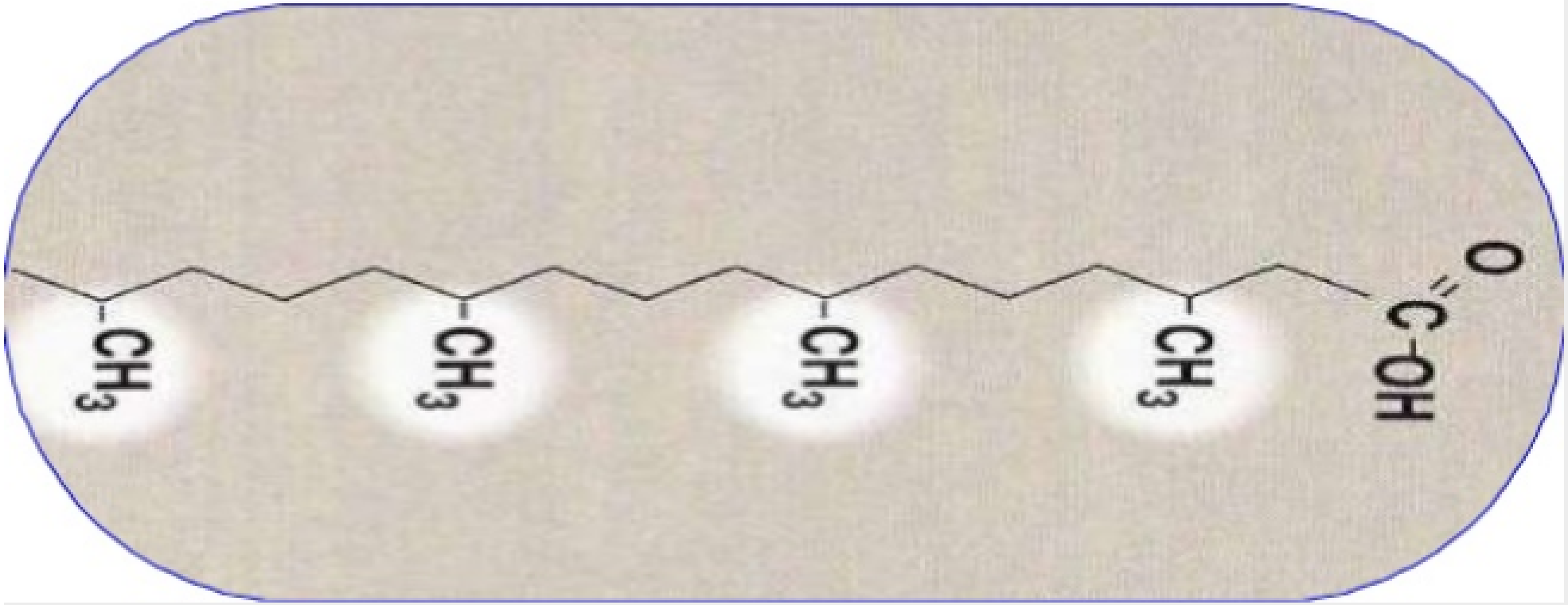
$$CH_3\text{-}(CH_2)_4\text{-}CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}(CH_2)_3\text{-}COOH$$

Signs and Symptoms of Essential Fatty Acids Deficiency

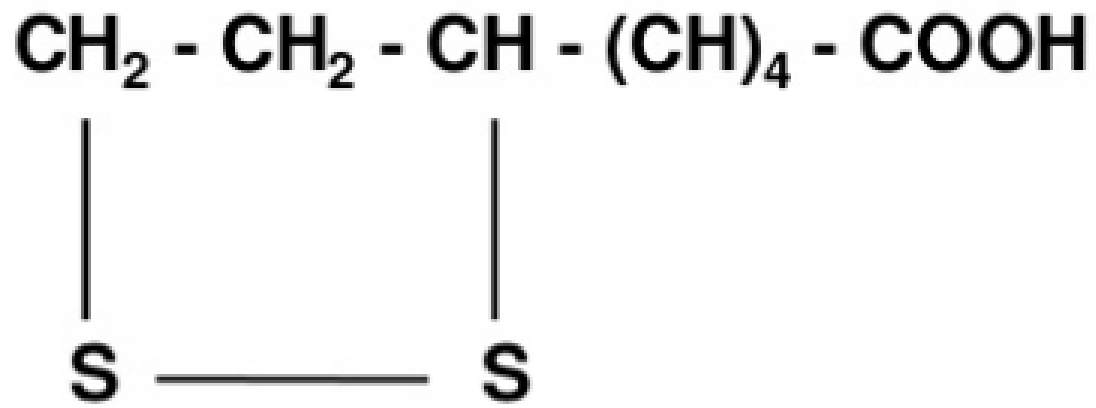
- Flaky, itchy skin
- Diarrhea
- Infections
- Retarded growth and wound healing
- Anemia

Branched Fatty Acids

- Phytanic acid (3,7,11,15 tetra methyl palmitic acid)
- It is present in milk lipids and animal fat.



Cyclic Fatty Acids



- Lipoic acid:
- It is a hydrogen carrier and coenzyme in oxidative decarboxylation of α-ketoacids e.g. pyruvate and α-ketoglutarate dehydrogenase complexes.