Lecture 3. Lipids

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Introduction

- **Lipids** (Greek: *lipos*, means fat or lard)

  - are a heterogeneous class of naturally occurring organic substances

  - are insoluble in water and highly soluble in one or more of the following solvents: ether, chloroform, benzene and acetone.This property sets them apart from proteins, carbohydrates, nucleic acids and other biomolecules

  - are widely distributed in the biological world

  - play a wide variety of roles in plant and animal tissues

- Lipids are concentrated source of energy.
- Lipids are the structural materials of cells and membranes
- Lipids serves as insulator for our body
- Lipids are the carrier / reservoir of fat soluble vitamins
- In food preparations lipids serves as a binding agent.

Classification of Lipids

1. **Simple lipids Such as:**

A. Terpens (Volatile hydrocarbons receive in locations such as the nose cells and sends them to the brain until you identify the smell)

B. Steroids(Hormones, There are from 30-40 steroid and has a different composition from each other and different function

Examples include cholesterol which creates sex hormones

C. Prostaglandine found in the prostate gland its working on lowering blood pressure also working on moving the non voluntary muscles.

D. Vitamines (A,D,E,K).

F. Coenzymes (important in biological oxidation reduction process)

2. Complex lipids Such as:

A. Glycerides. Such as animal fat and fat cells that around the heart and liver

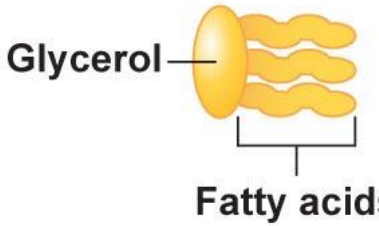
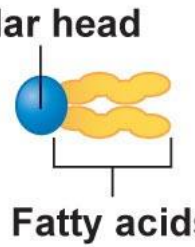
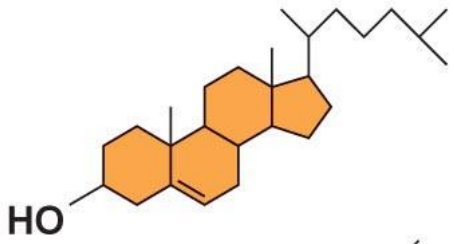
B. Phospholipids.

C. Sphingolipids

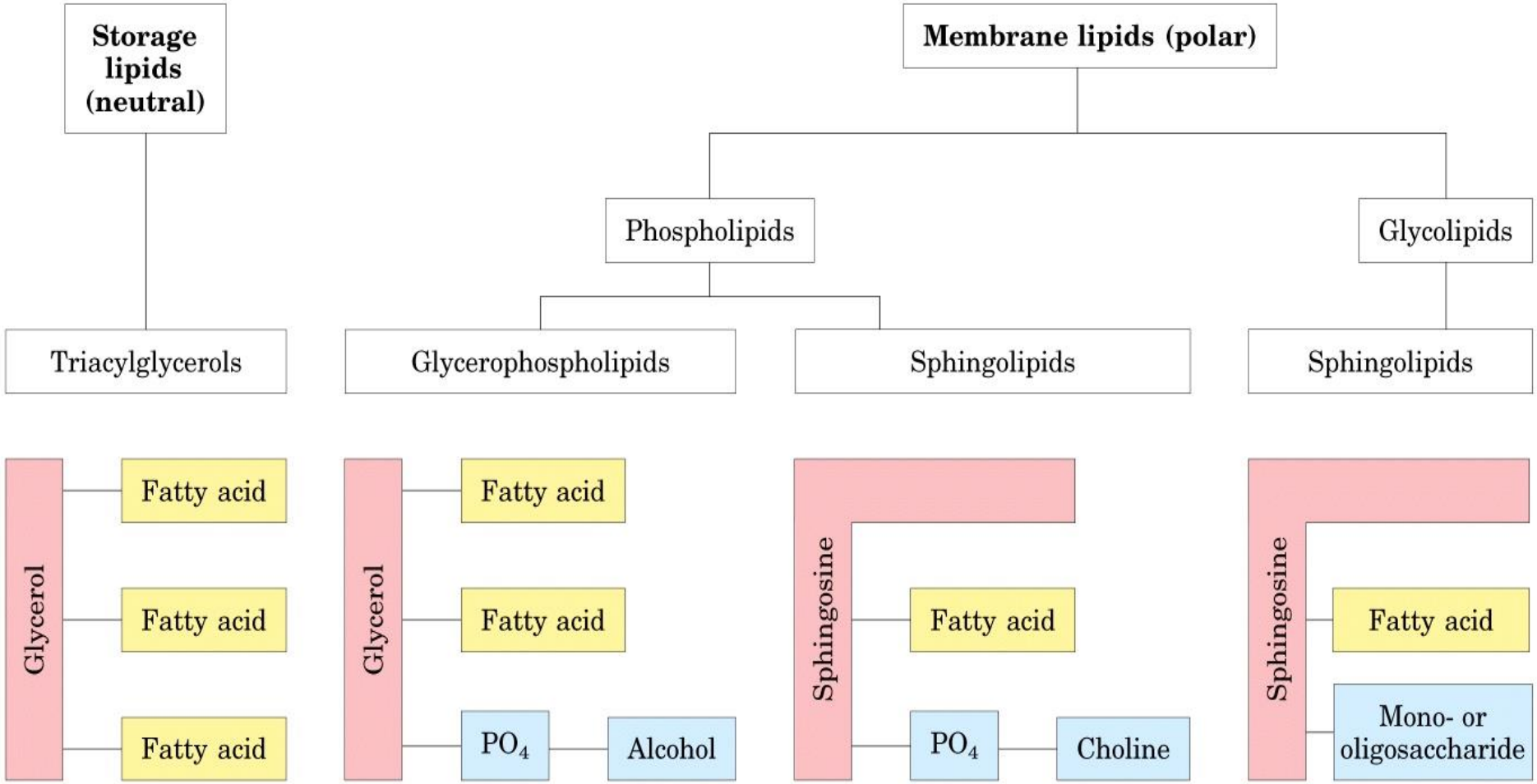
Present in the brain and formed a quarter of the weight of the brain

D. Waxes(Vegetable waxes)

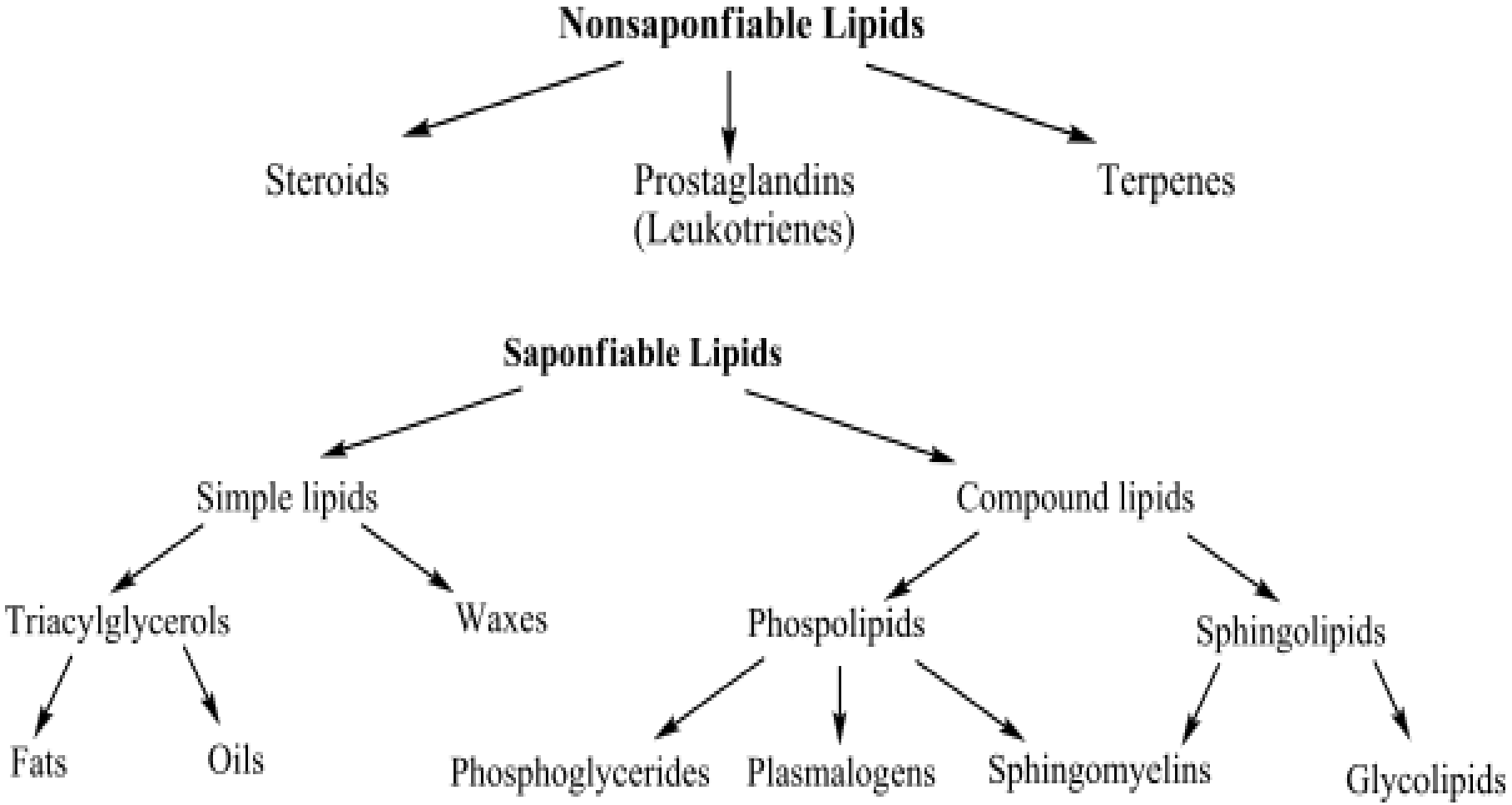
Quick Review

Lipid	Structure	Examples
Triglycerides		Saturated fat Unsaturated fat *Trans* fat
Phospholipids		Lecithin
Sterols	 	Cholesterol Sistanol

Classification of lipids

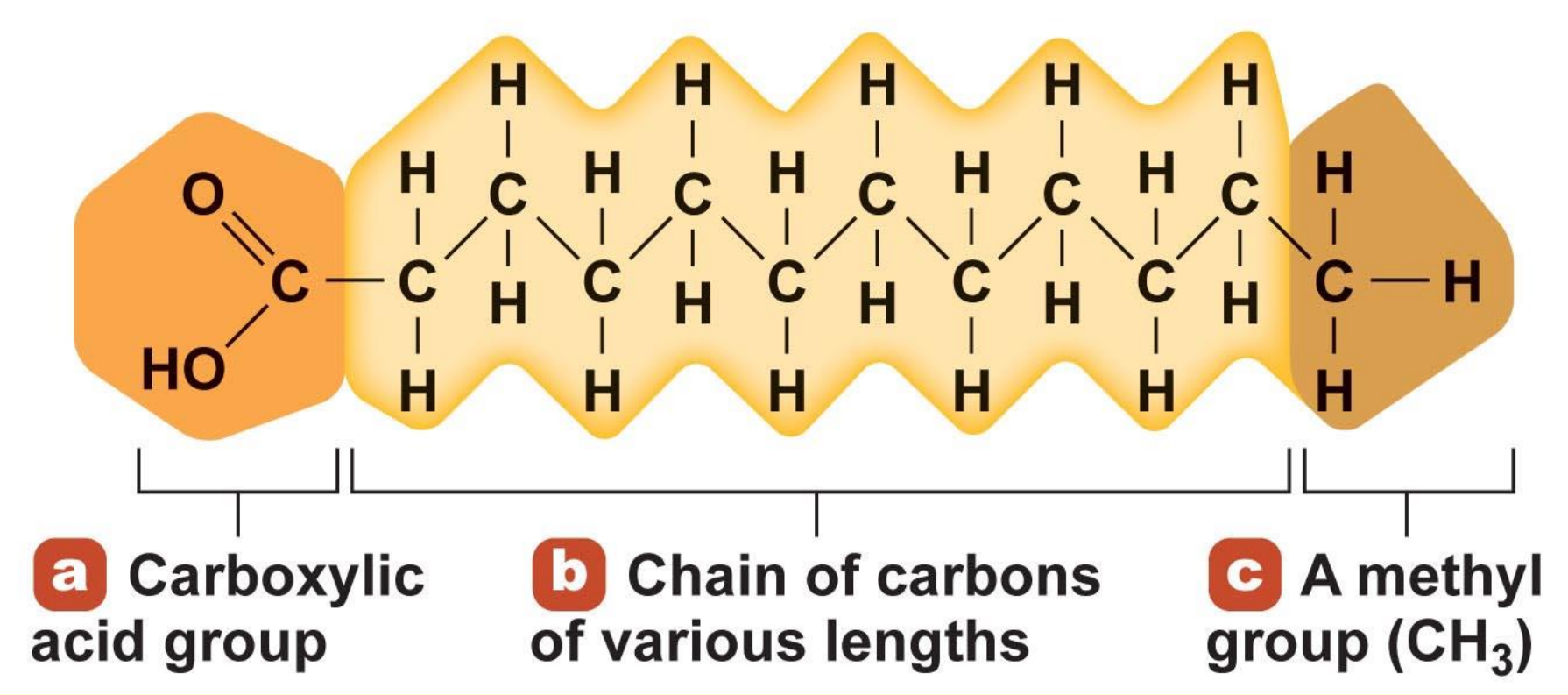


Classification of lipids



Fatty Acids

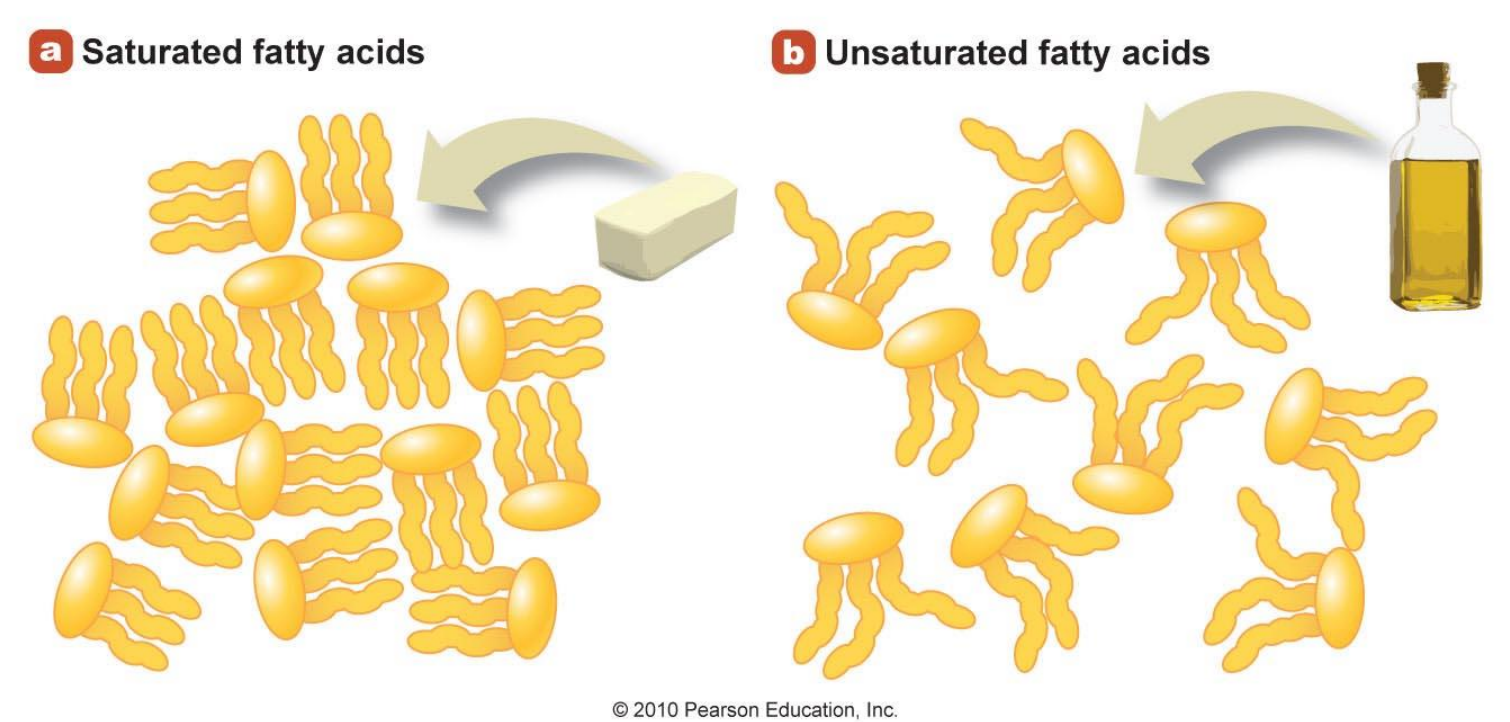
- Building blocks for triglycerides and phospholipids
- A chain of carbon and hydrogen atoms with a carboxyl group at the alpha end and a methyl group at the omega end



Fatty Acids

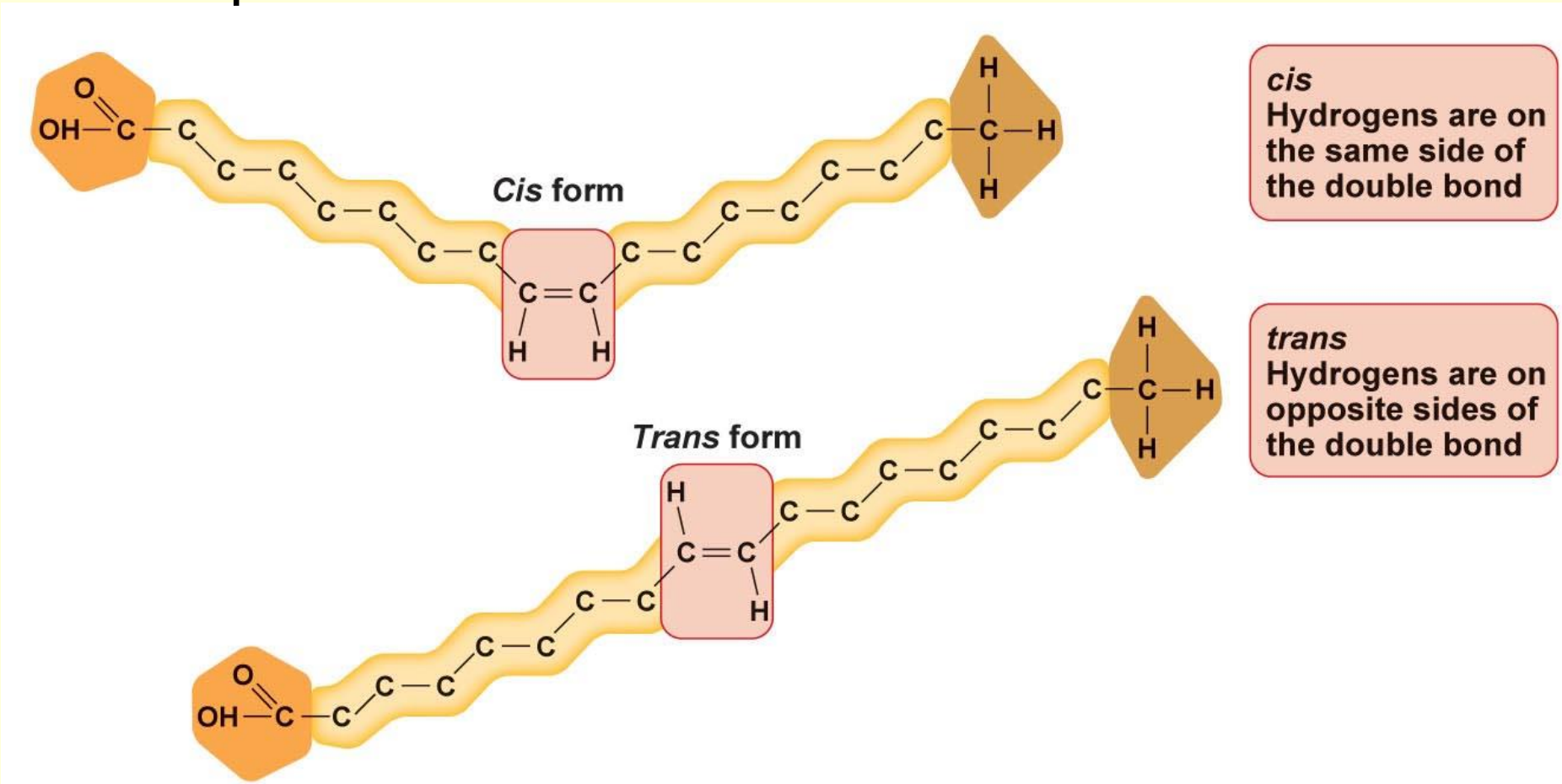
Definition:

- **Fatty acids are aliphatic mono-carboxylic acids that are mostly obtained from the hydrolysis of natural fats and oils.**
- **Have the general formula R-$(CH_2)_n$-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)**
- **Fatty acids are classified according to several bases as follows**:



Fatty Acids Vary in Shape

- Unsaturated fatty acids form two different shapes



I. According to presence or absence of double bonds they are classified into:

Saturated Fatty Acids

- **they contain no double bonds with 2-24 or more carbons.**
- **They are solid at room temperature except if they are short chained.**
- **They may be even or odd numbered.**
- **They have the following molecular formula, $C_nH_{2n+1}COOH$.**

Saturated fatty acids (**no double**)

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

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

Fatty Acids Commonly Found in Lipids

Some common *fatty acids*				
Common Name	**IUPAC name**	**Formula**	**Number of double bonds**	**Number of carbons**
Saturated fatty acids				
Palmitic	Hexadecanoic acid	$C_{15}H_{31}COOH$ ($CH_3(CH_2)_{14}COOH$)	0	16
Stearic	Octadecanoic acid	$C_{17}H_{35}COOH$ ($CH_3(CH_2)_{16}COOH$)	0	18
Unsaturated fatty acids				
Palmitoleic	9-hexadecenoic	$C_{15}H_{29}COOH$ ($CH_3(CH_2)_5CH=CH(CH_2)_7COOH$)	1	16
Oleic	9-octadecenoic acid	$C_{17}H_{33}COOH$ ($CH_3(CH_2)_7CH=CH(CH_2)_7COOH$)	1	18
Linoleic	9,12-octadecadienoic	$C_{17}H_{31}COOH$ ($CH_3(CH_2)_4(CH=CHCH_2)_2(CH_2)_6COOH$)	2	18
Linolenic	9,12,15-octadecatrienoic	$C_{17}H_{29}COOH$ ($CH_3CH_2(CH=CHCH_2)_3(CH_2)_6COOH$)	3	18

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).

1-Monounsaturated fatty acids:

1-Palmitoleic acid :

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

$$CH_3\text{-}(CH_2)_5CH = CH\text{-}(CH_2)_7\text{–}COOH$$

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.**

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

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**

1-Linoleic:

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

$$CH_3\text{-}(CH_2)_4\text{-}CH = CH\text{-}CH_2\text{-}CH{=}CH\text{-}(CH_2)_7\text{-}COOH$$

2-Linolenic acid:

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

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

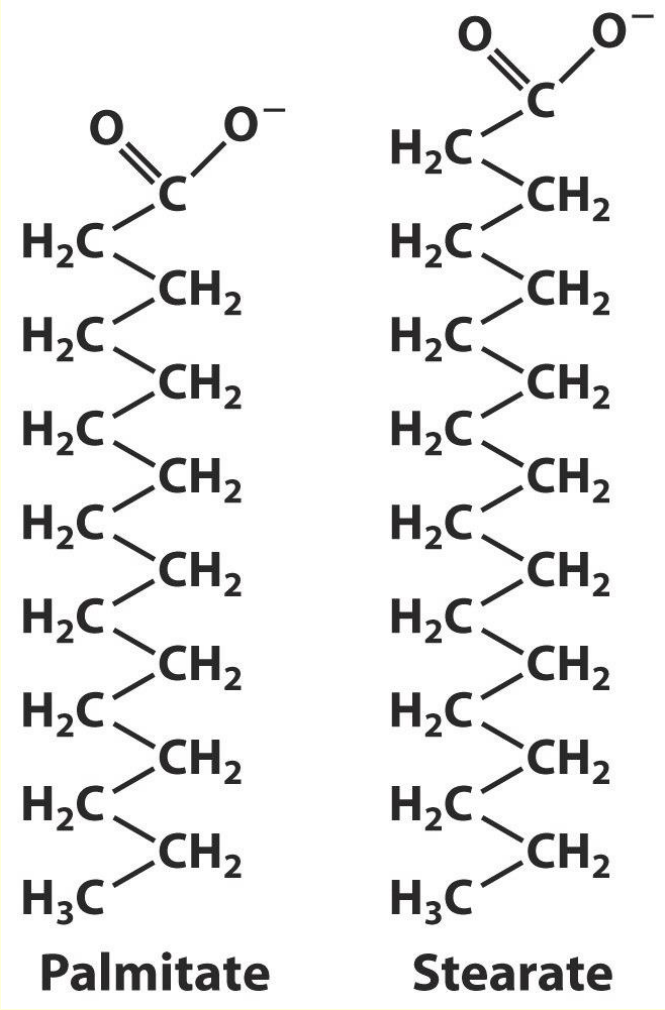
3-Arachidonic acid:

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

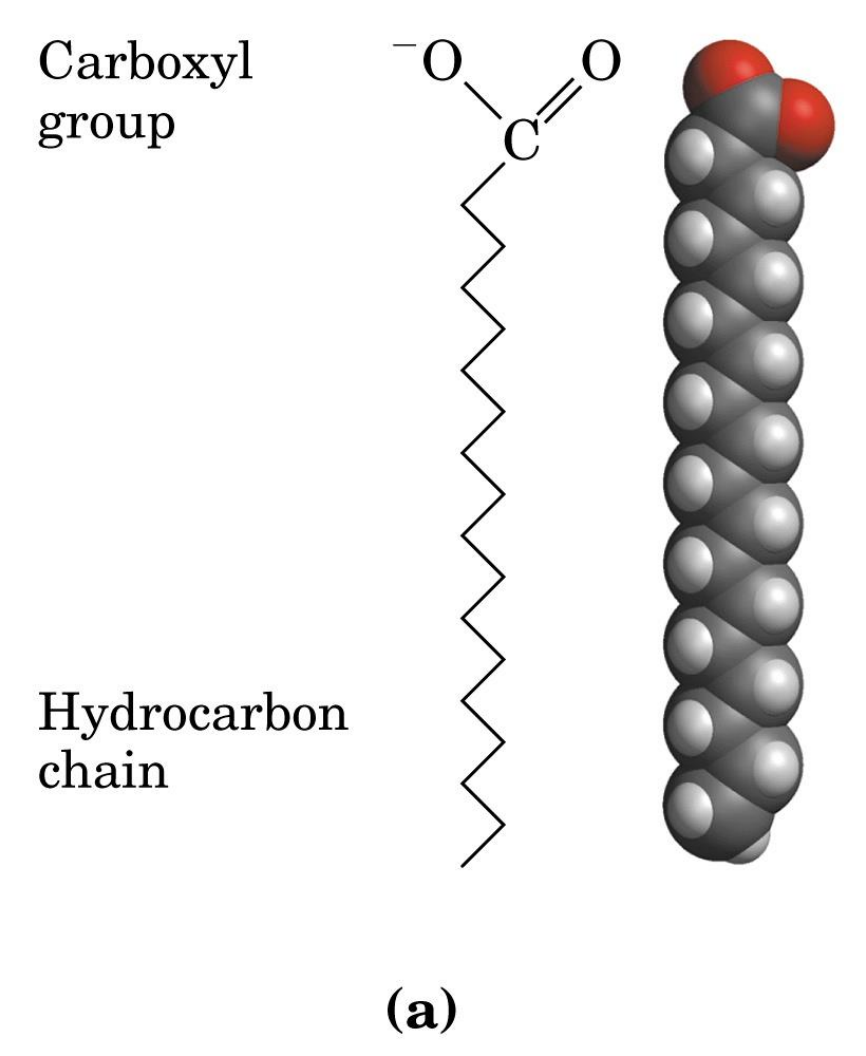
$$CH_3\text{-}(CH_2)_4\text{-}CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}(CH_2)_3\text{-}COOH$$

- The commonest fatty acids in animal fats are **palmitic, stearic and oleic acids.**
- The main difference between fats and oils is for **oils being liquid** at room temperature, whereas, **fats are solids.**
- This is mainly due to presence of larger percentage of **unsaturated** fatty acids in oils than fats that has mostly **saturated** fatty acids.

Saturated Fatty acids

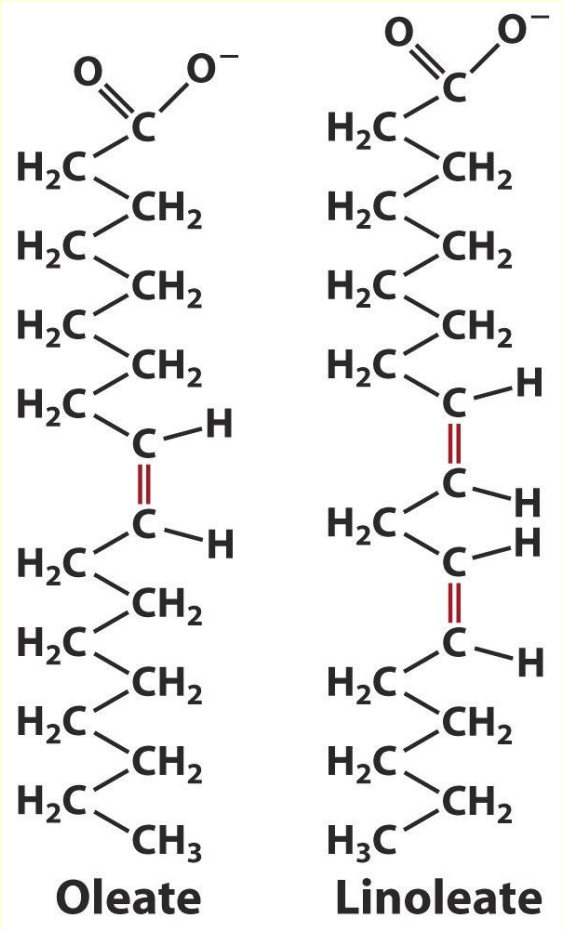


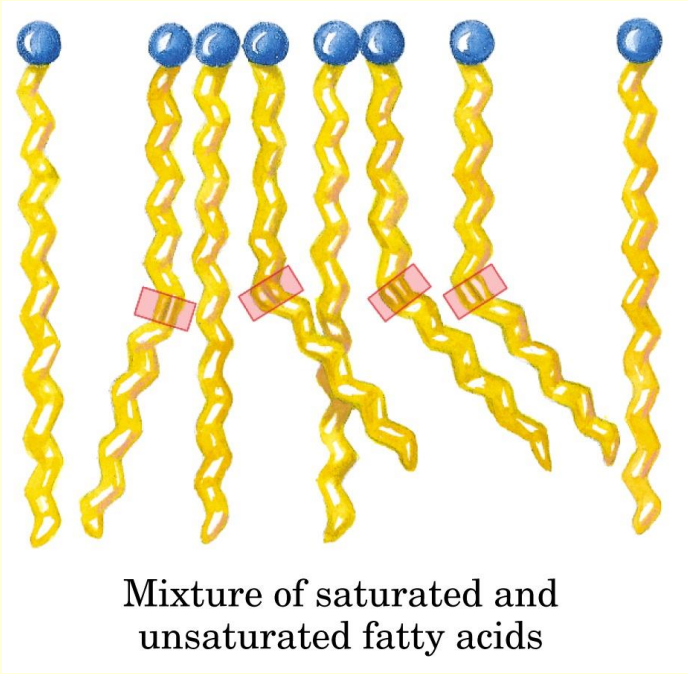
Stearic acid



The packing of fatty acids depends on their degree of saturation. Stearic acid is shown here in its usual extended conformation. Saturated fatty acids are tightly packed and stabilized by many hydrophobic interactions

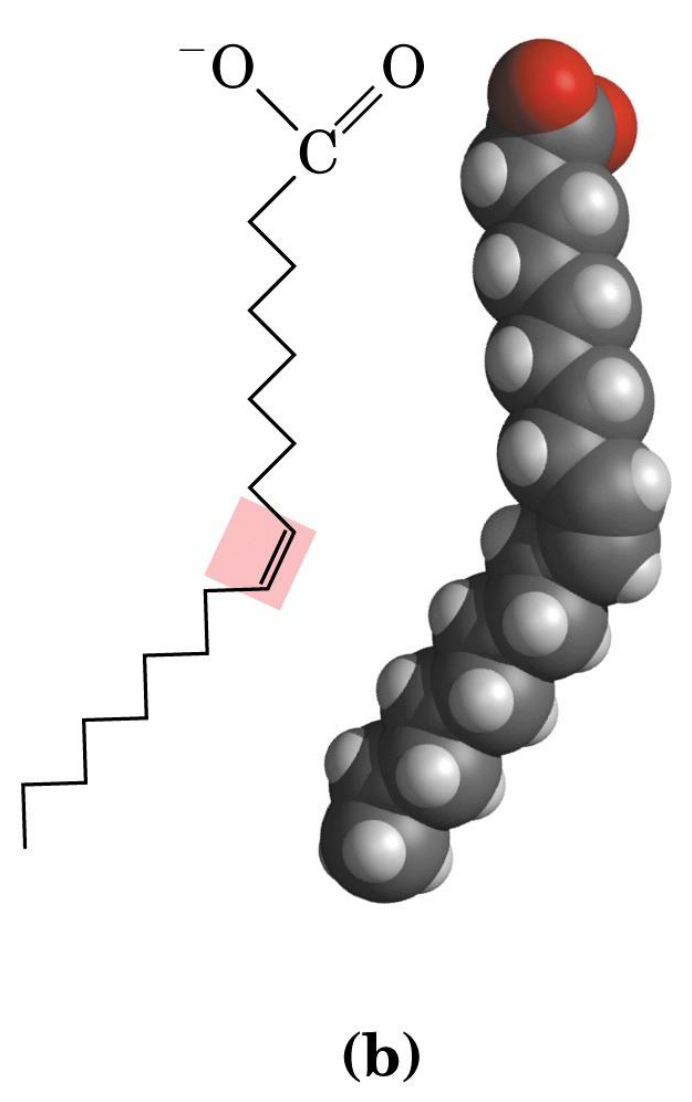
Unsaturated Fatty acids





Mixture of saturated and unsaturated fatty acids

Oleic acid



The double bond (shaded)introduces a rigid bend in the hydrocarbon tails. Fatty acids with one or several such bends cannot pack together as tightly as saturated fatty acids

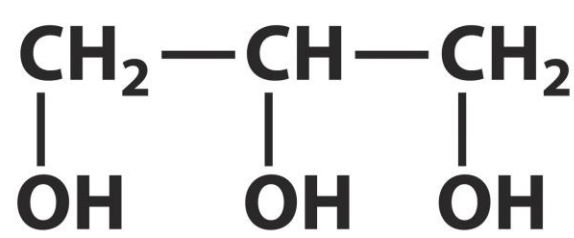
Waxes

- **Waxes**: Waxes are part of the lipid family. Waxes are esters of long-chain saturated and unsaturated fatty acids (having 14-36 carbon atoms) with long-chain alcohol(having 16-30 carbon atoms).
- Waxes are low- melting, stable solids which appear in nature in both plants and animals. A wax coat protects surface of many plant leaves from water loss and attack by microorganisms.
- Carnauba wax, a major ingredients of car wax and floor polish, comes from the leaves of a South American palm tree. Beeswax is largely myricyl palmitate , the ester of myricyl alcohol and palmitic acid
- Waxes also coat skin, hairs and feathers, and help keep them pliable and water-proof.

Triglycerides

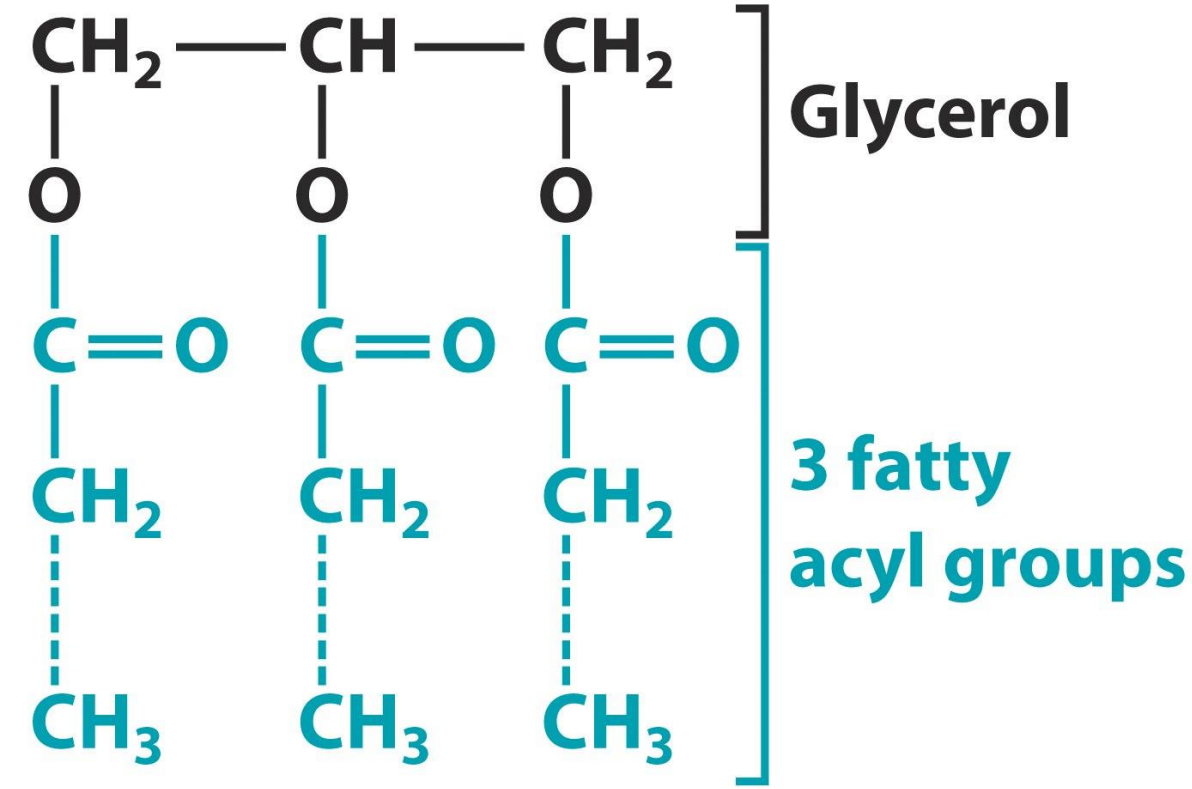
- The fats and oils found in animals and plants are triglycerides

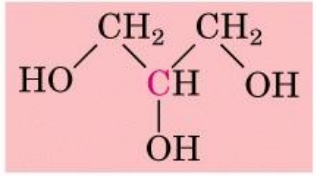
- Triglycerides are:
  - esters of fatty acids and glycerols
  - simple lipids
  - important as the storage form of fat in the human body



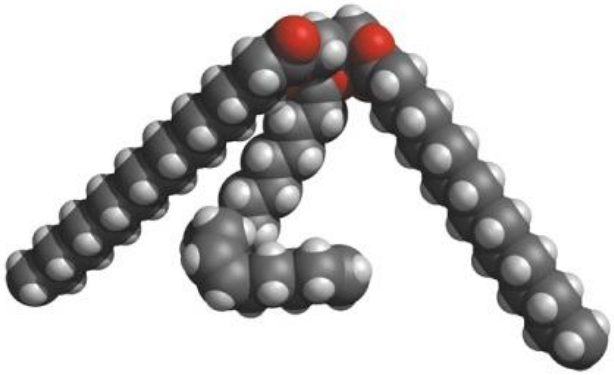
Glycerol

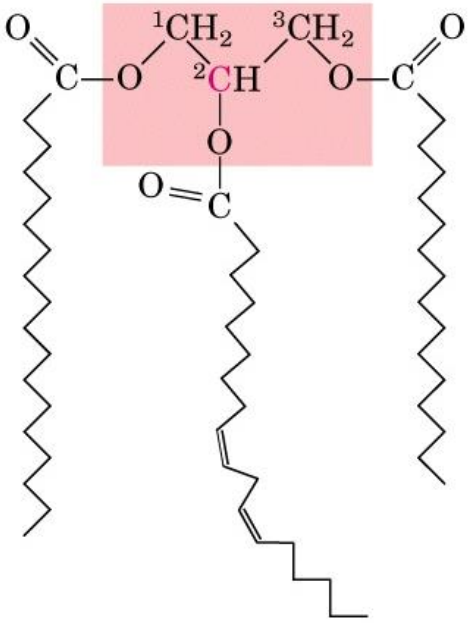
Triglycerides





Glycerol

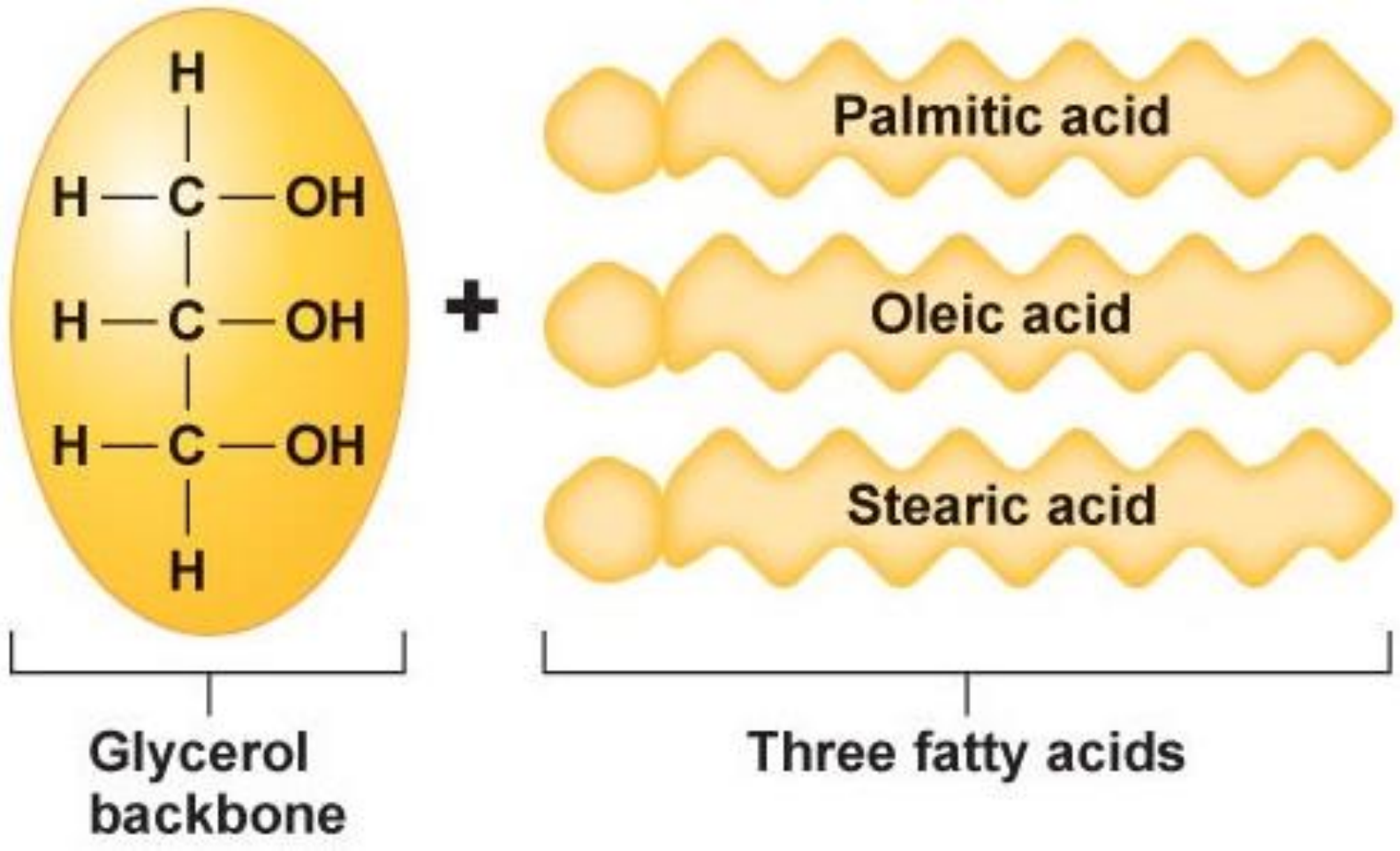




1-Stearoyl, 2-linoleoyl, 3-palmitoyl glycerol,
a mixed triacylglycerol

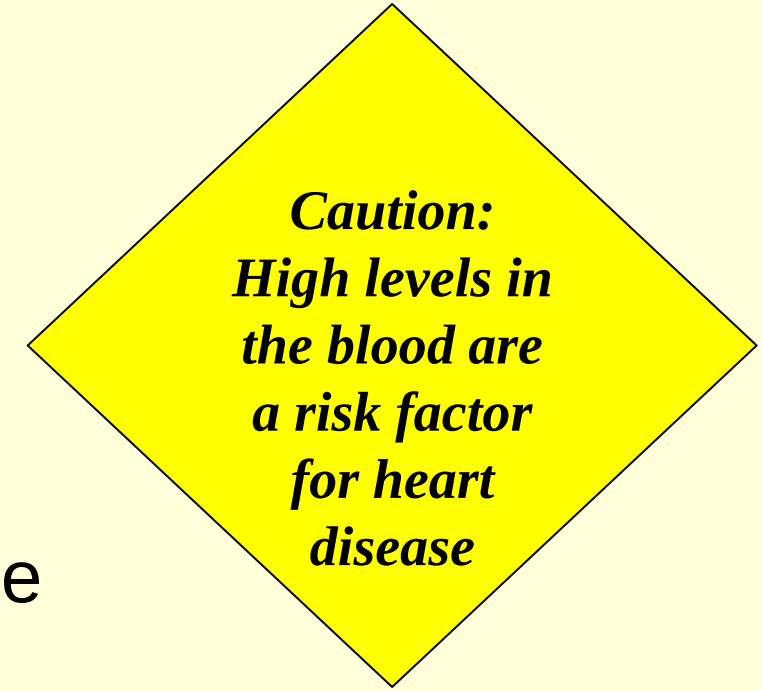
Triglycerides

- Three fatty acids connected to a glycerol backbone

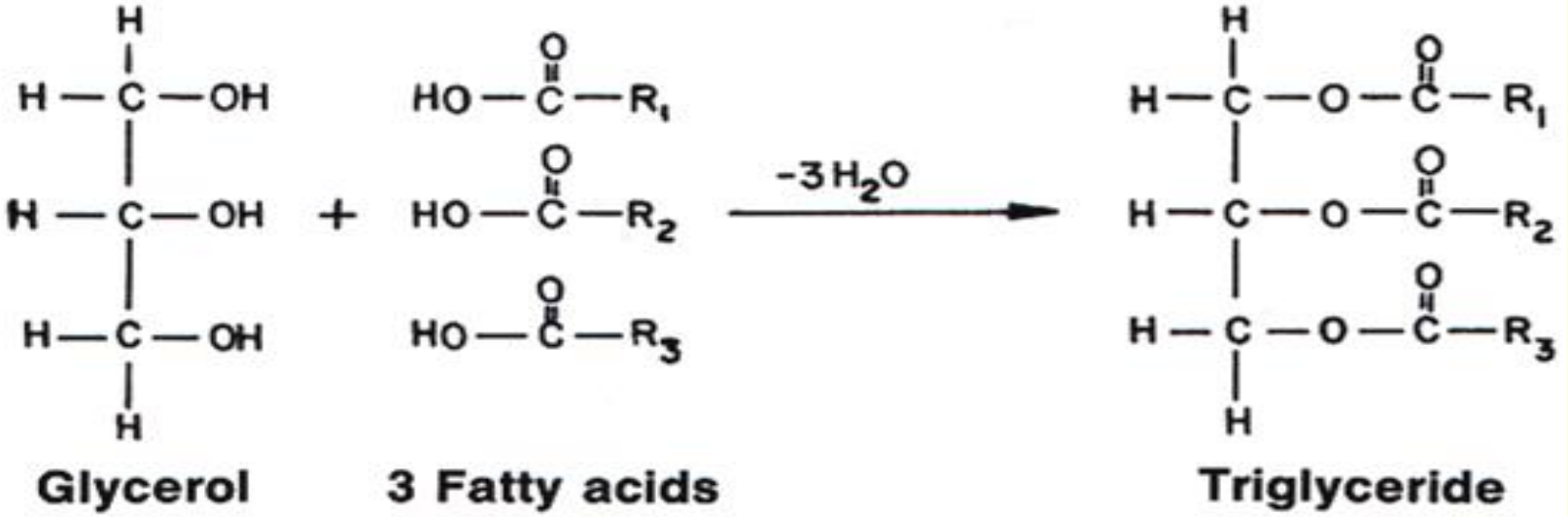


Triglycerides

- Most common lipid in both foods and the body
- Make up about 95% of lipids found in foods
- Functions
  - Add texture
  - Makes meats tender
  - Preserves freshness
  - Stores as adipose tissue for energy



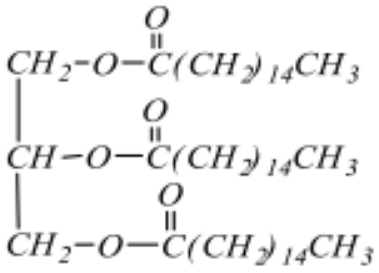
Formation of triglycerides



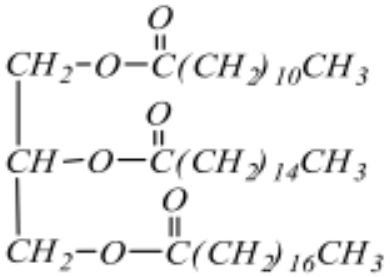
If all acid group are the same, the triglyceride is called a **simple glycerid**, otherwise the triglyceride is a **mixed glyceride** (complex triacylglycerols).

(**Simple** triacylglycerols are those in wich R^1, R^2, and R^3 are the same, i.e., three molecules of the same fatty acids react with glycerol. Complex triacylglycerols are those in wich R^1, R^2, R^3 are different).

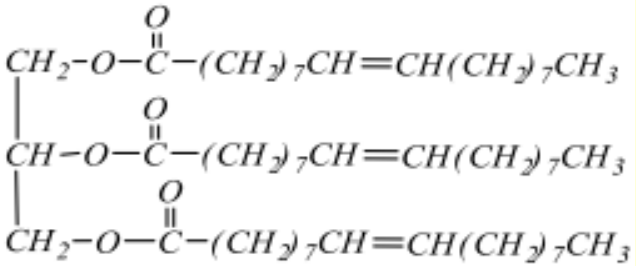
Naturally occurring triacylglycerols are complex triacylglycerols.



glyceryl tripalmitate
tripalmitin
(a simple glyceride; a fat)



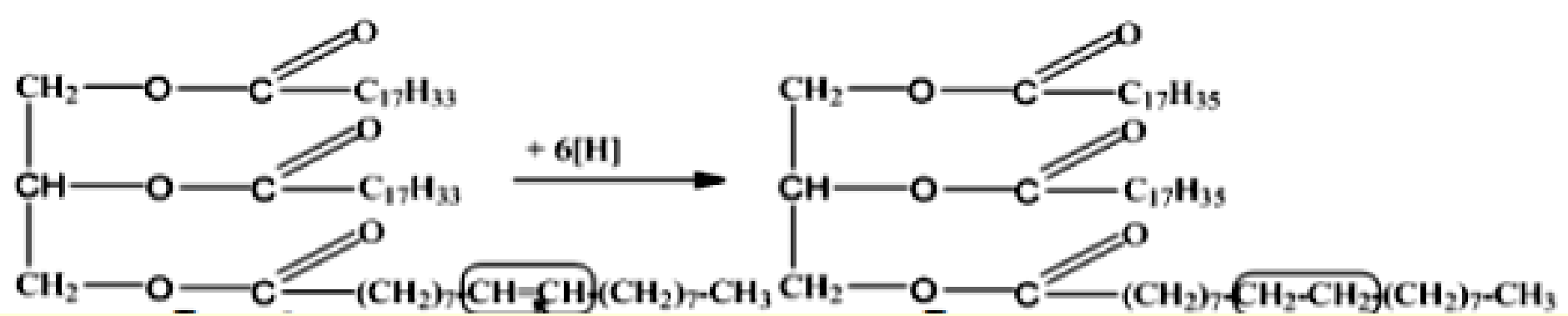
glyceryl lauropalmitosrearate
(a mixed glyceride; a fat)



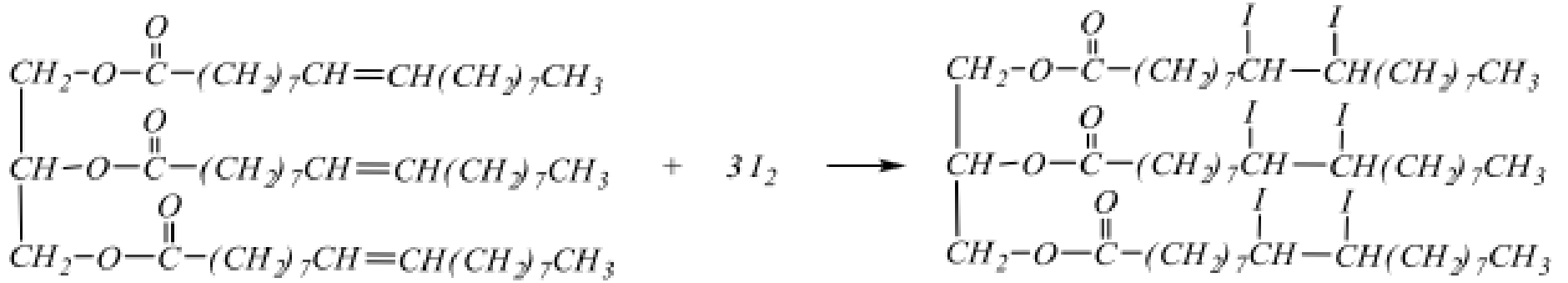
glyceryl trioleate, triolein
(a simple glyceride; an oil)

Chemical properties of triglycerides

Addition reactions



The **iodine number** of a triglyceride is the number of grams of I_2 reacting with $(1.00\times10^2\,g)$ 100g of the triglyceride. The iodine number indicates the degree of unsaturation in the fatty acid components.



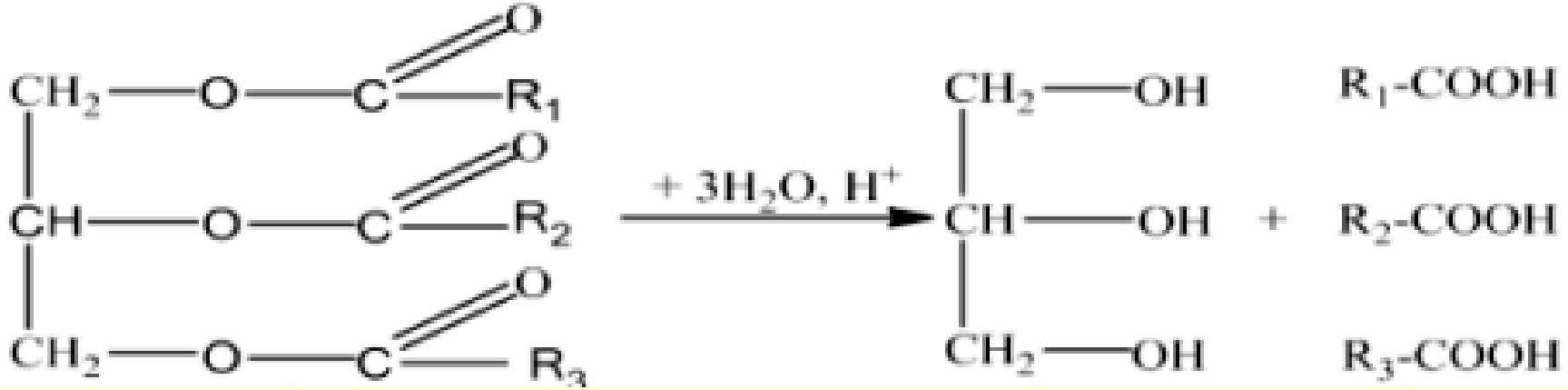
triolein

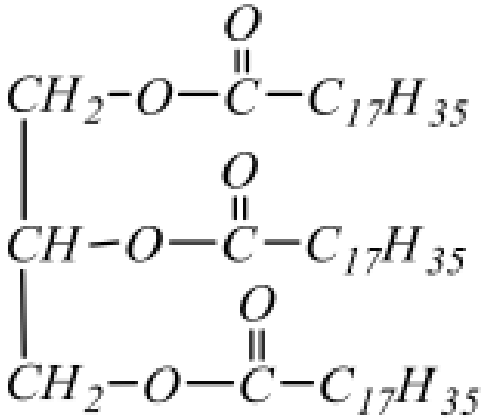
Oxidation cleaves the double bond, with each carbon of the double bond being converted to a *COOH* group.

Write the equation for oxidation of palmitoleic acid

$$CH_3(CH_2)_5CH=CH(CH_2)_7COOH \xrightarrow{[O]} CH_3(CH_2)_5COOH + HOOC(CH_2)_7COOH$$

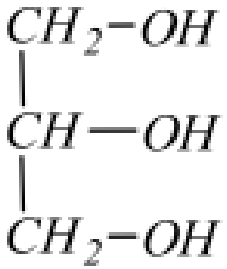
Hydrolysis process





tristearin
(glycerol tristearate)

+ $3KOH \longrightarrow$



glycerol

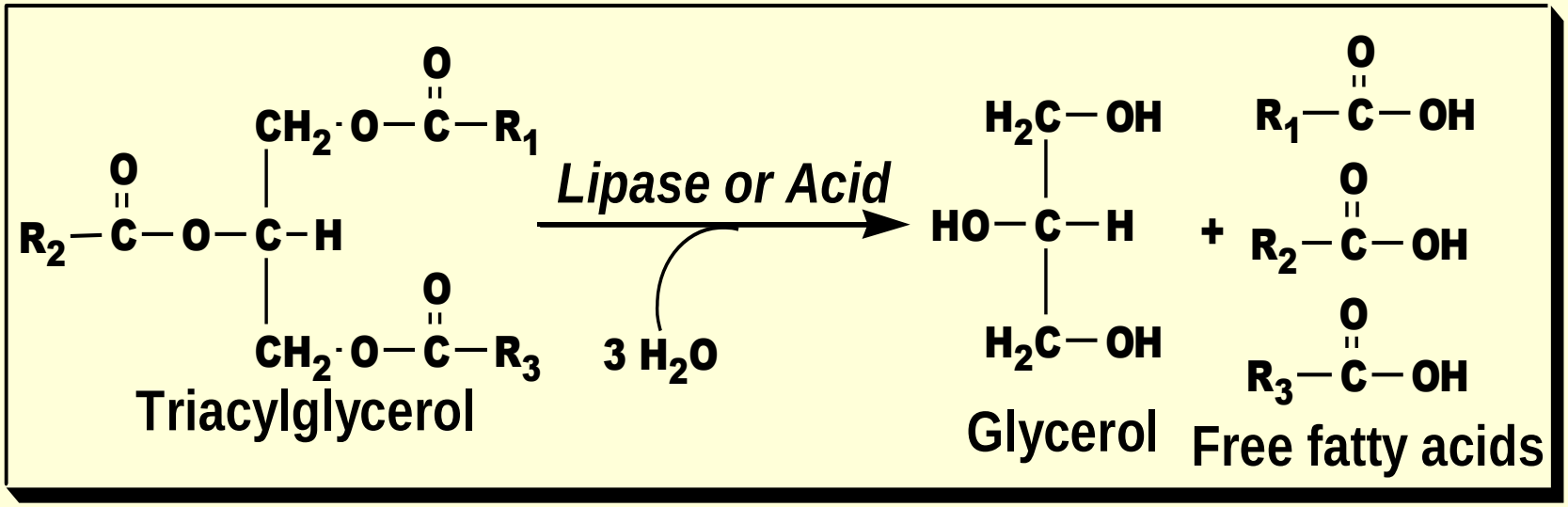
+ $3C_{17}H_{35}COOK$

potassium stearate
(a soap)

Chemical Properties of fats and oils:

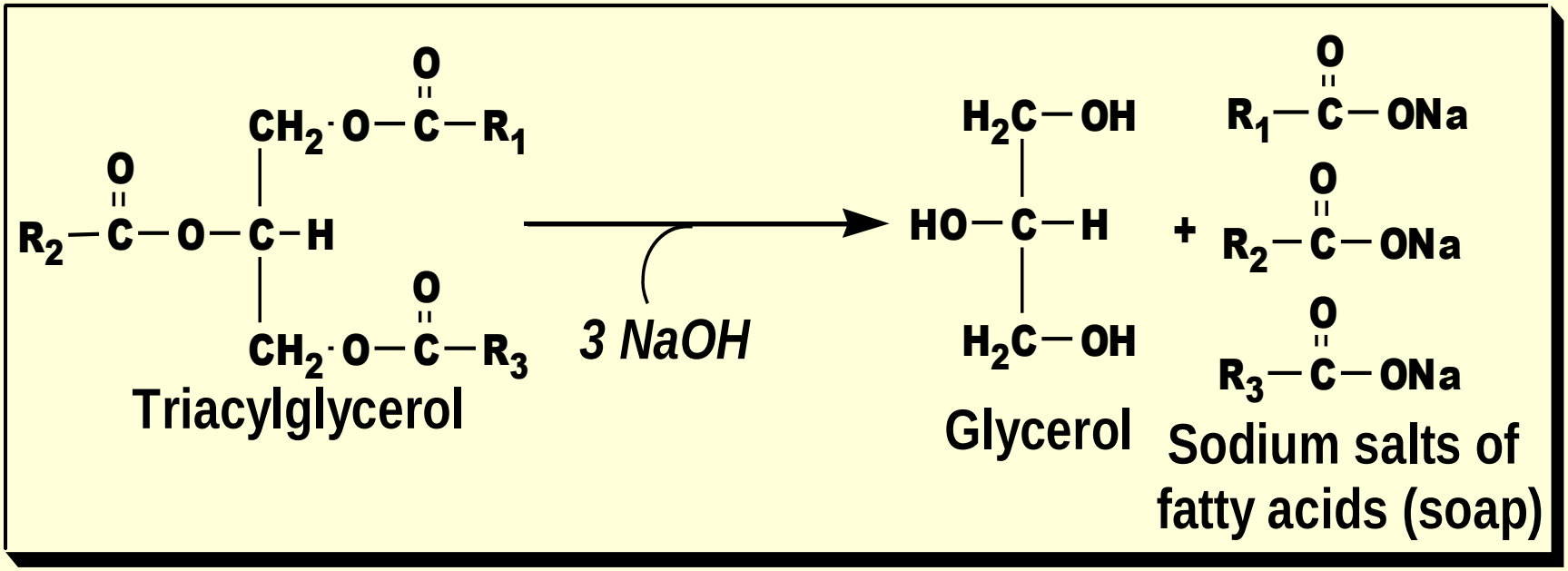
1-Hydrolysis:

- They are hydrolyzed into their constituents (fatty acids and glycerol) by the action of super heated steam, acid, alkali or enzyme (e.g., lipase of pancreas).
- - During their enzymatic and acid hydrolysis glycerol and free fatty acids are produced.



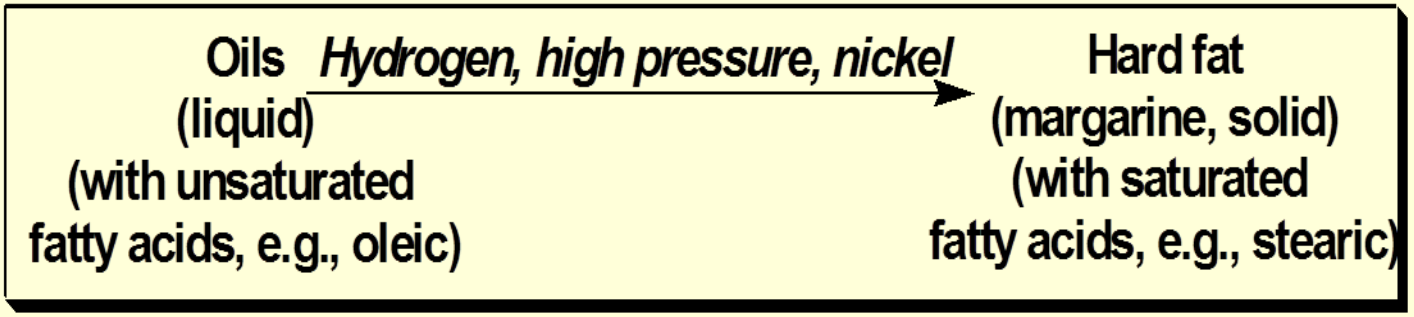
2-Saponification. Alkaline hydrolysis produces glycerol and salts of fatty acids (soaps).

- Soaps cause emulsification of oily material this help easy washing of the fatty materials



3-Hydrogenation or hardening of oils:

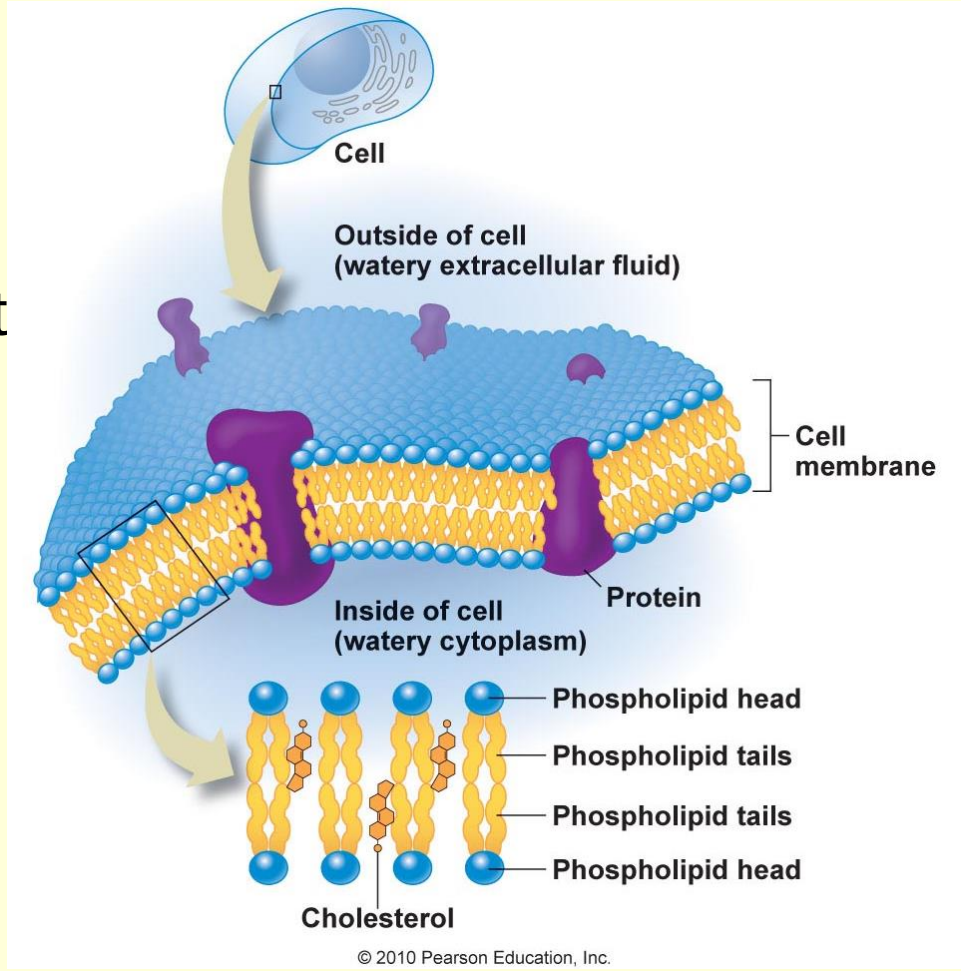
- **It is a type of addition reactions accepting hydrogen at the double bonds of unsaturated fatty acids.**
- **The hydrogenation is done under high pressure of hydrogen and is catalyzed by finely divided nickel or copper and heat.**
- **It is the base of hardening of oils (margarine manufacturing), e.g., change of oleic acid of fats (liquid) into stearic acid (solid).**



Structural lipids

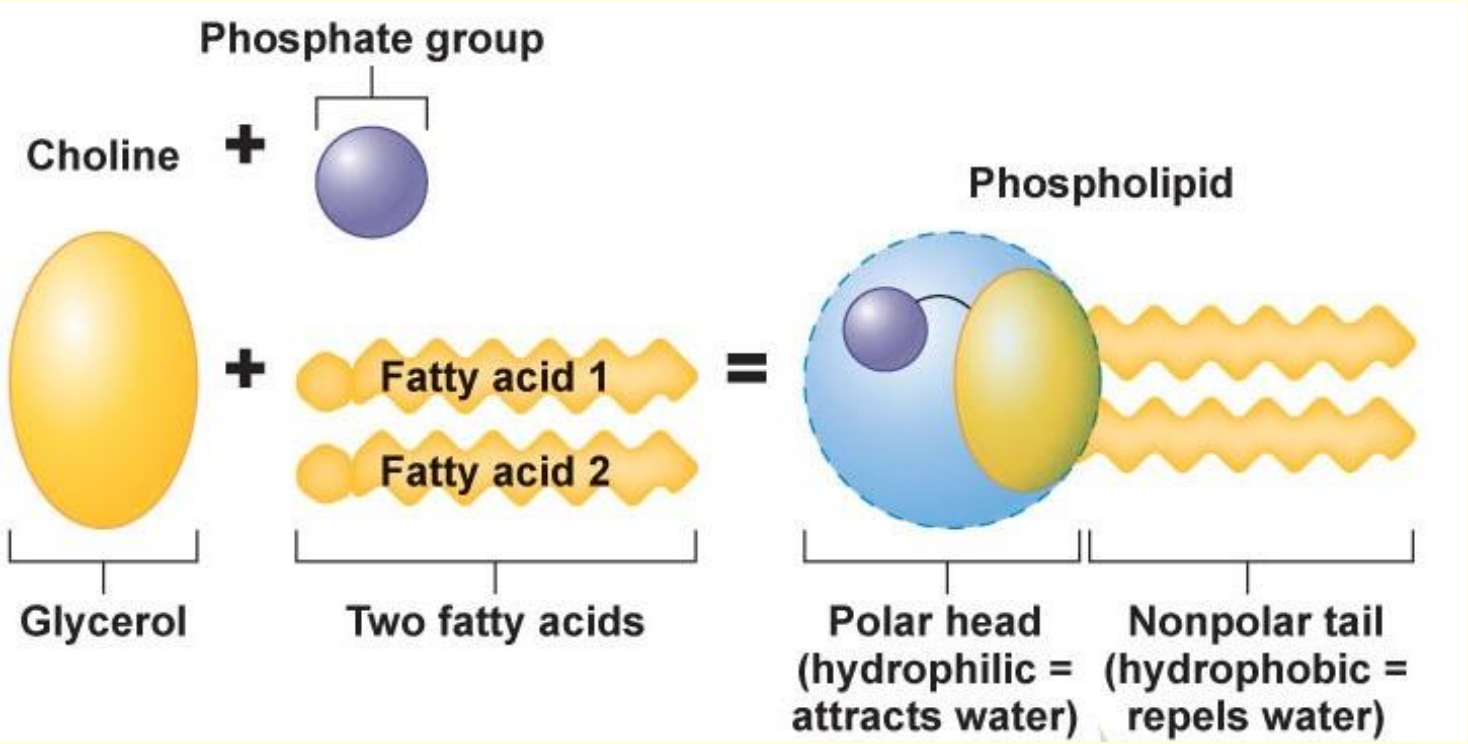
- Chemical analysis of the isolated materials shows that lipids are the major components of most membranes. This lipids are not triglycerides but another group of compound called **complex lipids**.

- There are two types of complex lipids:
  - Phospholipids
  - glycolipids



Phospholipids

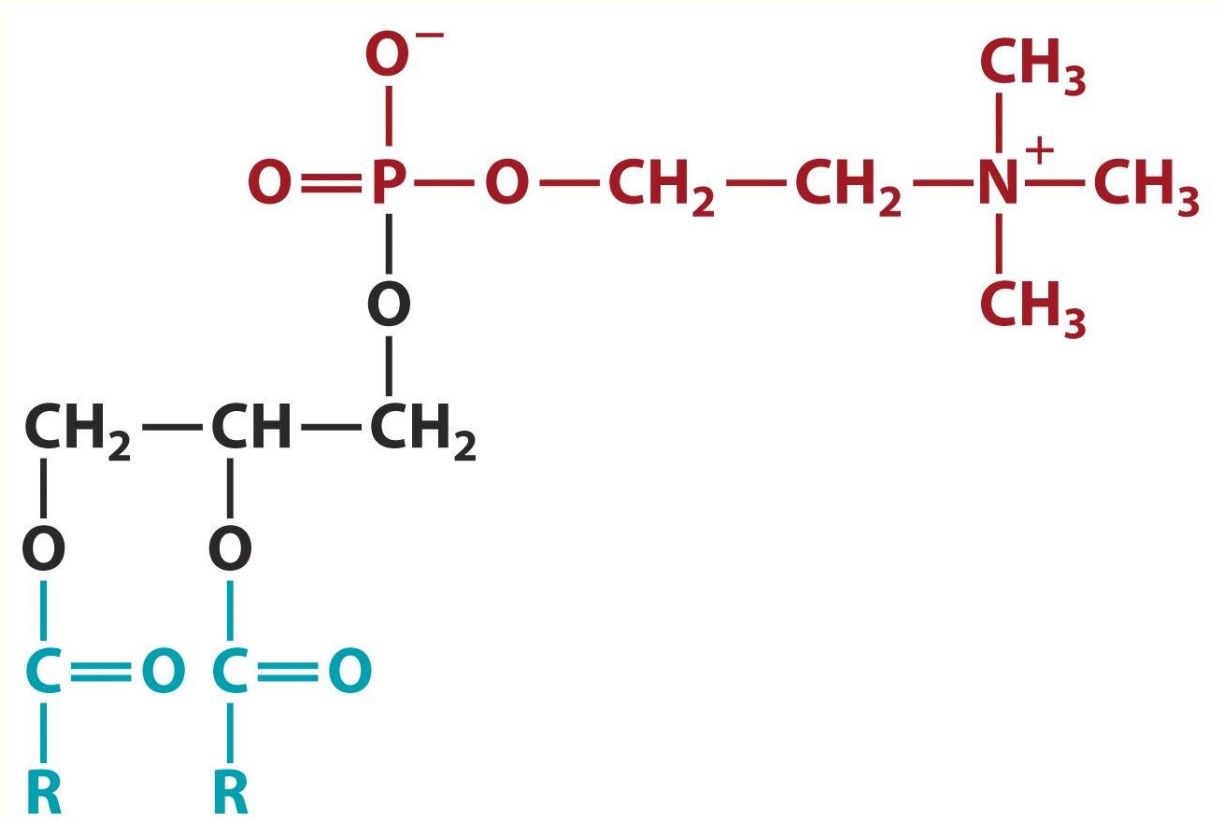
- Hydrophilic on one end; hydrophobic on the other
- Make up the phospholipid bilayer in the cell membrane
  - Lecithin (a.k.a. phosphatidylcholine)
    - A major phospholipid in the cell membrane
    - Used as an emulsifier in foods
- Synthesized by the liver



Complex Lipids

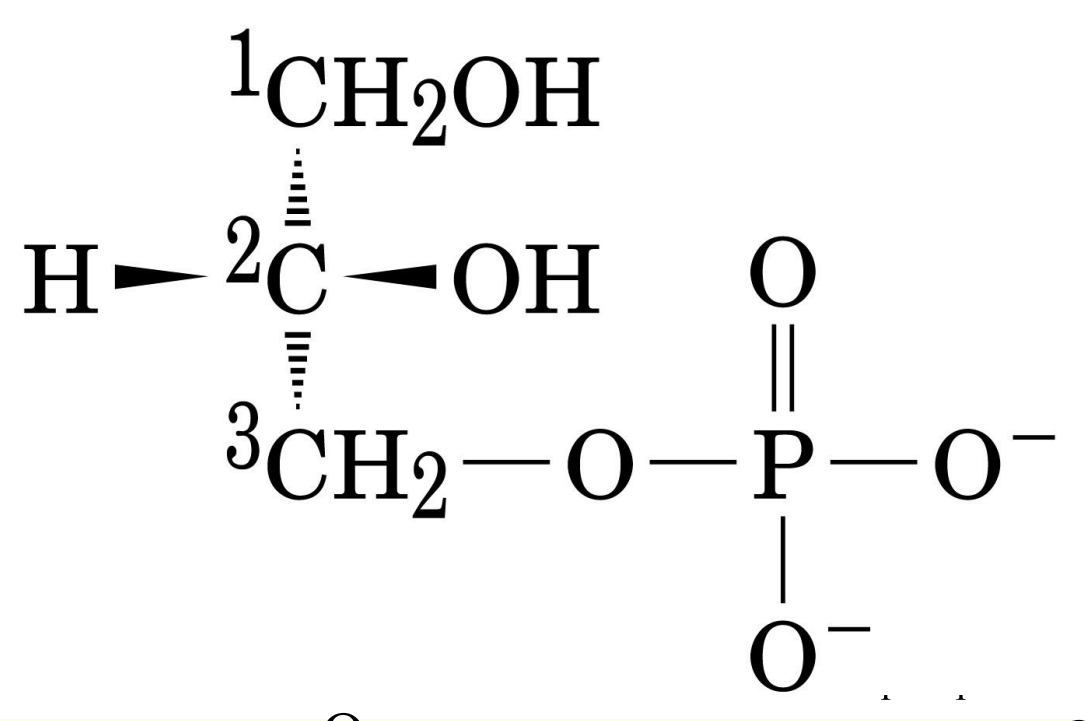
* **Phospholipids:** They are esters of phosphoric acids.There are two main types of phospholipids in cellular membranes:

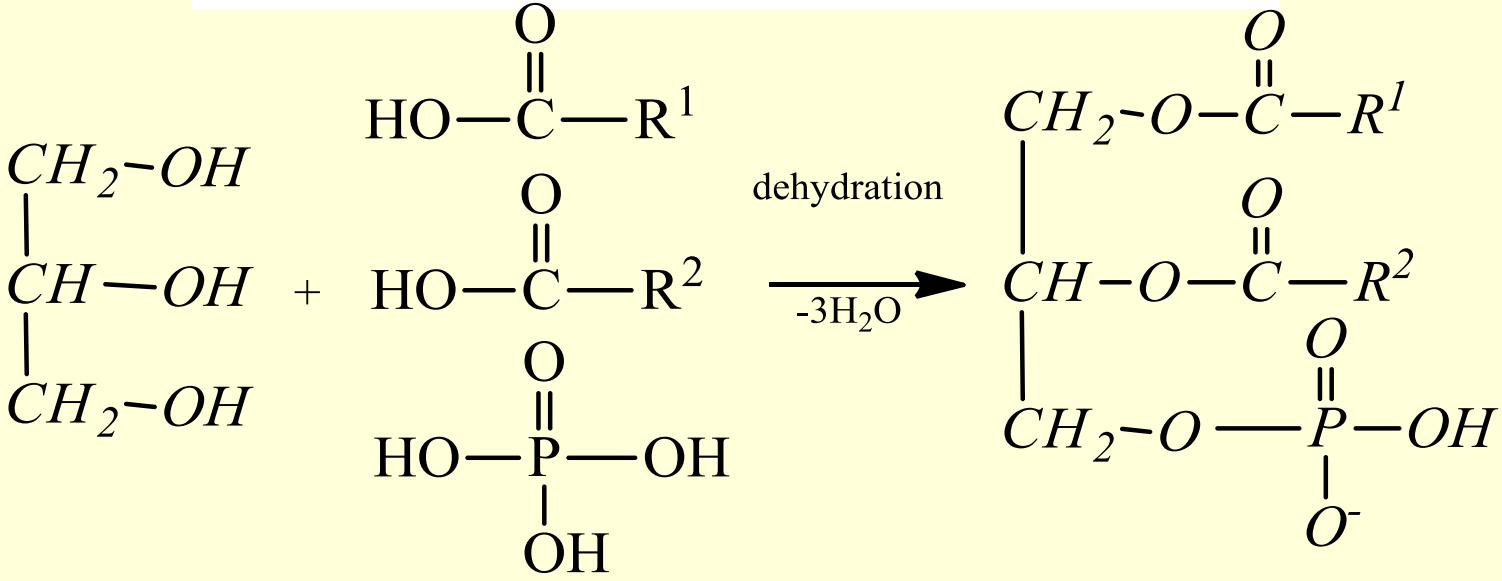
  Phosphoglycerides: They are also known as Phosphaitdyl choline (lecithin). They are built from long chain fatty acid, glycerol and phosphoric acids.



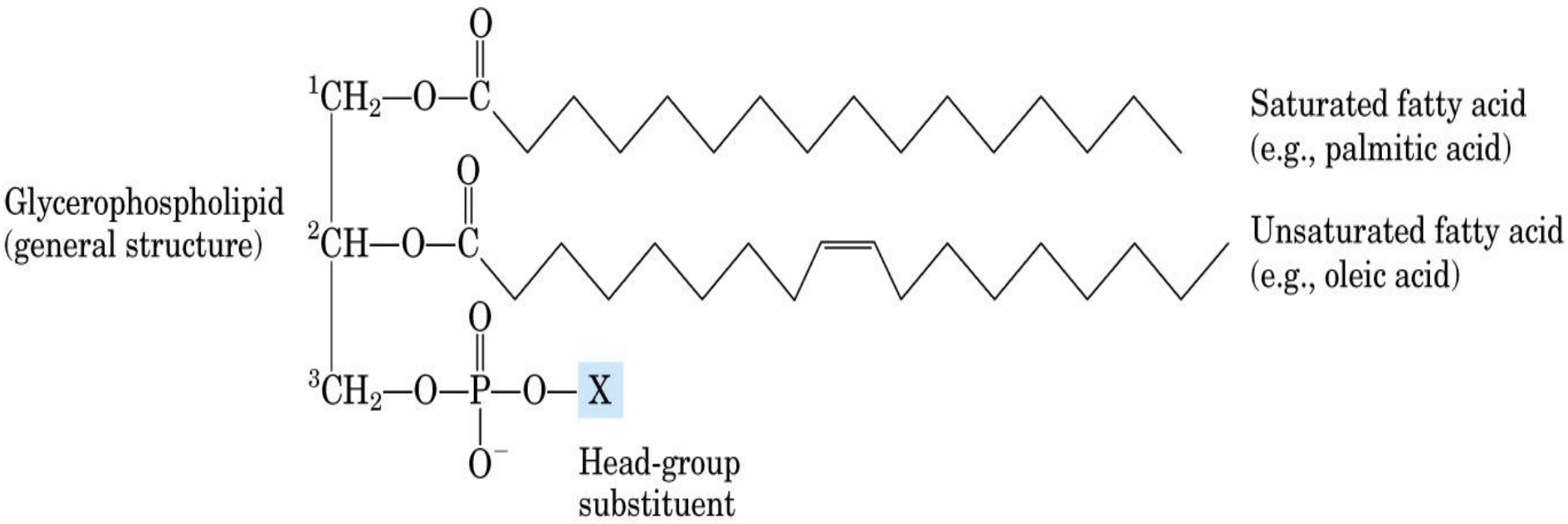
Phosphatidylcholine

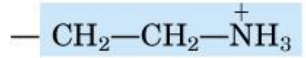
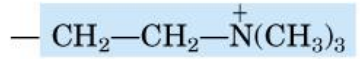
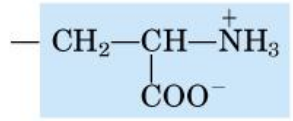
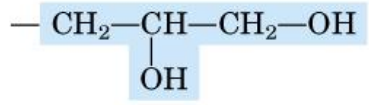
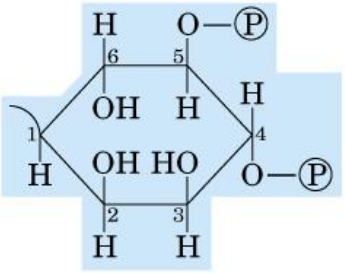
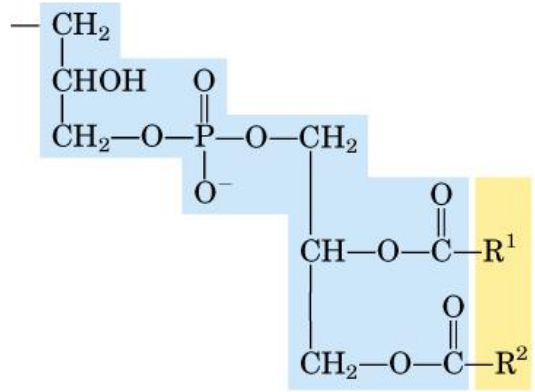
3-phosphoglycerol (building block for phosphoglycerides)

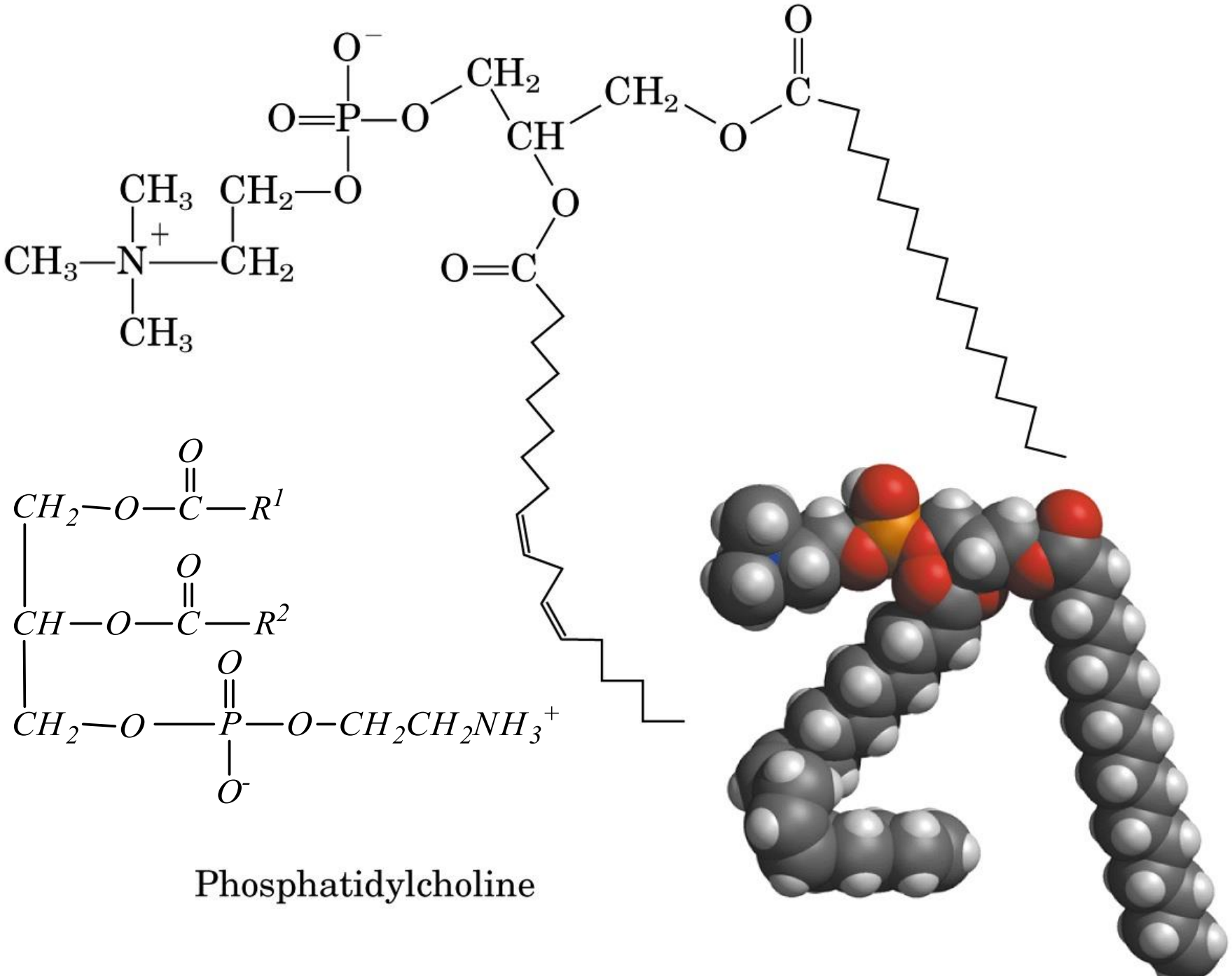




General structure of a glycerophospholipid. Note the glycerol-3-phosphate backbone



Name of glycerophospholipid	Name of X	Formula of X	Net charge (at pH 7)
Phosphatidic acid	—		−1
Phosphatidylethanolamine	Ethanolamine		0
Phosphatidylcholine	Choline		0
Phosphatidylserine	Serine		−1
Phosphatidylglycerol	Glycerol		−1
Phosphatidylinositol 4,5-bisphosphate	*myo*-Inositol 4,5-bisphosphate		−4
Cardiolipin	Phosphatidyl-glycerol		−2



Phosphatidylcholine

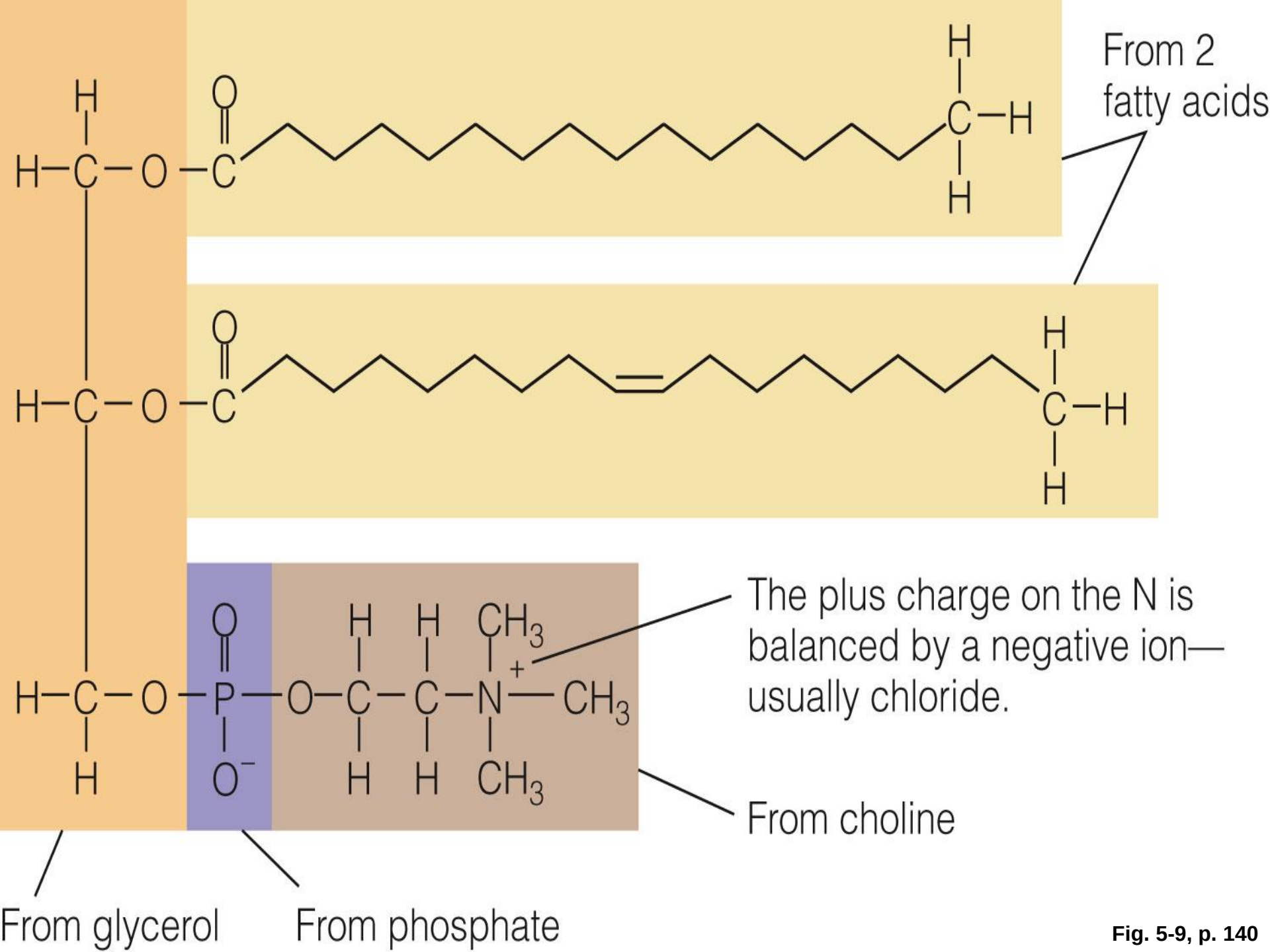
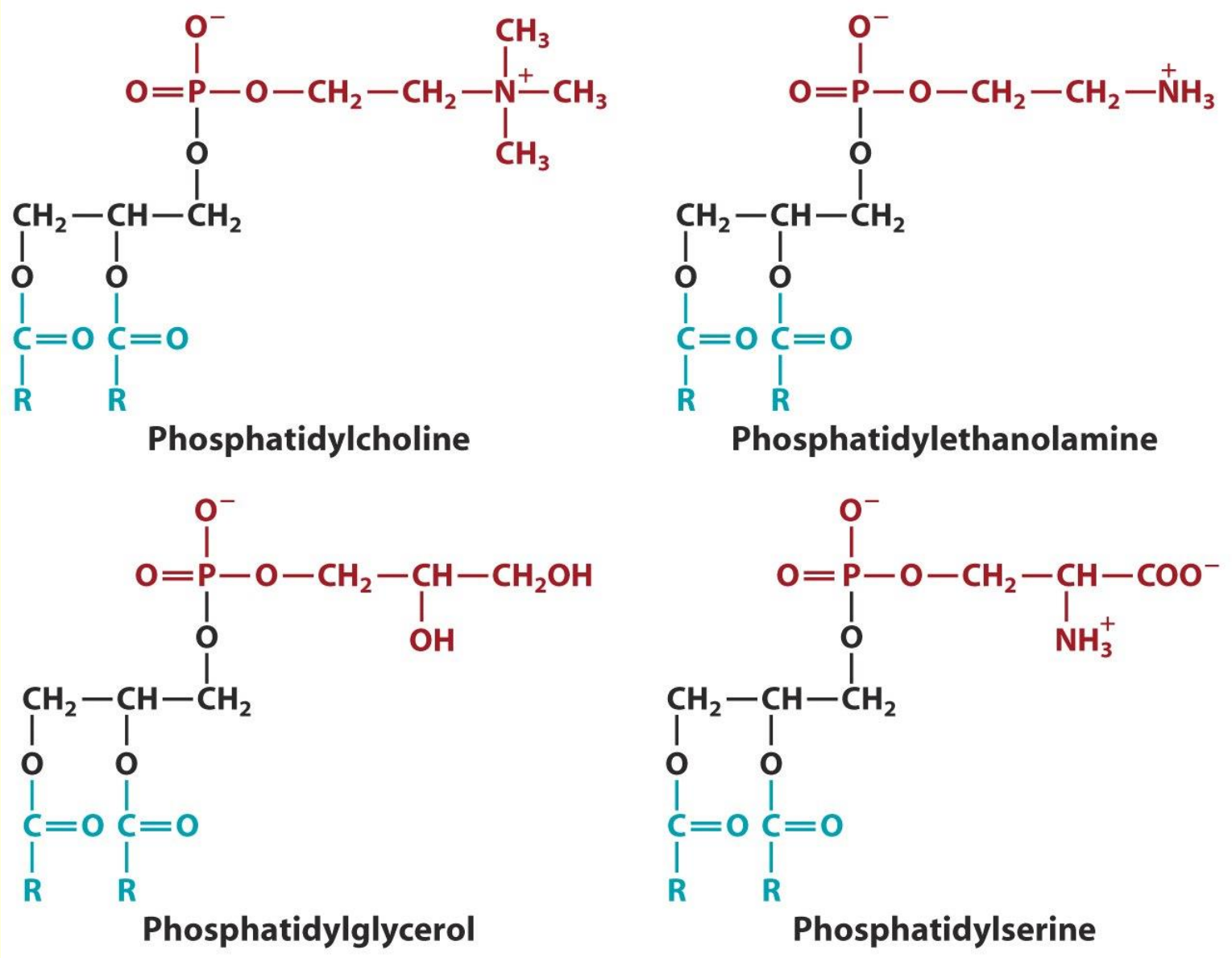
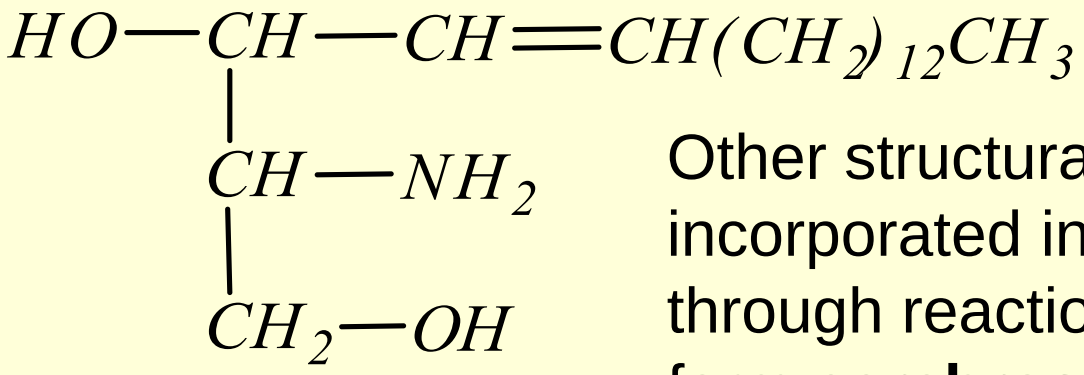

From 2 fatty acids
The plus charge on the N is balanced by a negative ion—usually chloride.
From choline
From glycerol
From phosphate

Fig. 5-9, p. 140

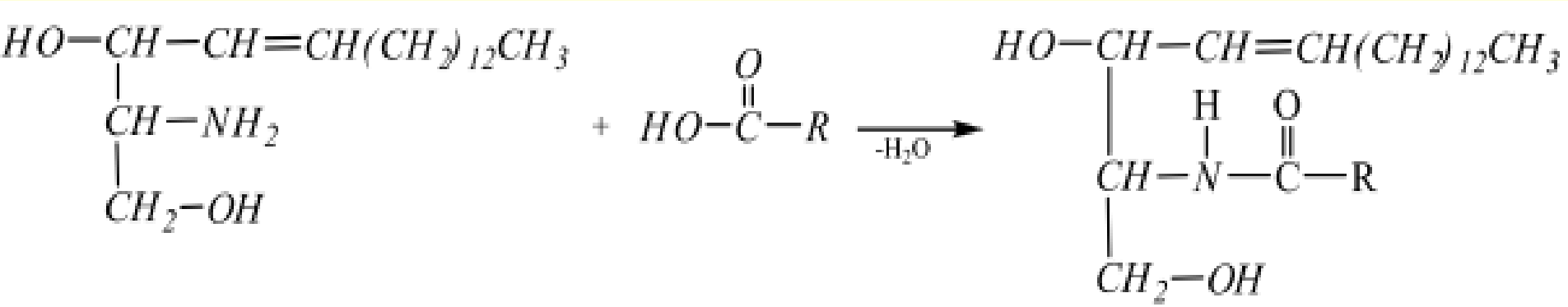
Glycerophospholipids

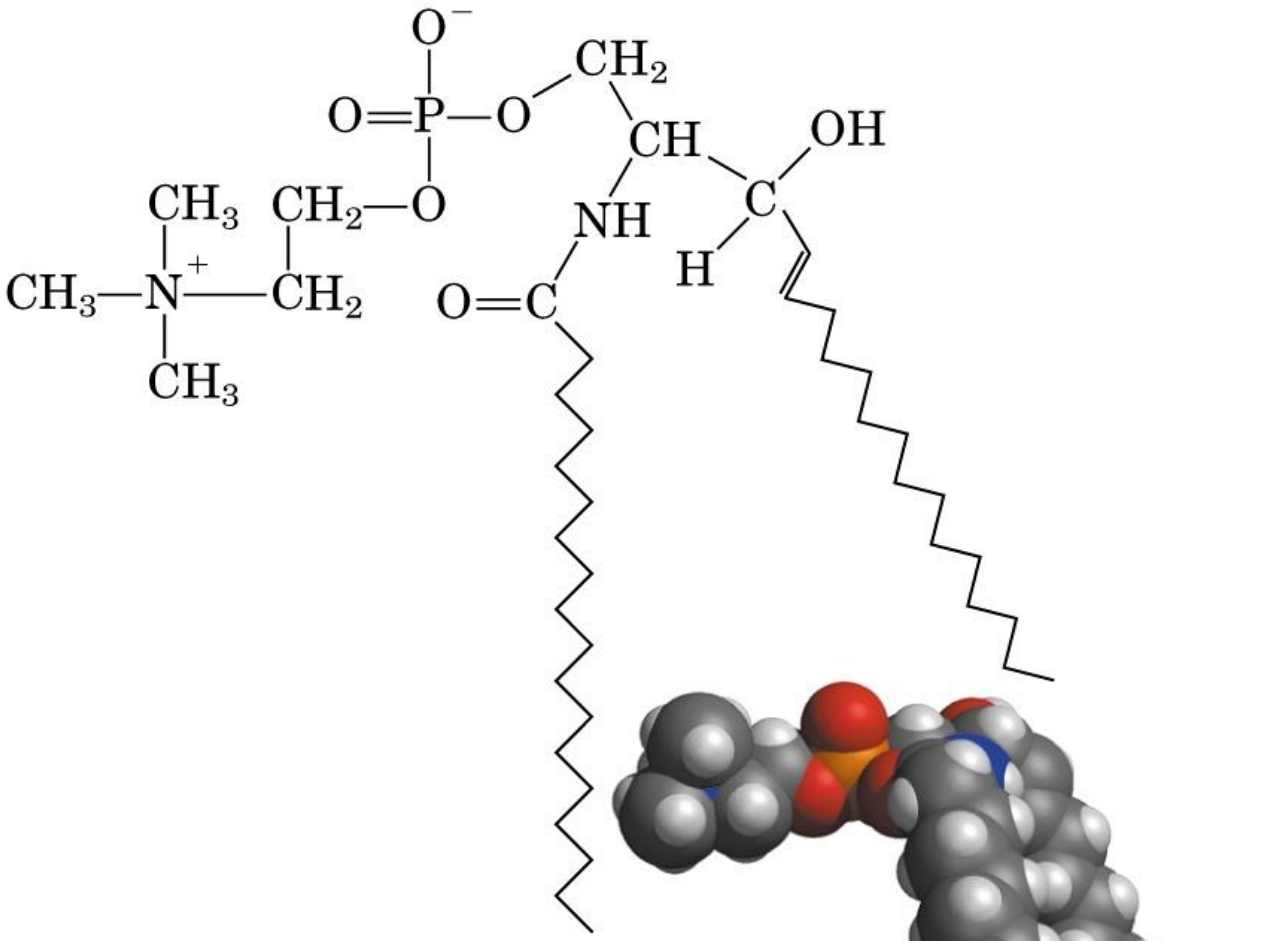


sphingomyelins: They do not contain glycerol. Instead, they contain sphingosine, a long-chain unsaturated amino alcohol. Only one fatty acid is attached to the sphingosine. Sphingomylins are found in brain and nervous tissue and in the myelin sheath, the protective coat of nerves.

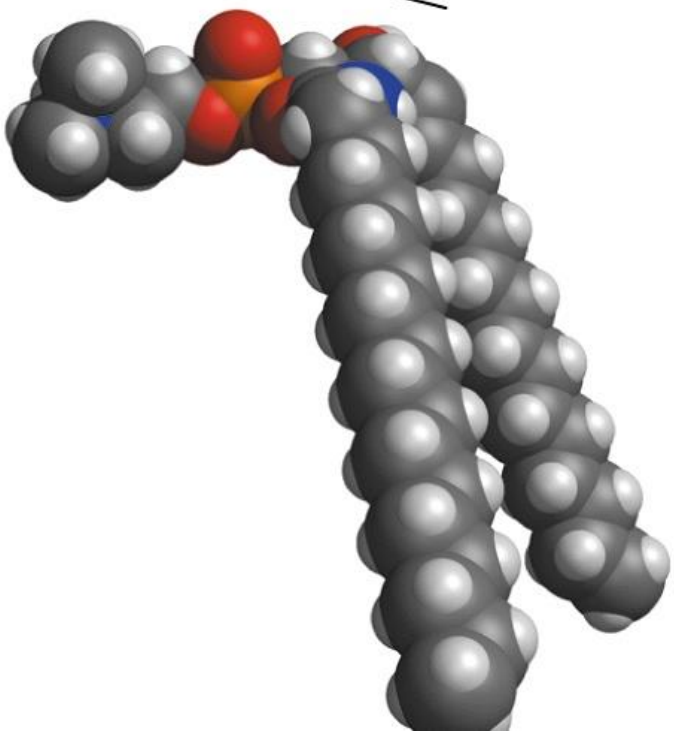


Other structural units are incorporated into sphingosine through reactions at the *OH* group to form **cerebrosides**.

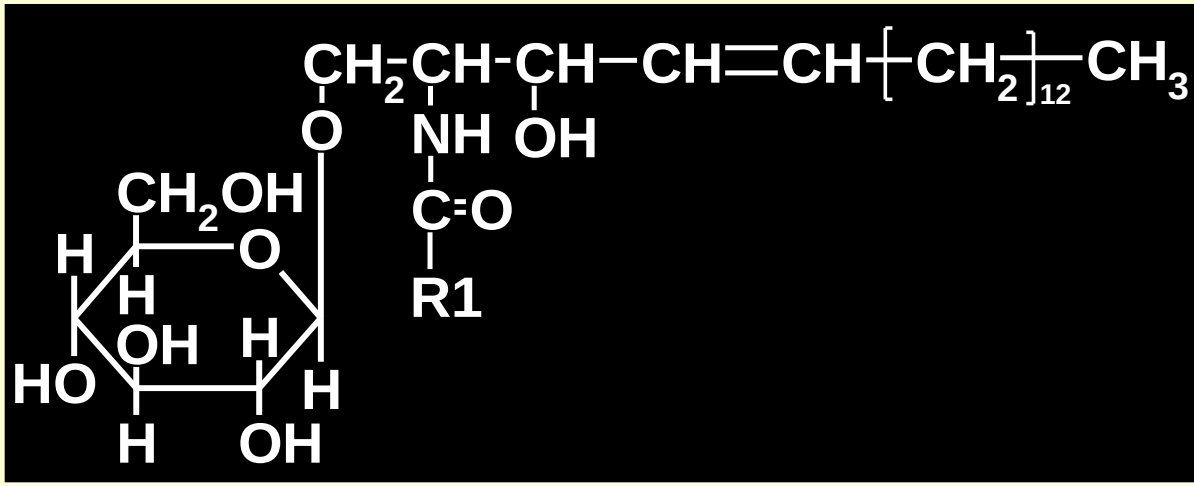




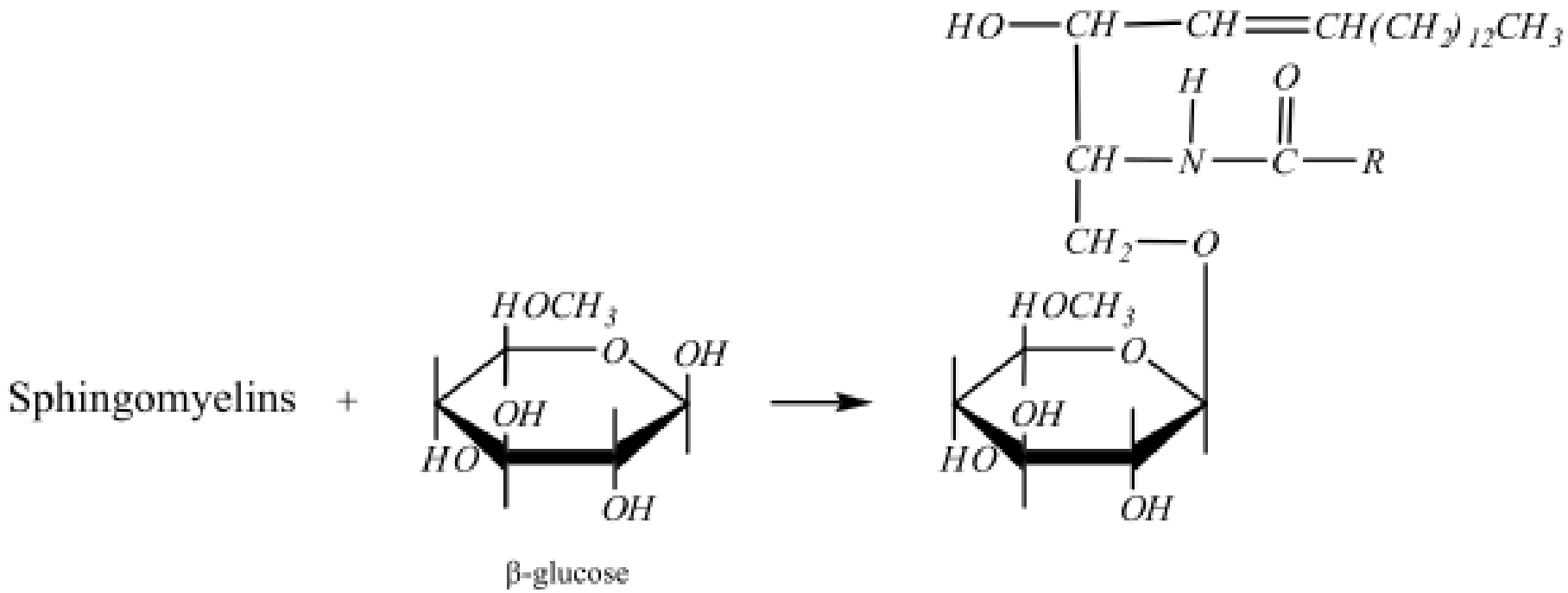
Sphingomyelin



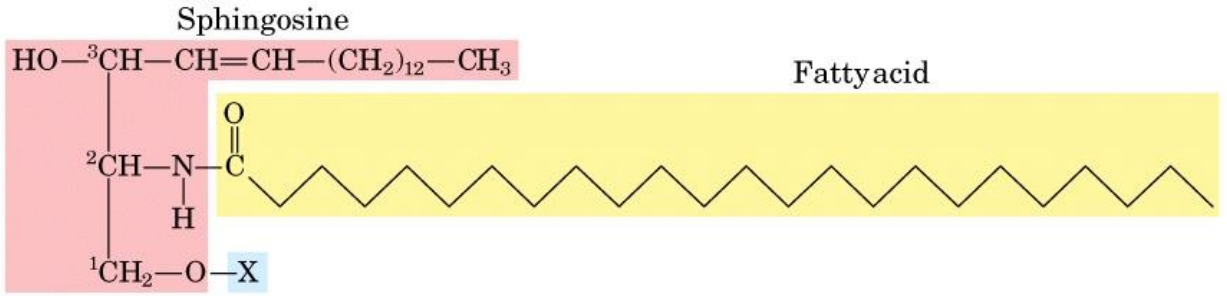
Cerebroside (Glycolipid)

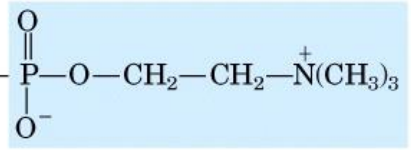
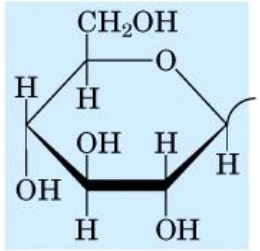
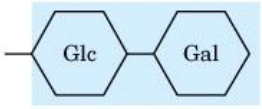
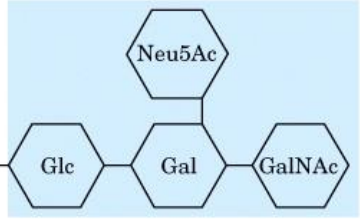


Cerebrosides, also referred to as **glycolipids**, contain a saccharide unit attaches by acetal formation at the *OH* of shingosine.



Sphingolipid (general structure)



Name of sphingolipid	Name of X	Formula of X
Ceramide	—	—H
Sphingomyelin	Phosphocholine	
Neutral glycolipids Glucosylcerebroside	Glucose	
Lactosylceramide (a globoside)	Di-, tri-, or tetrasaccharide	
Ganglioside GM2	Complex oligosaccharide	

Complex Lipids

Glycolipids: A lipid molecule that contains carbohydrates, which is usually a simple sugar like glucose or galactose

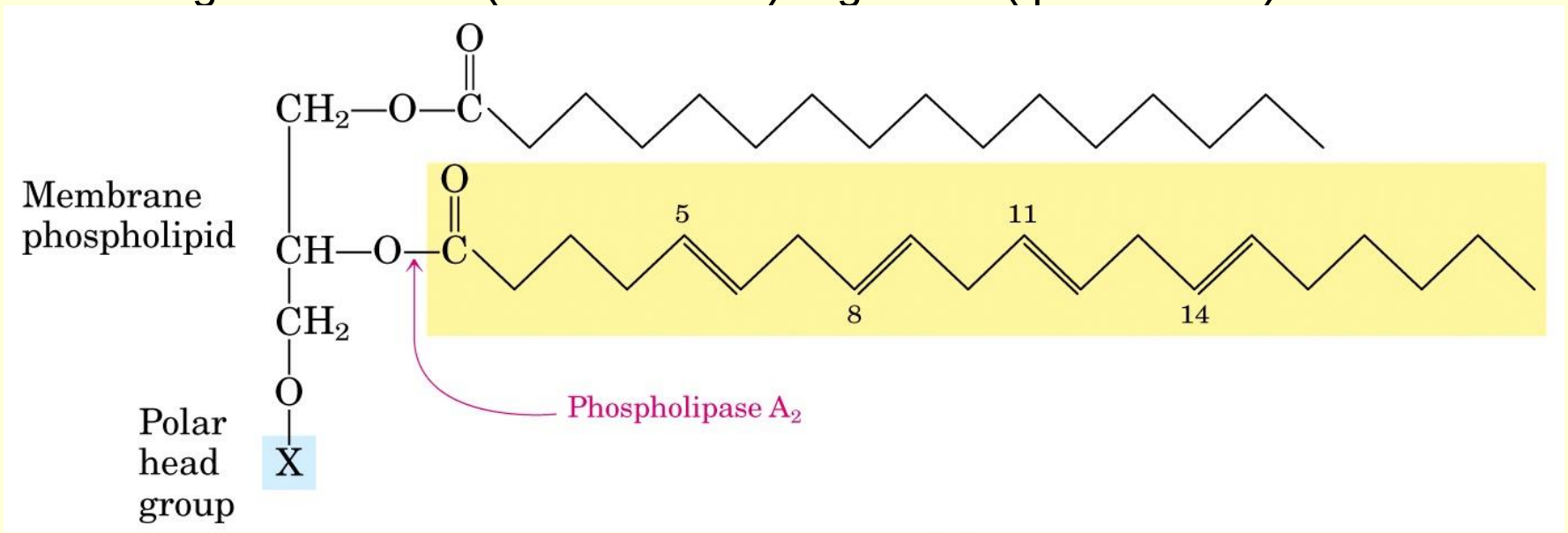
They are also called **cerebrosides** because of their abundance in brain.

Membrane lipids

Phospholipids: naturally aggregate in form of bilayers (which fuse to form spherical liposomes)

- glycerophospholipids
- sphingophospholipids

Sterols: e.g. cholesterol (animal sterol) ergosterol(plant sterol).

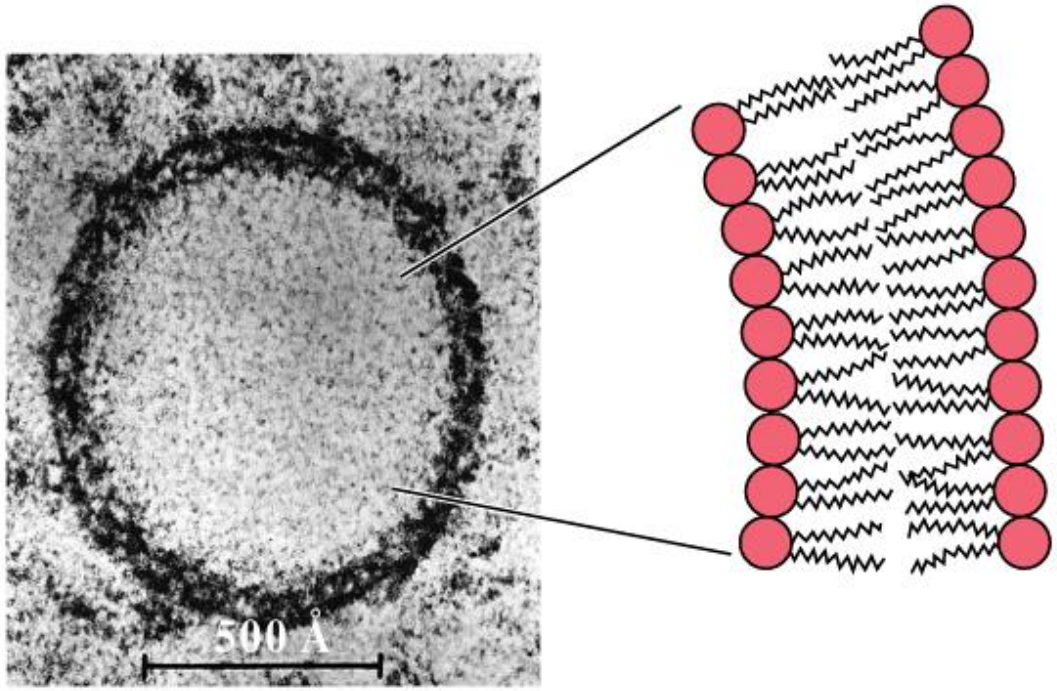


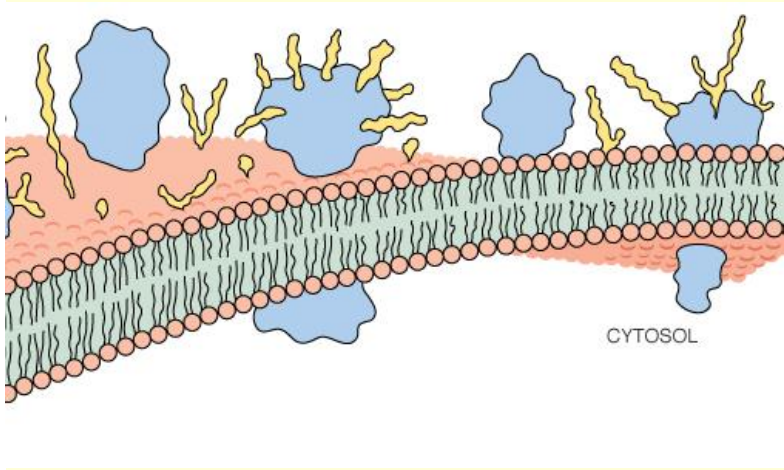
Lipid bilayers

The fundamental component of a biological membrane is **lipid bilayer**.

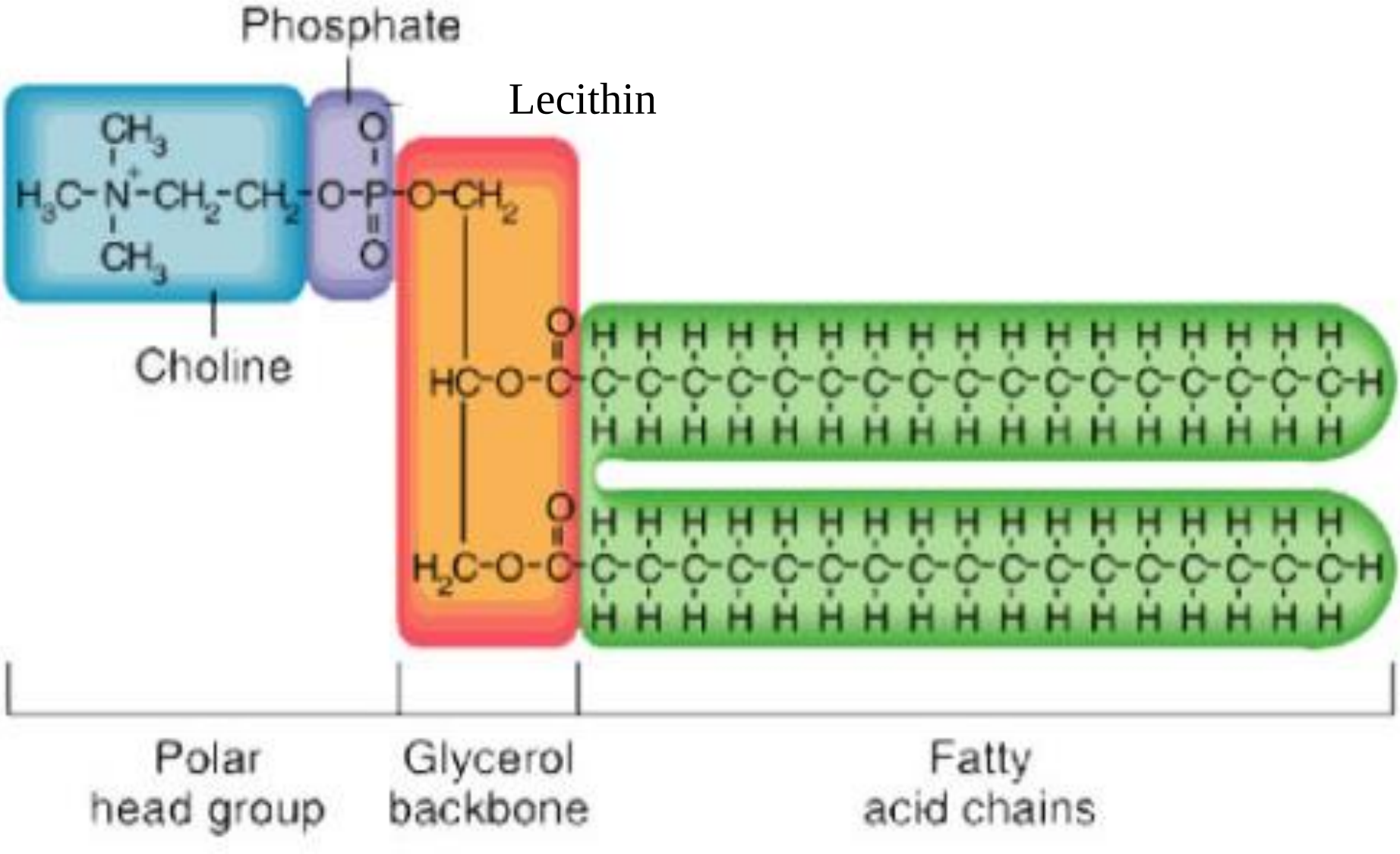
In a vigorously shaked mixture of phosphatidyl choline and water, the lipid molecules form microscopic sphere.

These lipid sphere or **liposome** are packages of solvent surrounded by a lipid bilayer- *a two layer thick wall of phosphatidyl choline*

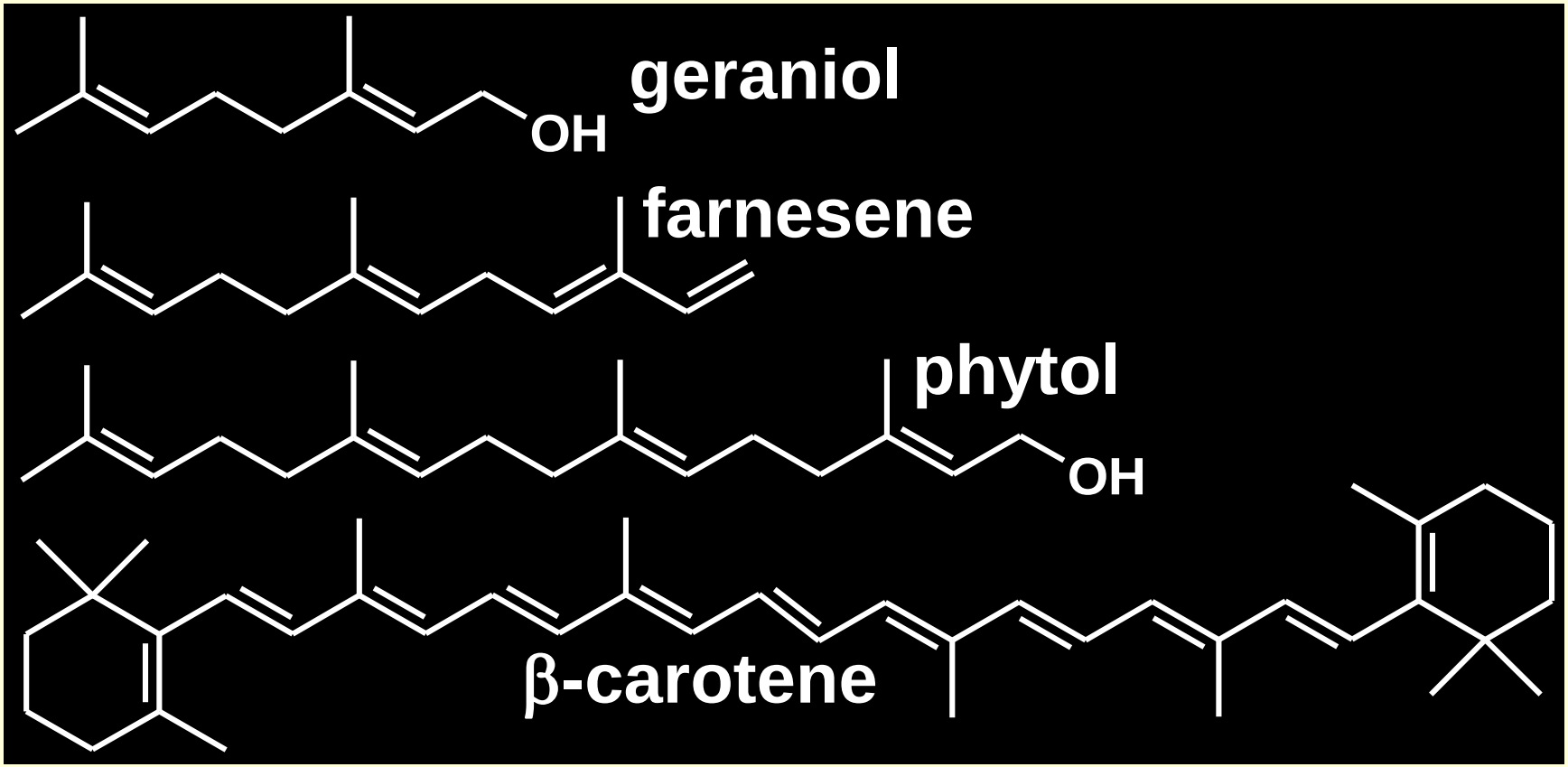




Lecithin

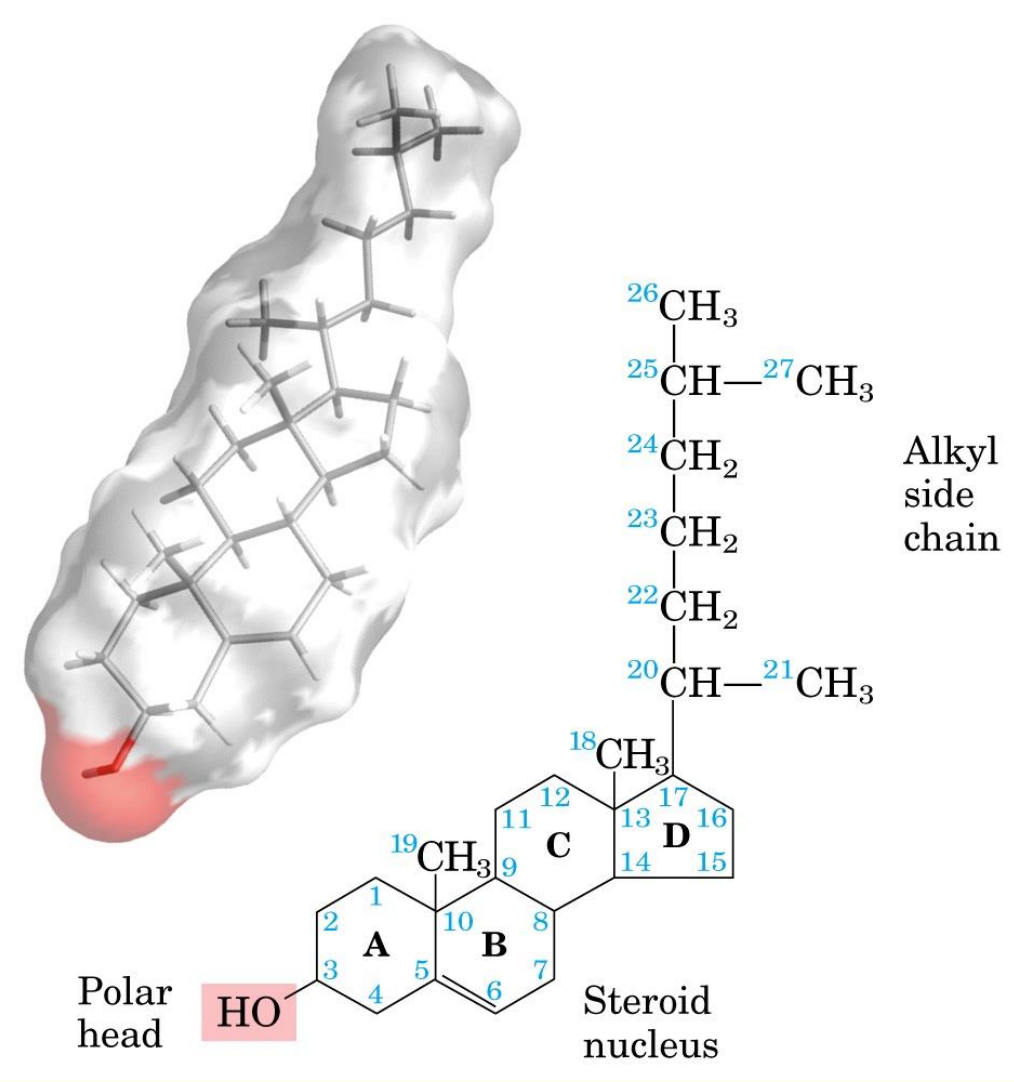

Phosphate
Choline
Polar
head group
Glycerol
backbone
Fatty
acid chains

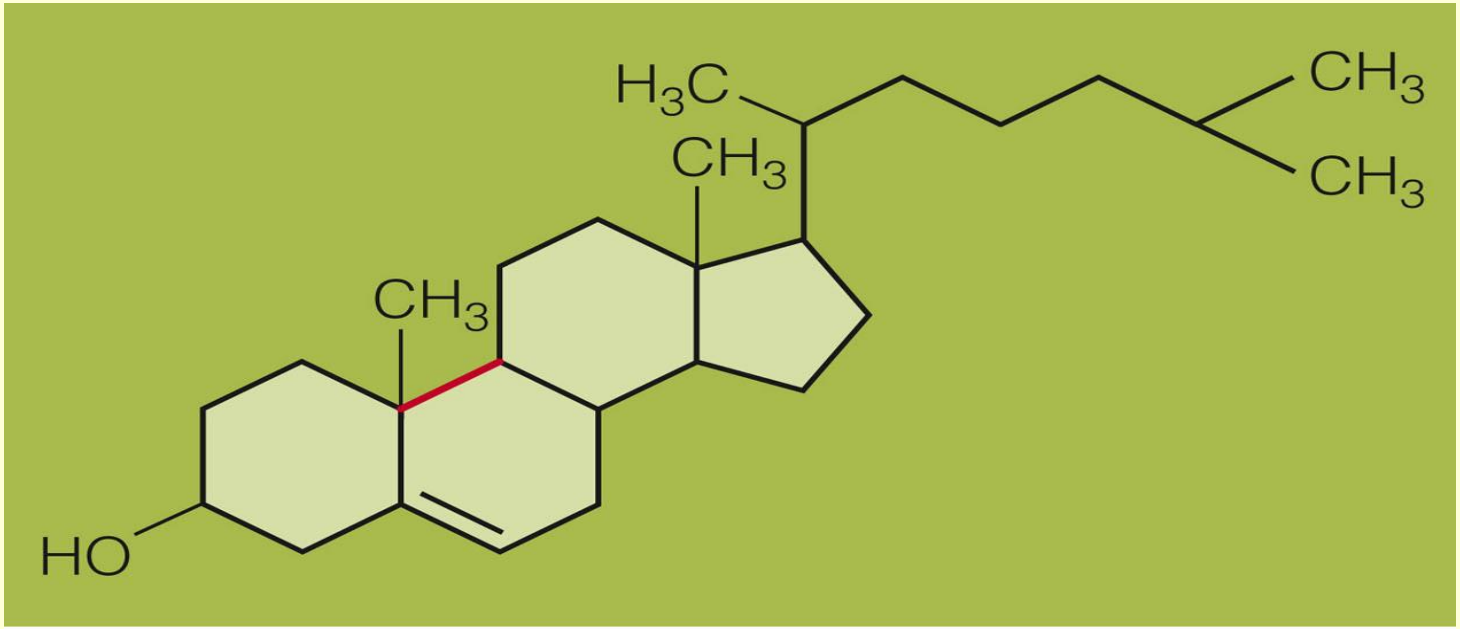
Terpenes



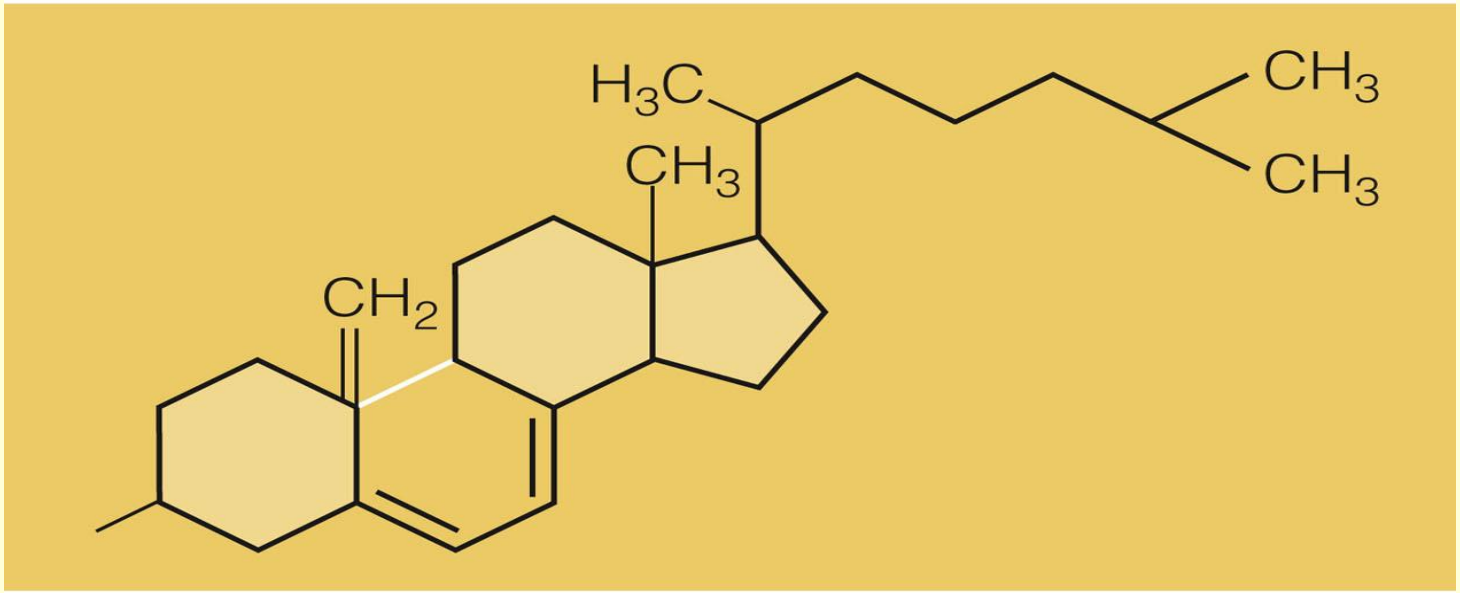
Steroids

- Steroids are a family of lipids found in plants and animal
  - A steroid contains four fused carbon ring: 17 carbon atoms make the structural unit of steroids known as steroid nucleus.
  - Steroid nucleus is found in a number of extremely important biological molecules: cholesterol, adrenocorticoid hormones, the sex hormone and bile acids.

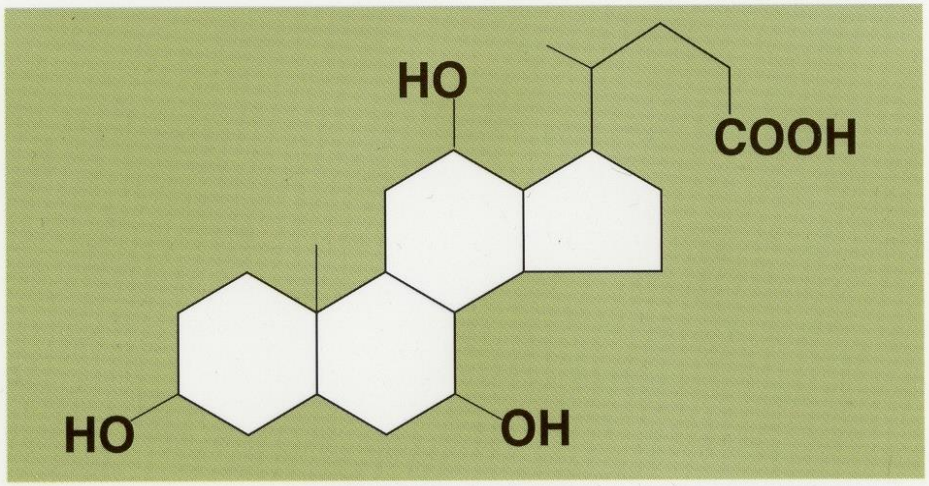




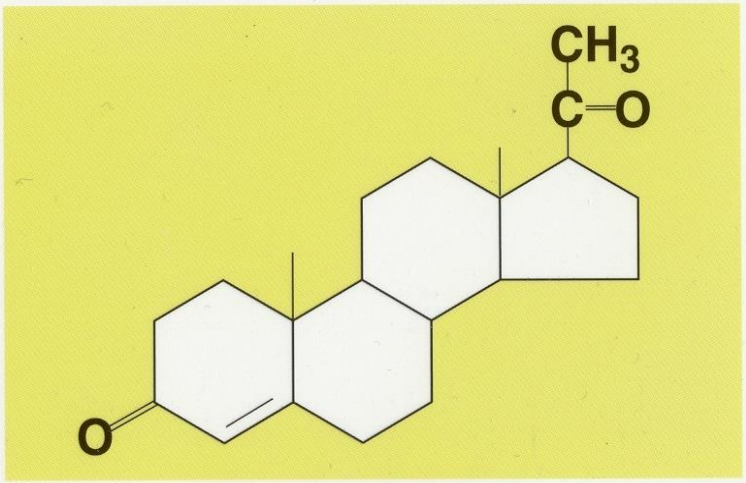
Cholesterol



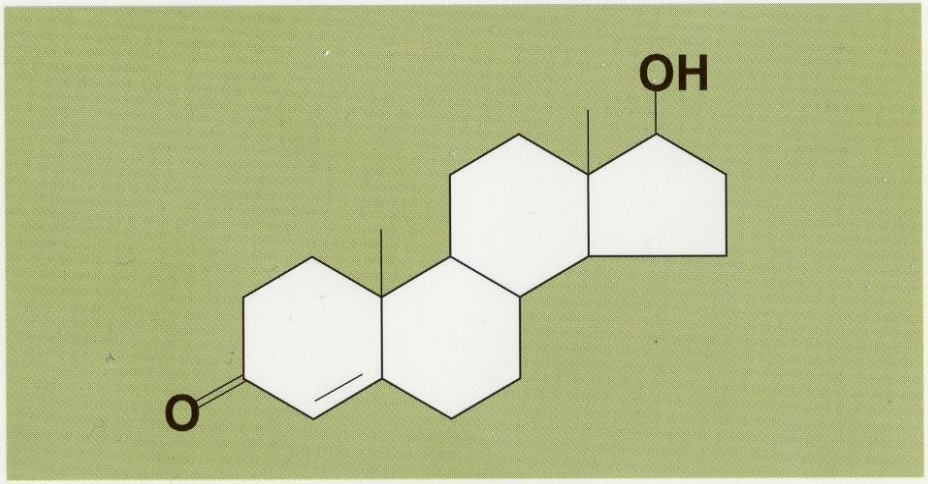
Vitamin D_3



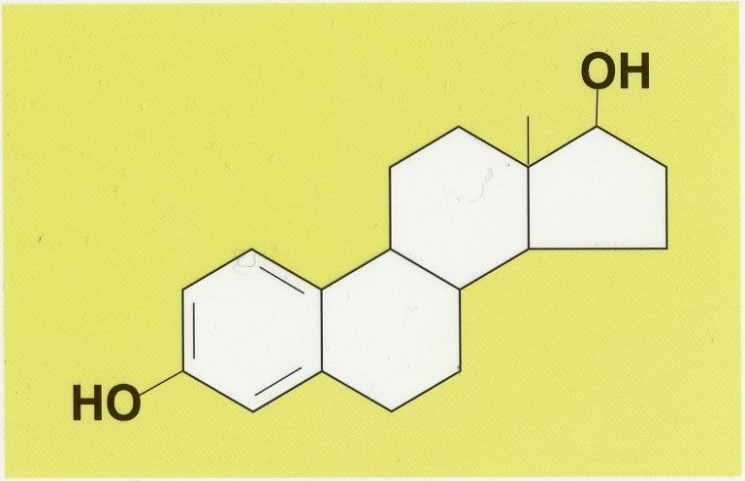
Cholic Acid



Progesterone



Testosterone

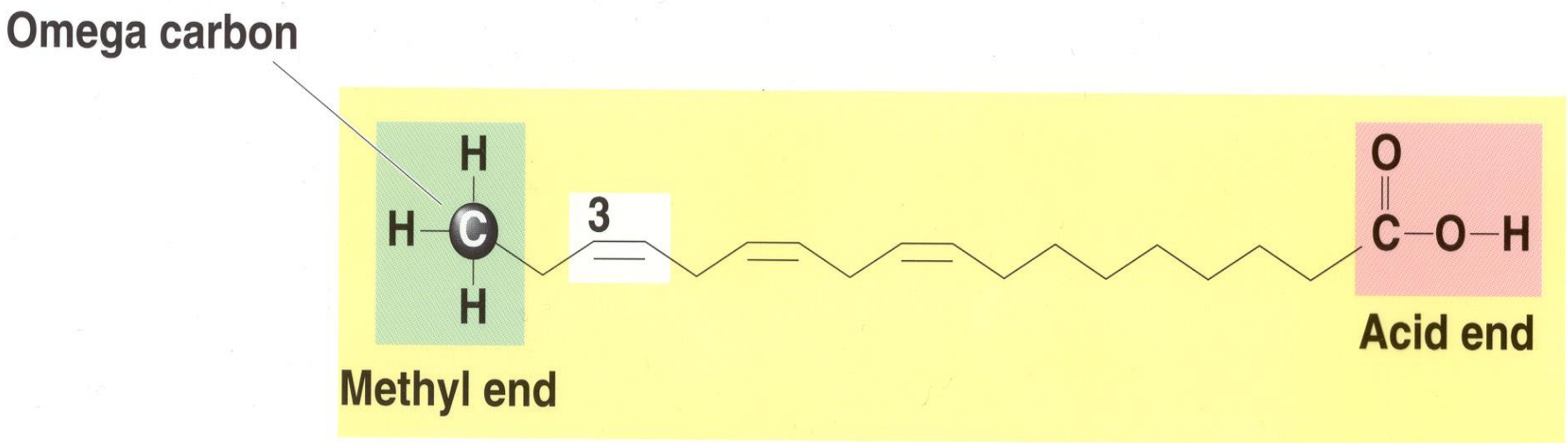


Estradiol

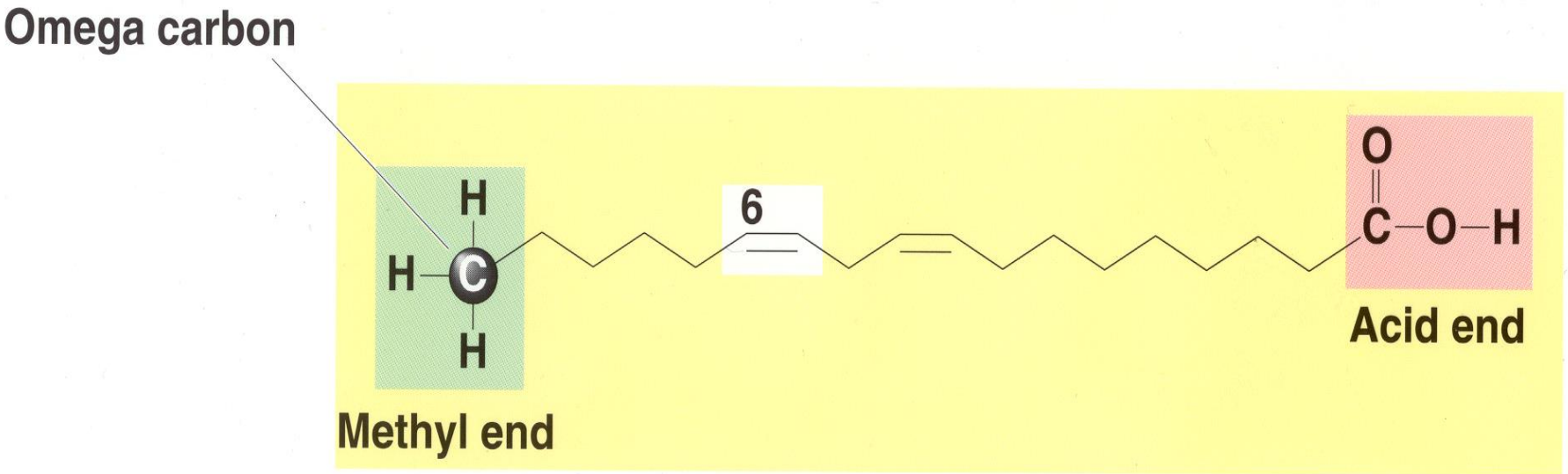
Enrichment Cholic Acid and the Sex Hormones

Good sources of 'omega-6 fatty acids'

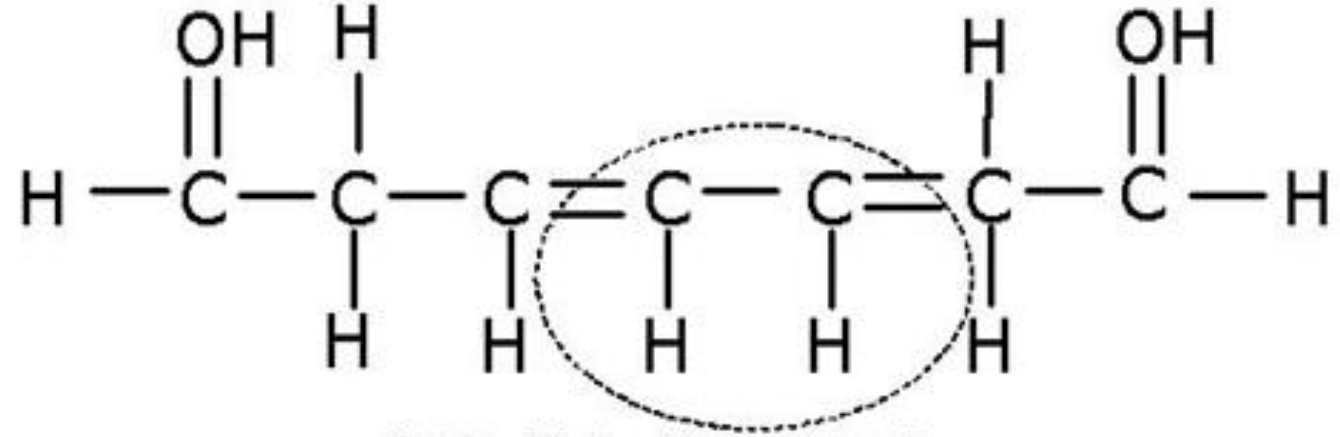
- Most vegetable oil, Sunflower oil, Corn oil, Soybean oil
- Cotton seeds oil
- Pumpkin seeds
- Nuts and cereals
- Poultry, eggs
- Avocado



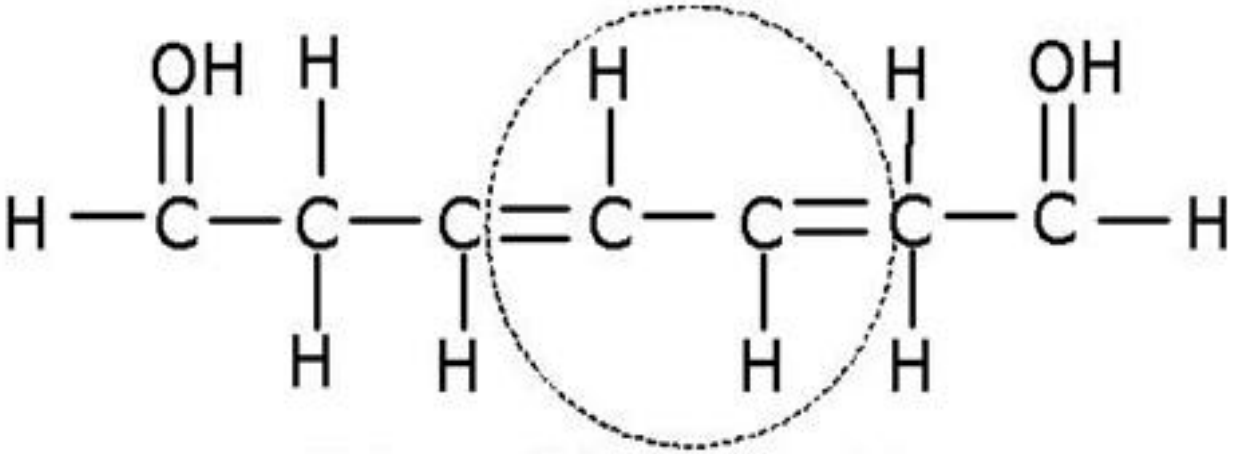
Linolenic acid, an omega-3 fatty acid



Linoleic acid, an omega-6 fatty acid



"Cis" fatty acid



"Trans" fatty acid

Major Food Sources of *Trans* Fat for American Adults