Lipids: classification, structure and biological role.

By: Dr. Debalina Basu

LIPIDS

Lipids are a class of biological molecules defined by low solubility in water and high solubility in nonpolar solvents.

As molecules that are largely hydrocarbon in nature, lipids represent highly reduced forms of carbon and, upon oxidation in metabolism, yield large amounts of energy. Lipids are thus the molecules of choice for metabolic energy torage.

Classification

By structure:

1. Simple: fats, oils, waxes, steroids.
2. Complex: phospholipids, spingolipids, glygolipids.
3. They derivatives: hormones, fat-solubility vitamins

On the basis of whether they undergo hydrolysis reactions in alkaline solution:

1. Saponifiable **lipids** can be hydrolyzed under alkaline conditions to yield salts of fatty acids.
2. Nonsaponifiable **lipids** do not undergo hydrolysis reactions in alkaline solution.

Biological functions

- The most important role of lipids is as a fuel. Thus fat is the most concentrated form in which potential energy can be stored.
- Since fat is a bad conductor of heat, it provides excellent insulation.
- Fat may also provide padding to protect the internal organs.
- Some compounds derived from lipids are important building blocks of biologically active materials.
- Lipoproteins are constituents of cell walls.
- One more important function of dietary lipids is that of supplying the so-called essential fatty acids

Fatty acids

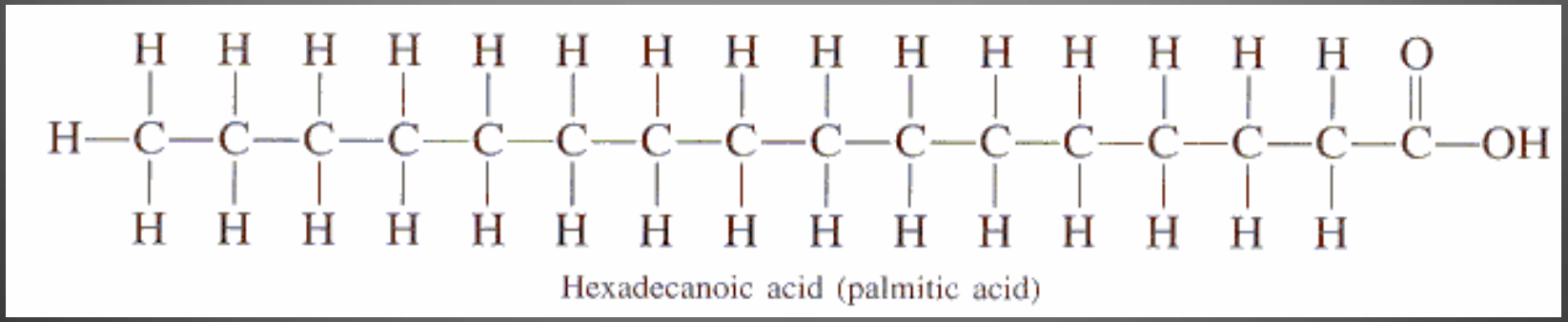
– are saponifiable lipid building blocks.

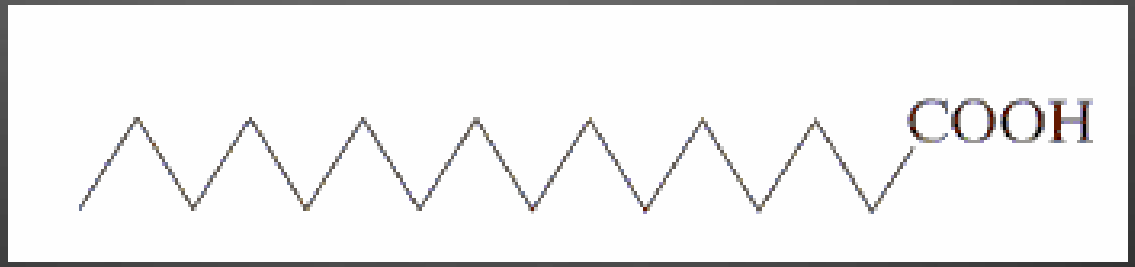
Fatty acids are naturally occurring carboxylic acids with an unbranched carbon chain and an even number of carbon atoms. The pathway by which fatty acids are biosynthesized they almost always contain an even number of carbon atoms. Long-chain fatty acids (12 to 26 carbon atoms) are found in meats and fish; medium-chain fatty acids (6 to 10 carbon atoms) and short-chain fatty acids (fewer than 6 carbon atoms) occur primarily in dairy products.

There are saturated and unsaturated Fatty acids.

Saturated fatty acid

- Fatty acid chains that contain only carbon-carbon single bonds are referred to as **saturated.**
- Palmitic acid:

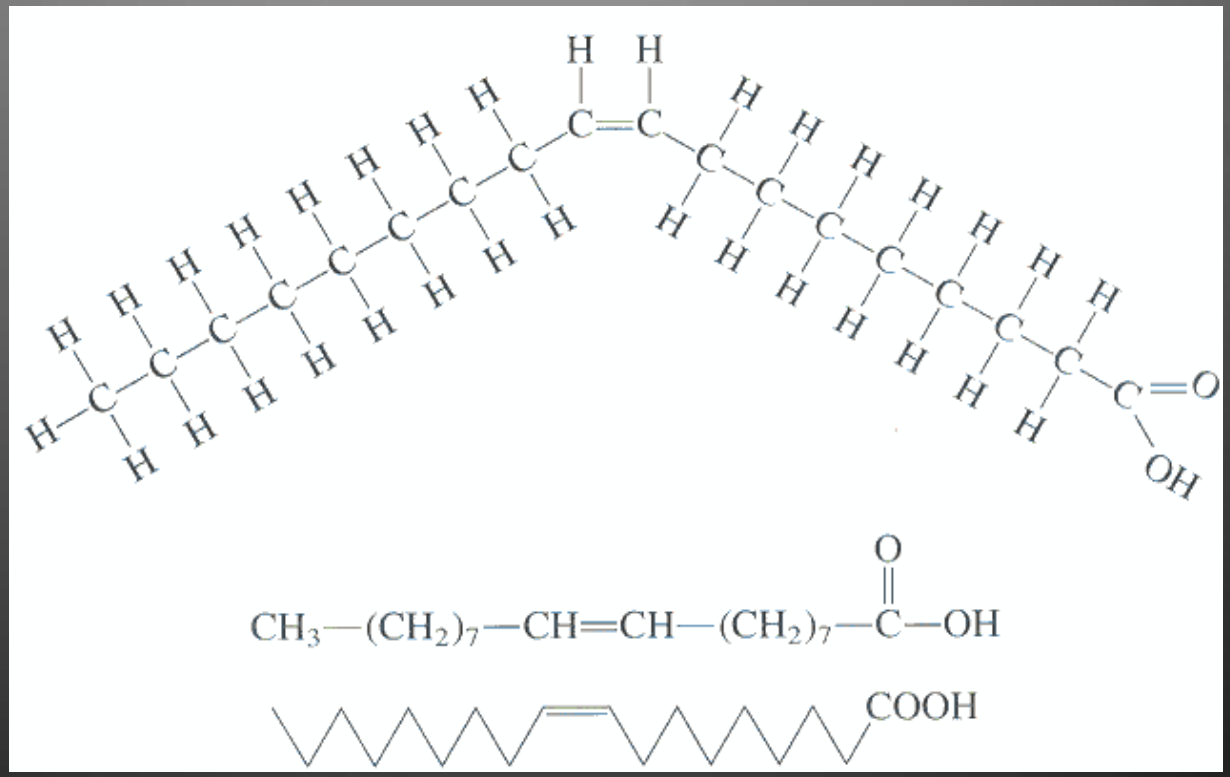




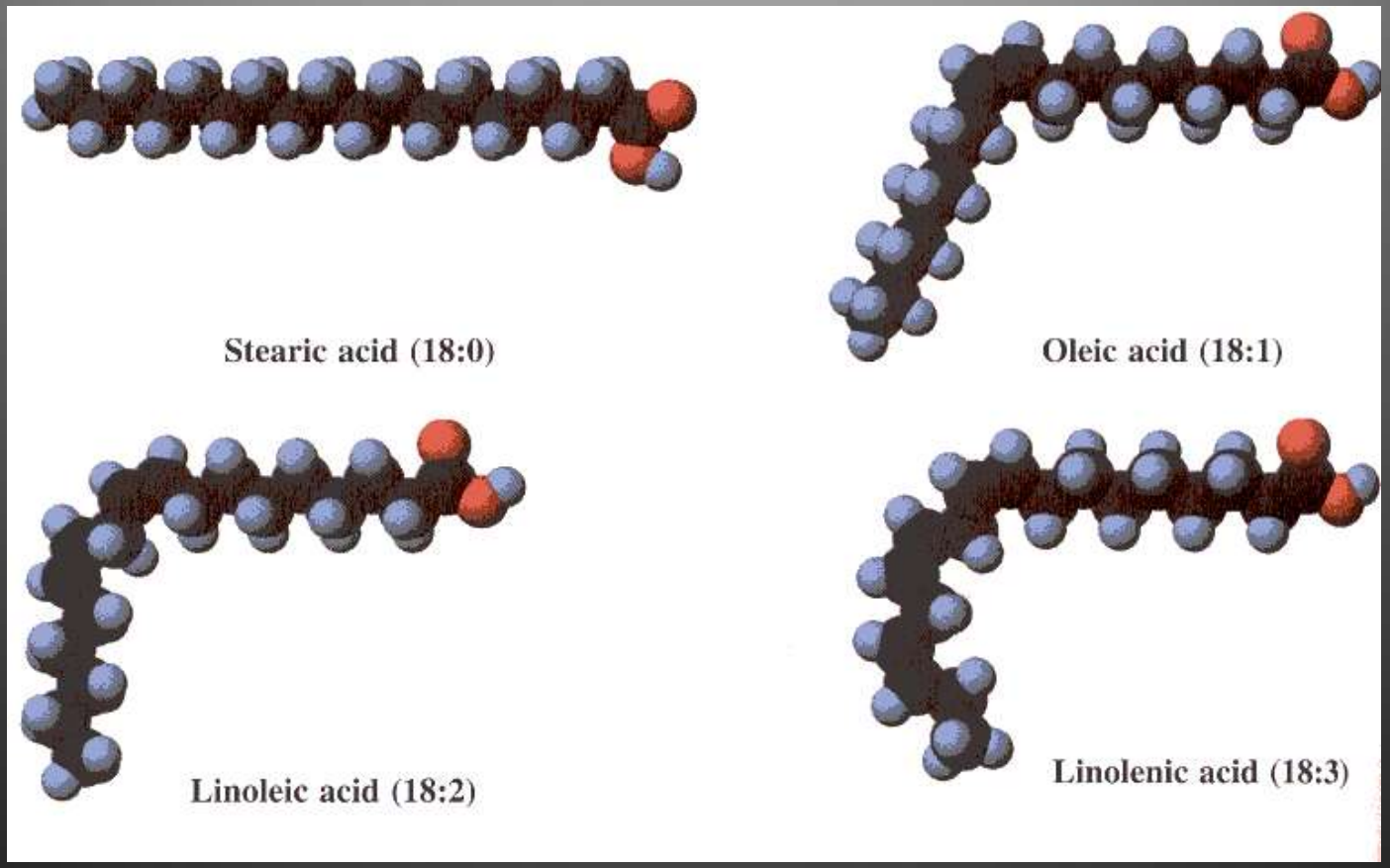
Unsaturated fatty acid

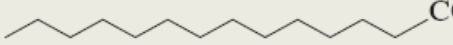
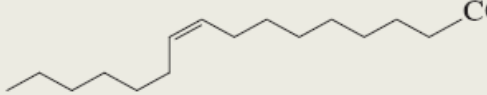
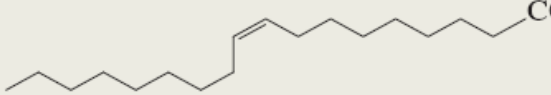
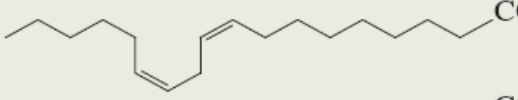
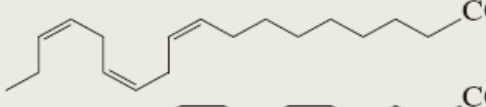
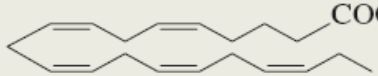
- Those molecules that contain one or more double bonds are said to be **unsaturated.**
- There are mono- and polyunsaturated fatty acids.

Oleic acid:

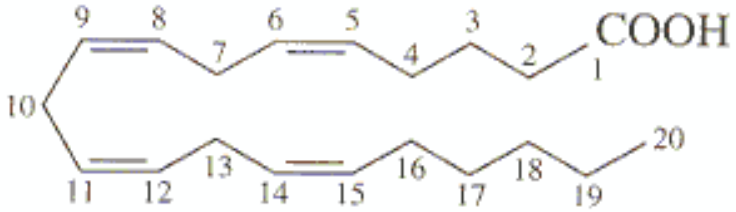


Structure of fatty acids

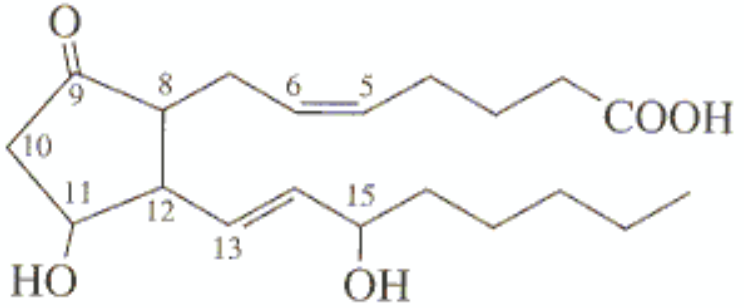


Number of carbons	Common name	Systematic name	Structure	Melting point °C
Saturated				
12	lauric acid	dodecanoic acid		44
14	myristic acid	tetradecanoic acid		58
16	palmitic acid	hexadecanoic acid		63
18	stearic acid	octadecanoic acid		69
20	arachidic acid	eicosanoic acid		77
Unsaturated				
16	palmitoleic acid	(9*Z*)-hexadecenoic acid		0
18	oleic acid	(9*Z*)-octadecenoic acid		13
18	linoleic acid	(9*Z*,12*Z*)-octadecadienoic acid		−5
18	linolenic acid	(9*Z*,12*Z*,15*Z*)-octadecatrienoic acid		−11
20	arachidonic acid	(5*Z*,8*Z*,11*Z*,14*Z*)-eicosatetraenoic acid		−50
20	EPA	(5*Z*,8*Z*,11*Z*,14*Z*,17*Z*)-eicosapentaenoic acid		−50

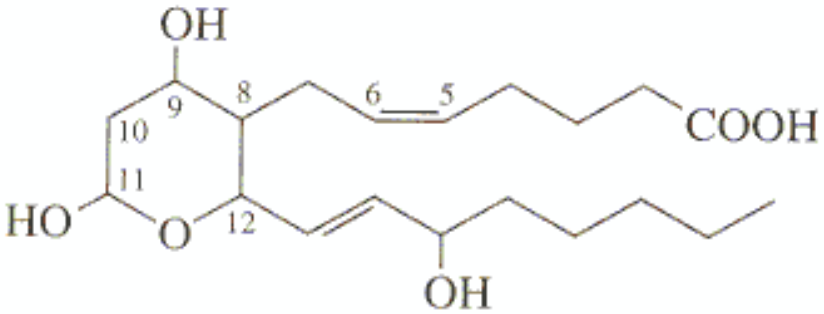
Prostaglandins are derivative of fatty polyunsaturated acids



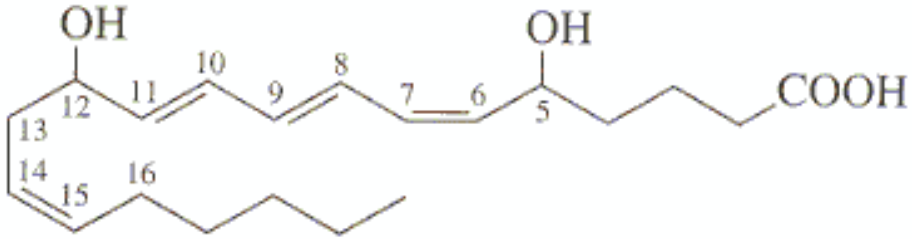
(a) Arachidonic acid



(b) Prostaglandin E_2



(c) Thromboxane B_2

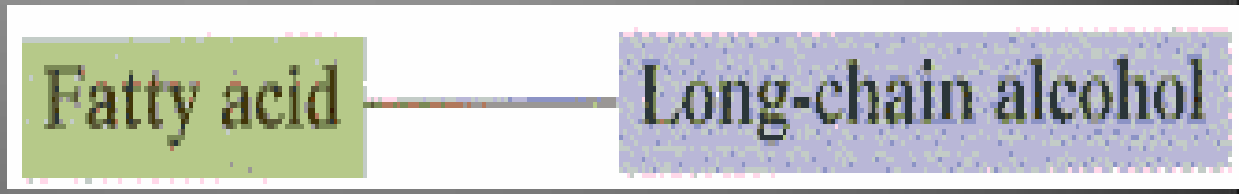


(d) Leukotriene B_4

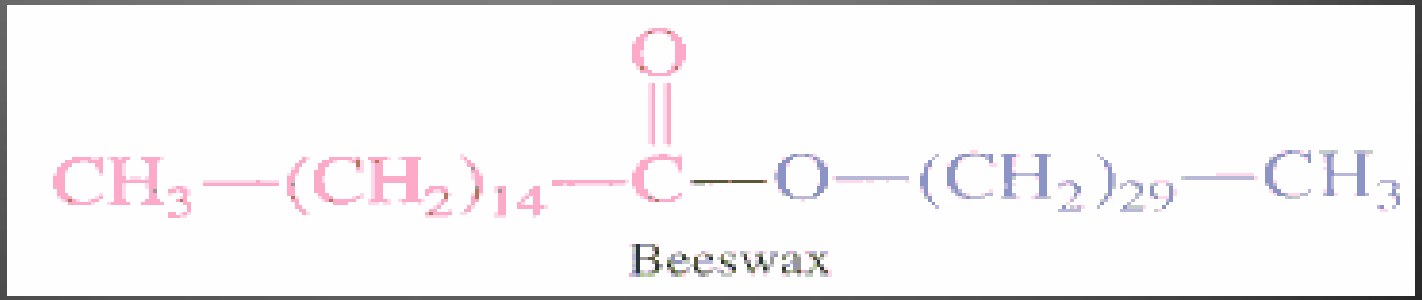
Waxes

A **wax** is a monoester formed from the reaction of a long-chain monohydroxy alcohol with a fatty acid molecule.

The block diagram:



Example



Biological role: They serve as protective coatings on leaves, stems, and fruit of plants and the skin and fur of animals.

Layers of honeycomb in a beehive

$CH_3(CH_2)_{24}\overset{\overset{O}{\|}}{C}O(CH_2)_{29}CH_3$

a major component of
beeswax
structural material
of beehives

$CH_3(CH_2)_{30}\overset{\overset{O}{\|}}{C}O(CH_2)_{33}CH_3$

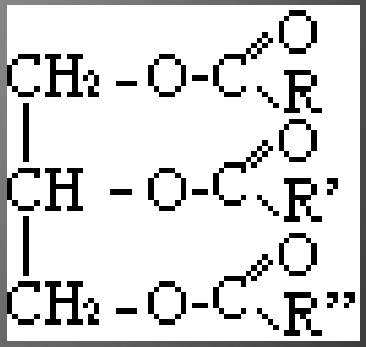
a major component of
carnauba wax
coating on the leaves
of a Brazilian palm

$CH_3(CH_2)_{14}\overset{\overset{O}{\|}}{C}O(CH_2)_{15}CH_3$

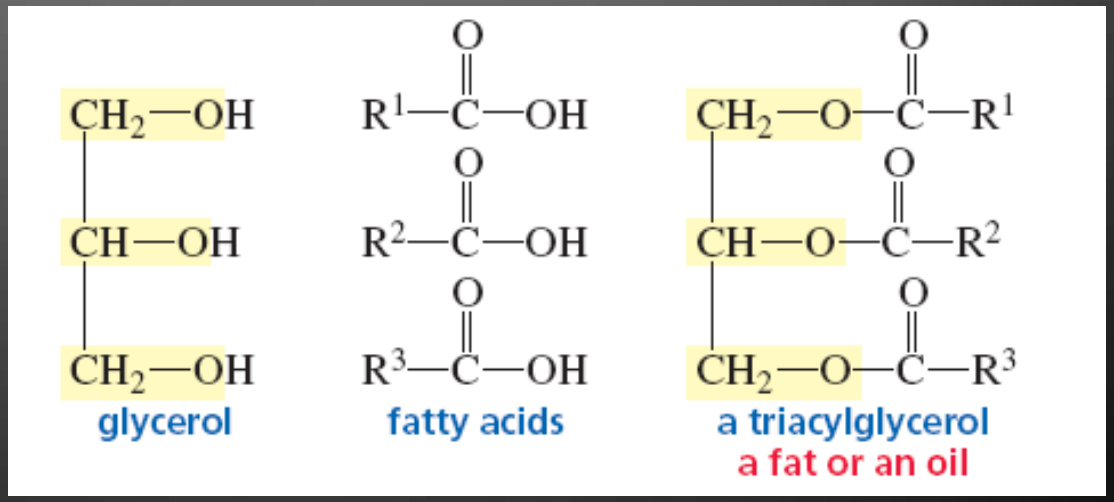
a major component of
spermaceti wax
from the heads of
sperm whales

Oils and fats

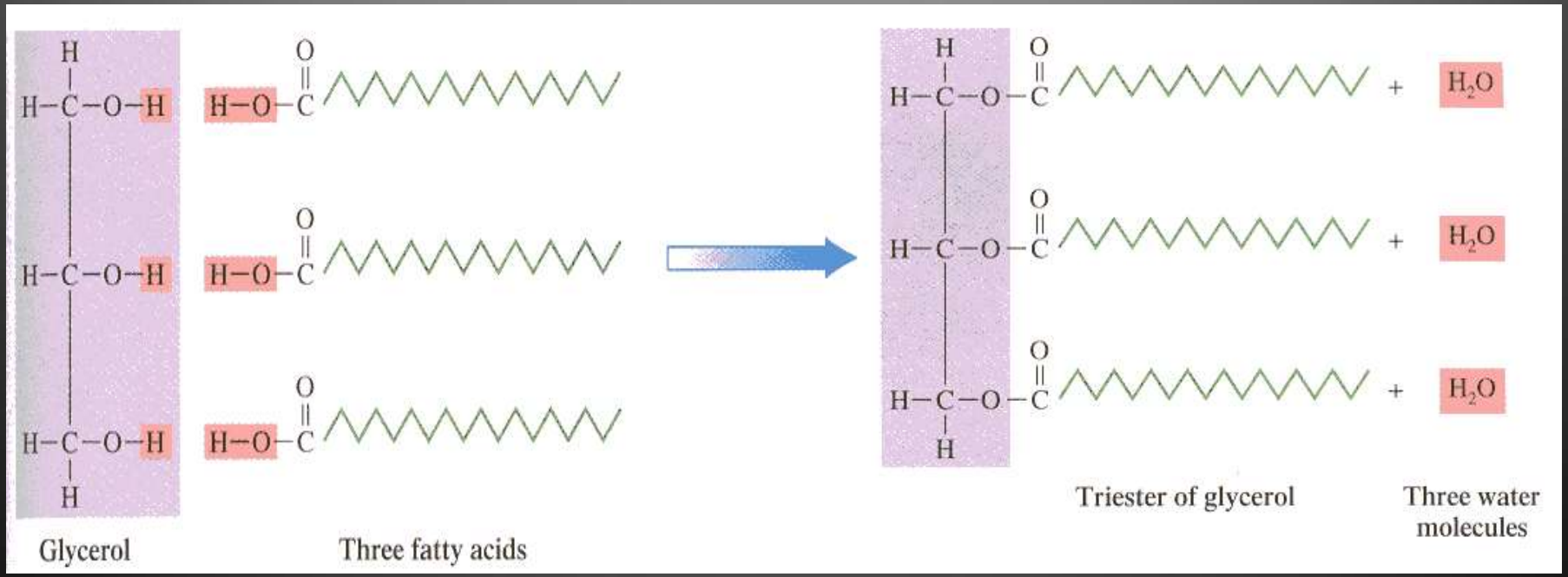
- Fatty acid esters of the thihydric alcohol – glycerol are called acylglycerol or glicerides; “neutral fart”



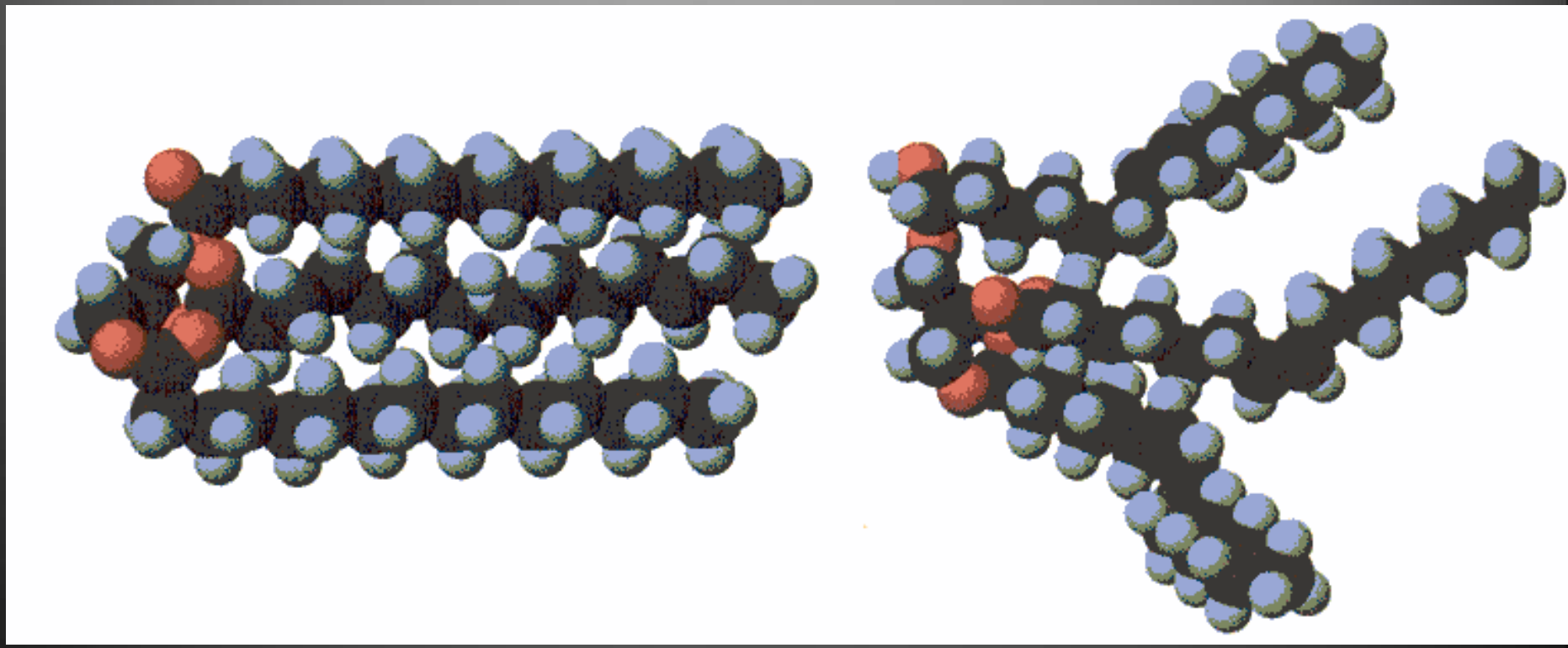
- Reaction formation of triacylglicerols



Reaction formation of triacylglicerol



Structure of thiacylglycerol

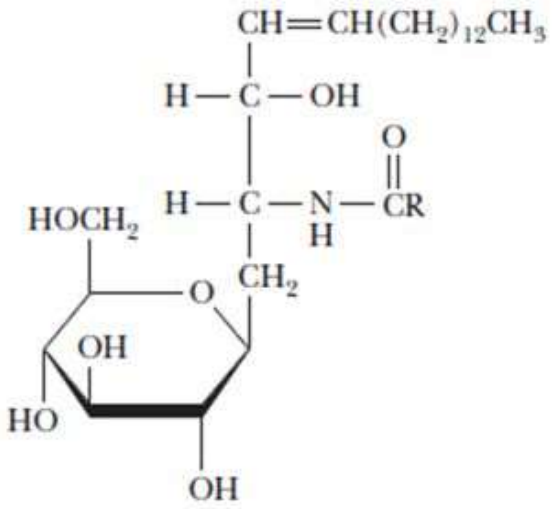


Fat

Oil

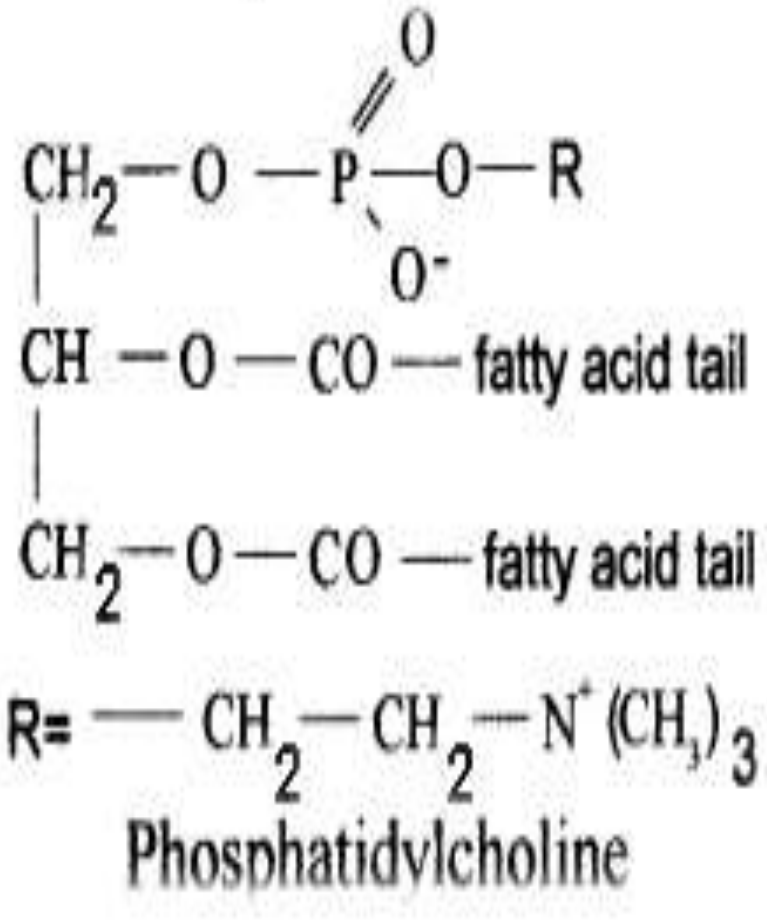
Glycolipids

- Carbohydrate bound to lipid
- Ceramides are the parent compound – sugar is attached to the primary alcohol group of ceramide through glycosidic bonds – forming cerebroside
- Sugar residue; glucose or galactose
- Found in nerve and brain membrane cells
- Glycolipids often found as markers on cell membranes
- Example of glycolipids: ganglioside



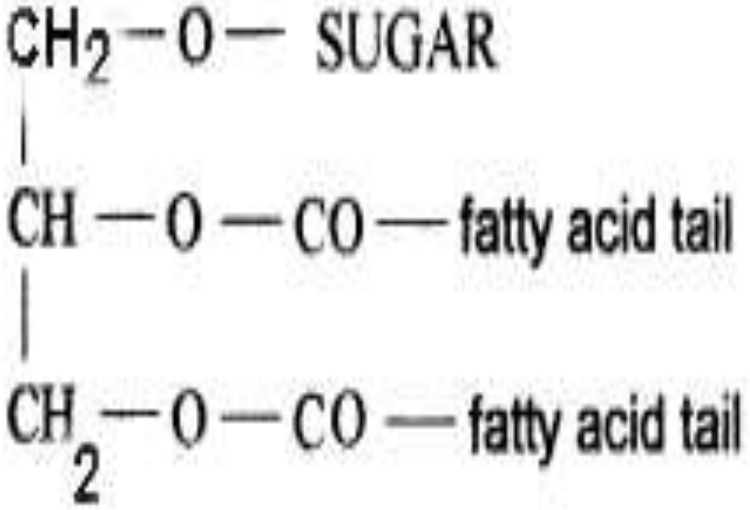
A Glucocerebroside

Phospholipid

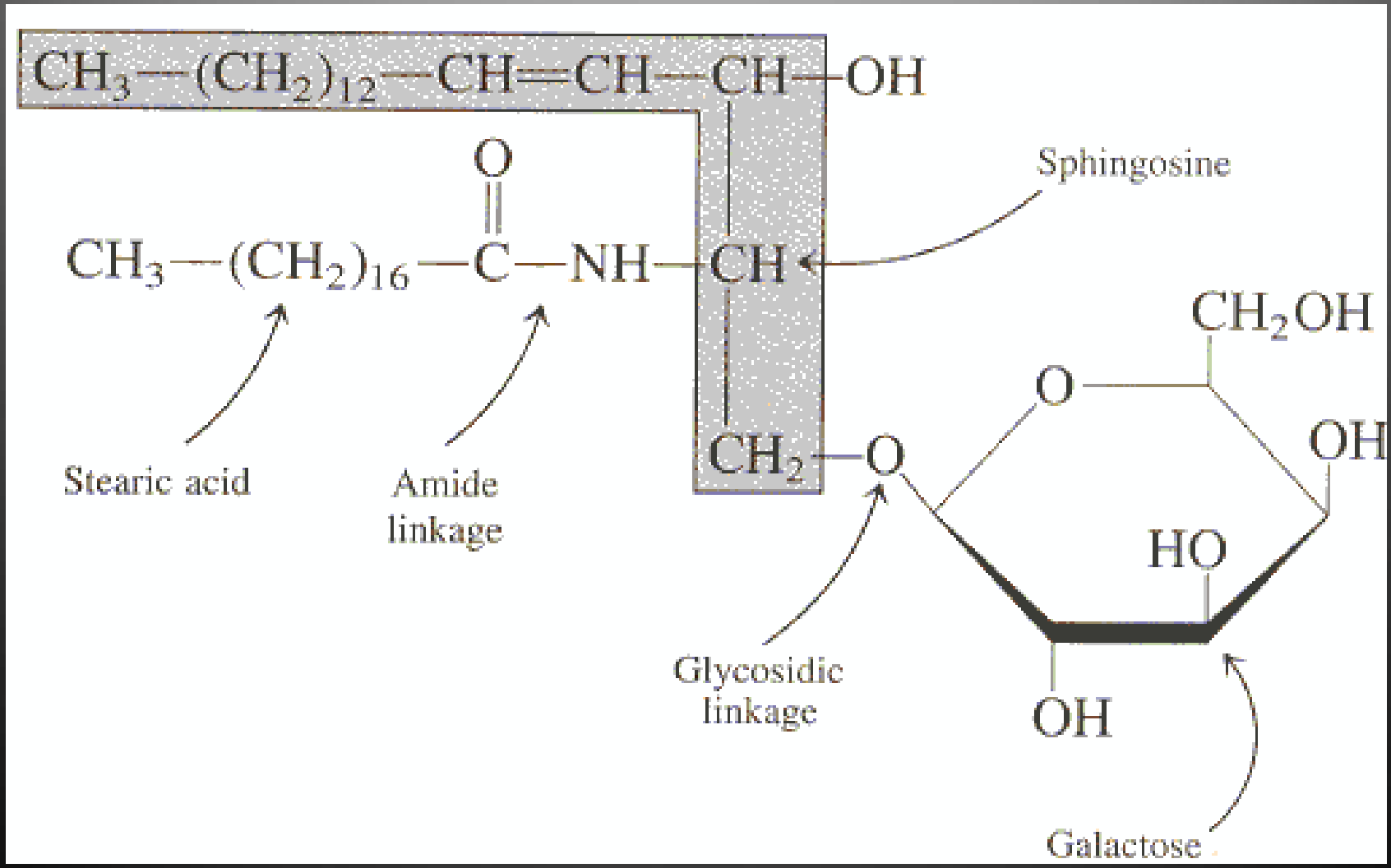


Phosphatidylcholine

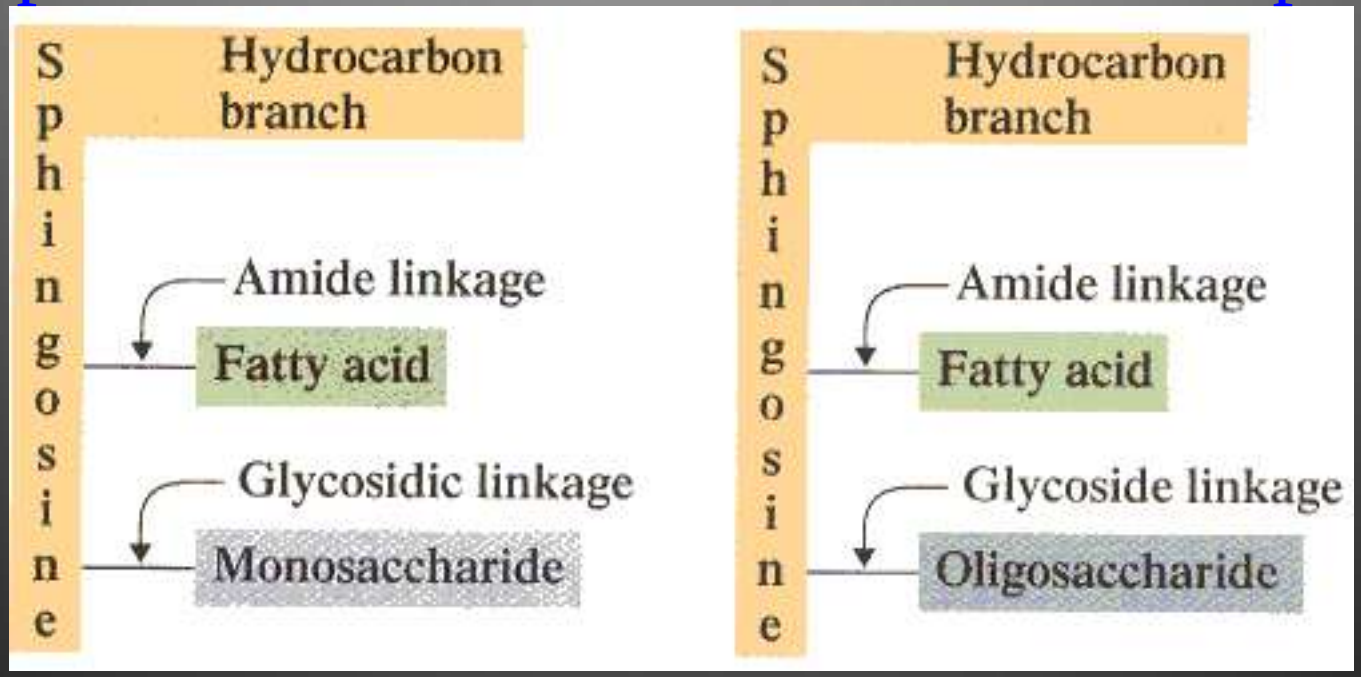
Glycolipid



Glycolipid


CH3—(CH2)12—CH=CH—CH—OH
O
CH3—(CH2)16—C—NH—CH
Sphingosine
Stearic acid
Amide linkage
CH2—O
Glycosidic linkage
CH2OH
O
OH
HO
OH
Galactose

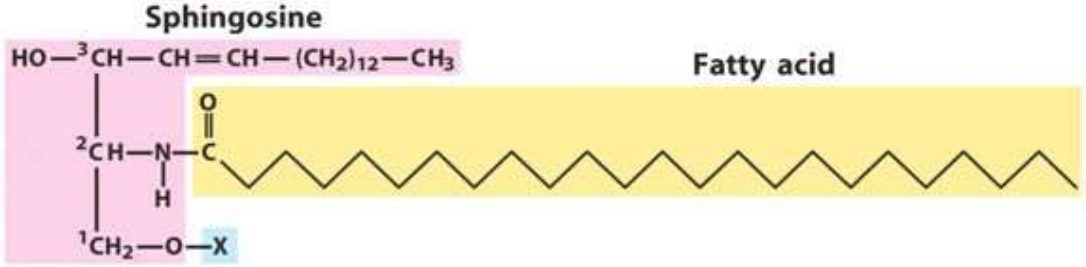
- **Cerebrosides,** the simplest of such carbohydrate-containing lipids, usually have a glucose or galactose as the carbohydrate unit.
- **Gangliosides** contain more complex carbohydrate heads; up to seven monosaccharide units are present.

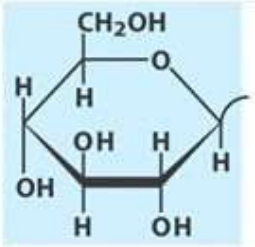
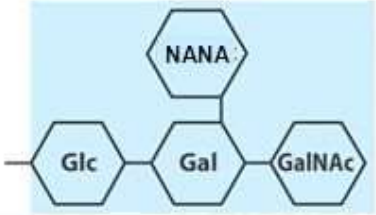


Cerebrosides **Gangliosides**

Glycolipid Structure and Function

- Sugar derivatives of **sphingolipids**
- Involved in intracellular communication
- Mainly on outer surface of plasma membrane
- **Cerebrosides**
  - **Ceramide** w/ monosaccharide (Glu or Gal)
- **Gangliosides**
  - **Ceramide** w/ complex oligosaccharide
  - High concentrations in neural cells



Name of sphingolipid	Name of X	Formula of X
Ceramide	—	— H
Glucosylcerebroside	Glucose	
Ganglioside GM2	Complex oligosaccharide	

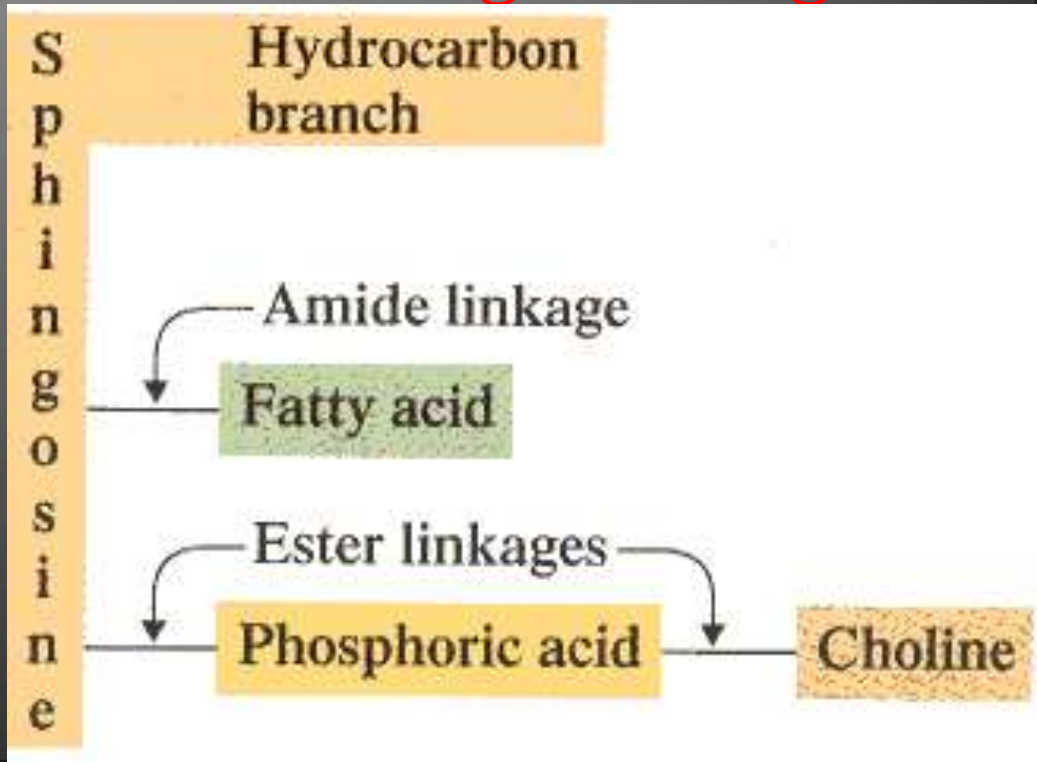
Functions of Glycolipid

- The glycolipids are an essential part of cell membranes.
- Glycolipids also help determine the blood group of an individual.
- Glycolipids act as receptors at the surface of the red blood cell.
- some viruses, bacteria (eg., cholera) use glycolipids on their cell surface as well. This helps the immune system destroy and clear the pathogen from the body.

Sphingolipids in which the esterifying group is phosphoric acid to which choline is attached are called **sphingomyelins.**

Sphingomyelins are found in all cell membranes and are important structural components of the myelin sheath, the protective and insulating coating that surrounds nerves

Sphingornyelins



Phospholipides

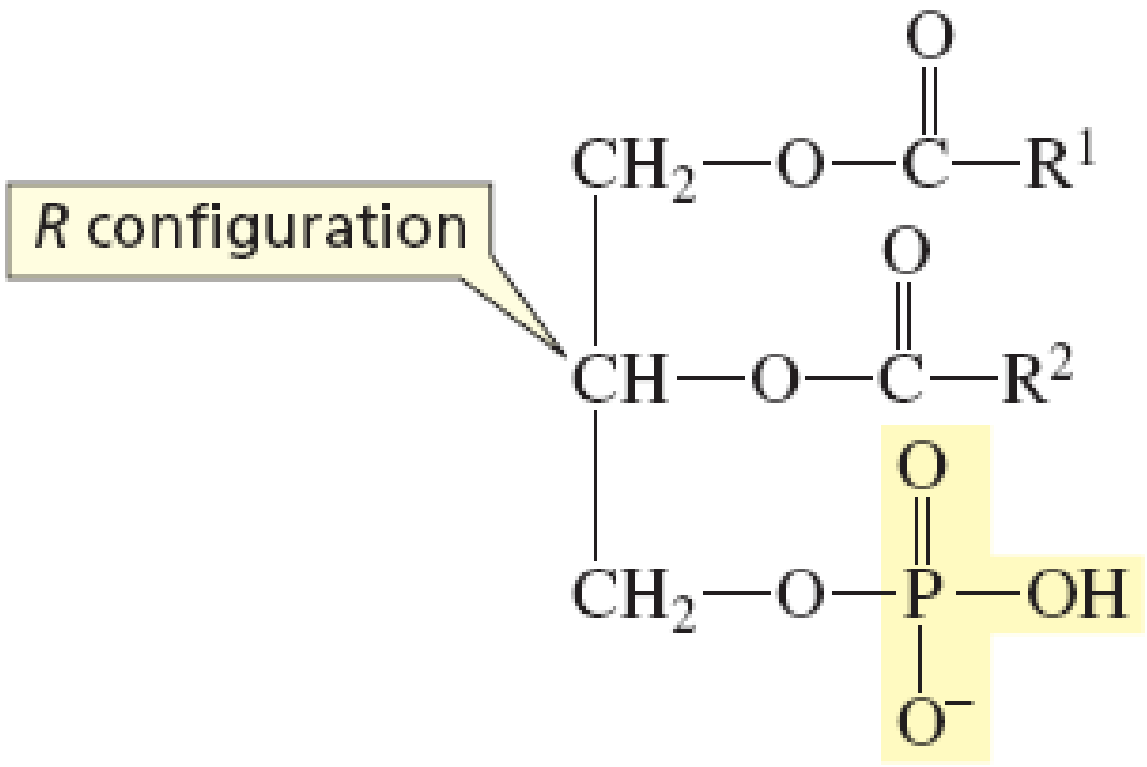
- **Phosphoacylglycerols** are triesters of glycerol in which two -OH groups are esterified with fatty acids and one the third is esterified with phosphofic acid, which in turn is esterified to an alcohol.

a)Phosphatidylethanolamines

b)Phosphatidylcholines

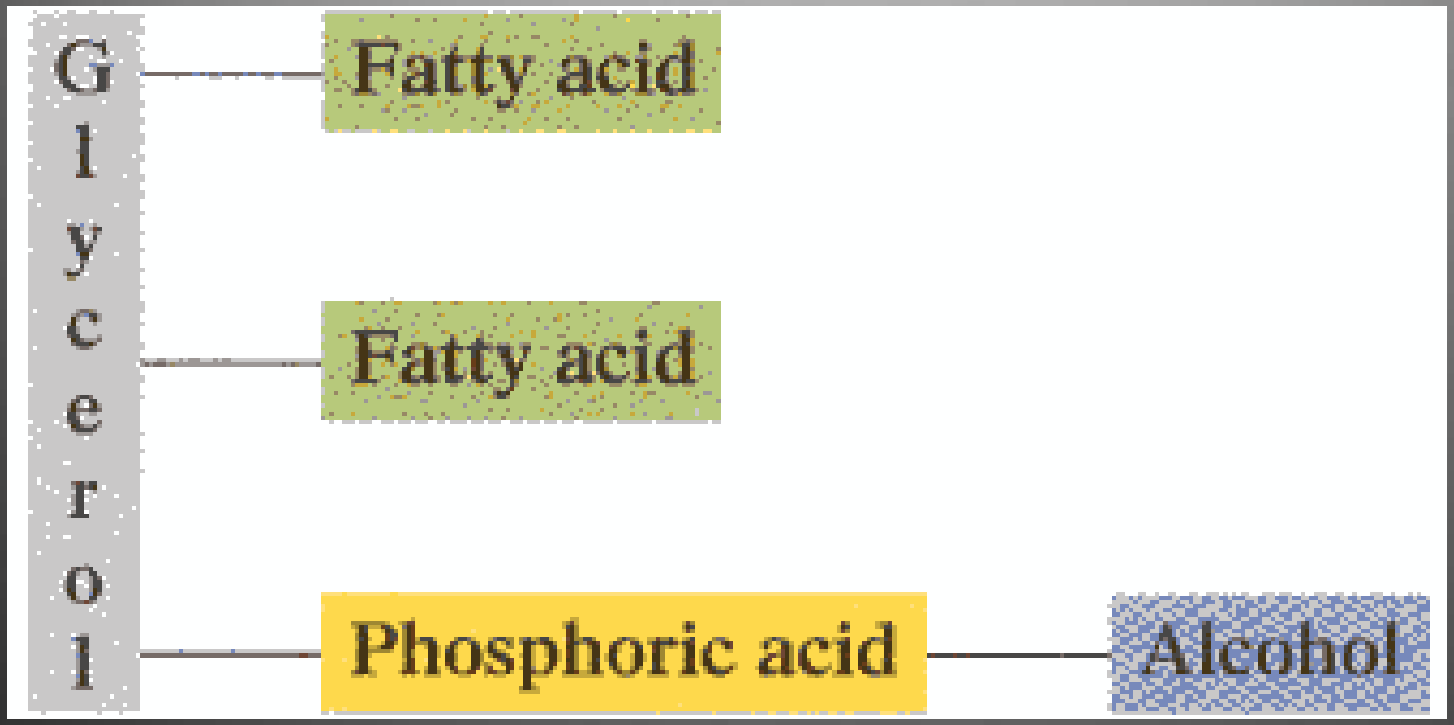
c)Phosphatidylserines

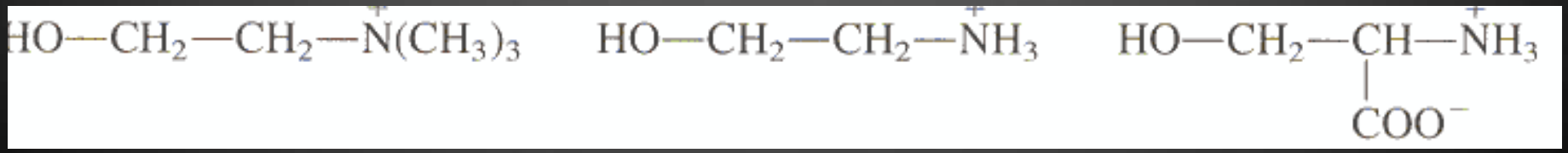
- **Phosphosphingolipid** are esters of dialcohol sphingosine in which a fatty acid in amide linkage on the amino group and the phosphorylcholine group attached by way of the terminal alcohol group.



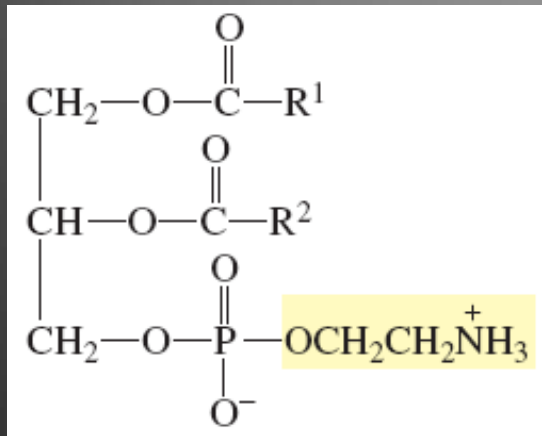
a phosphatidic acid

Phosphoacylglycerols

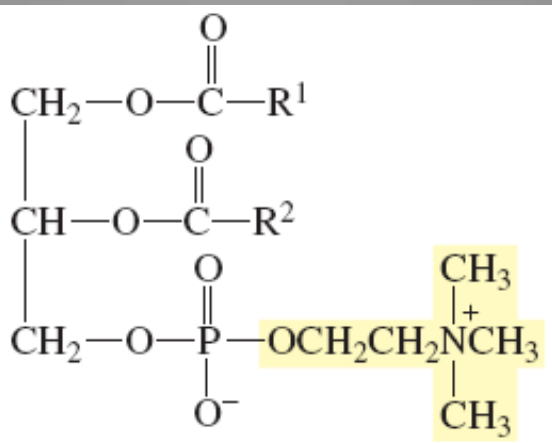




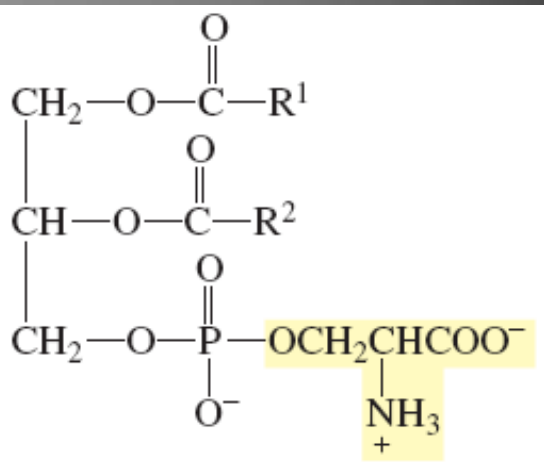
Choline Ethanolamine Serine



a phosphatidylethanolamine
a cephalin



a phosphatidylcholine
a lecithin



a phosphatidylserine

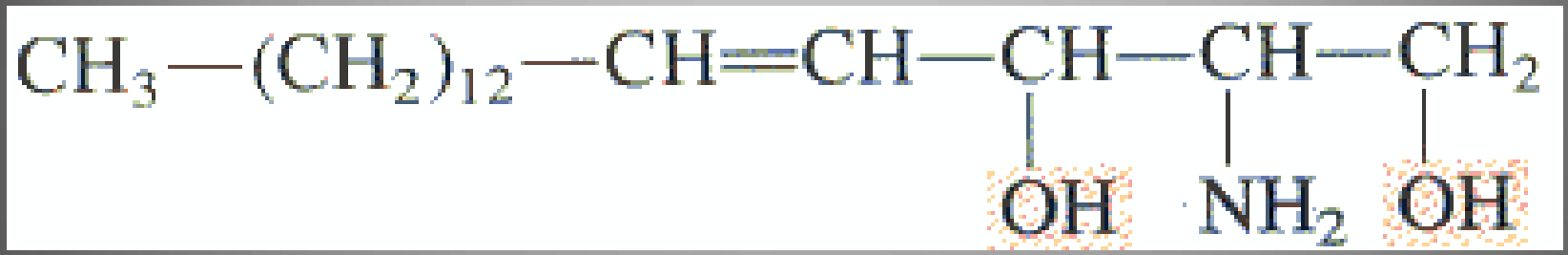
2-Sphingophospholipids

Sphingomyelin: it is a sphingophospholipid

Not contain glycerol but contain alcoholcalled : sphingosine,

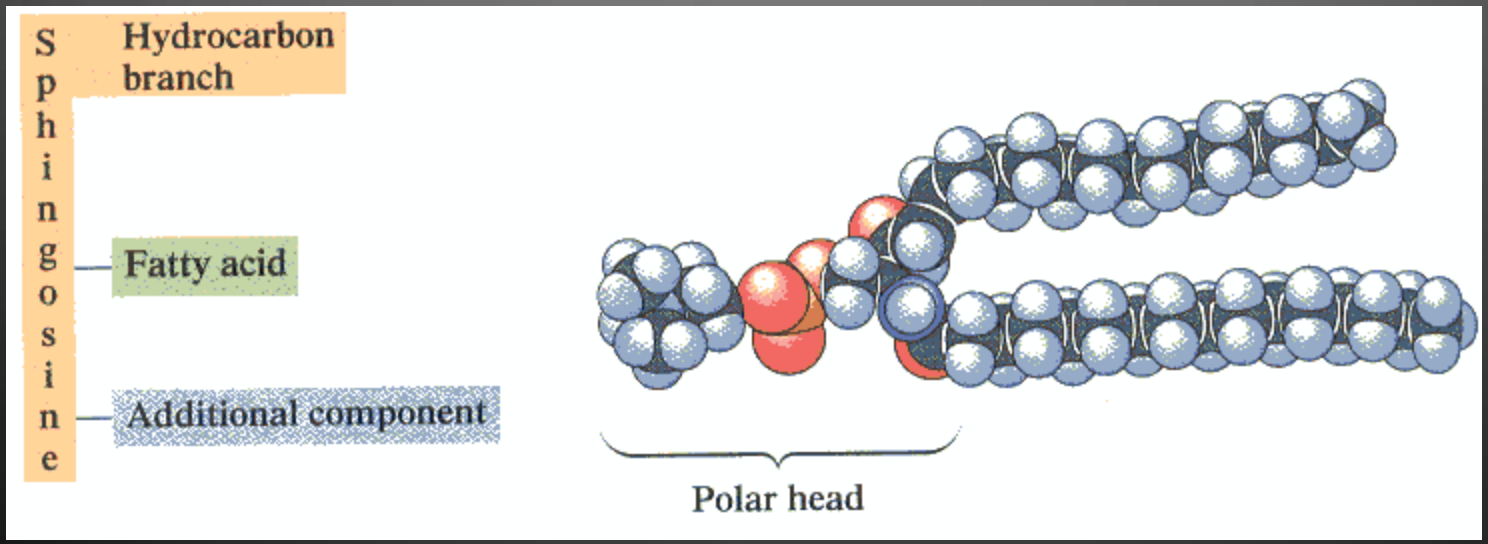
Fatty acid is attached to amino group of sphingosine and phosphorylcholine (phosphate + choline) is attached to the last OH group.

Sources: present in high amount in brain and nerve tissues.

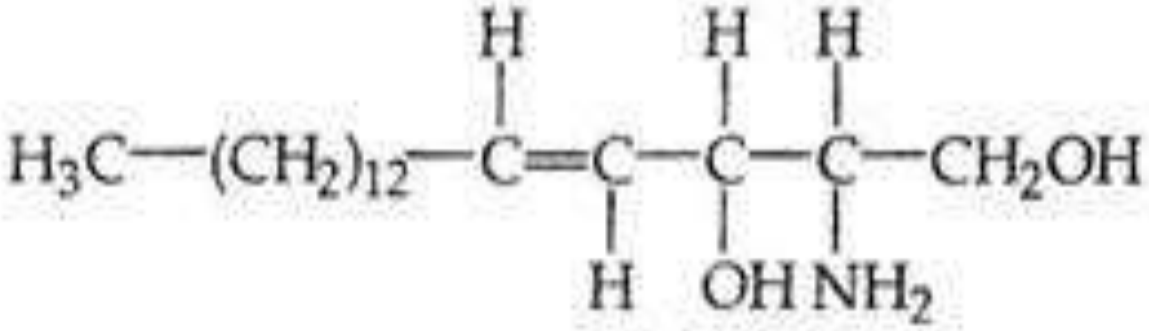


Sphingosine

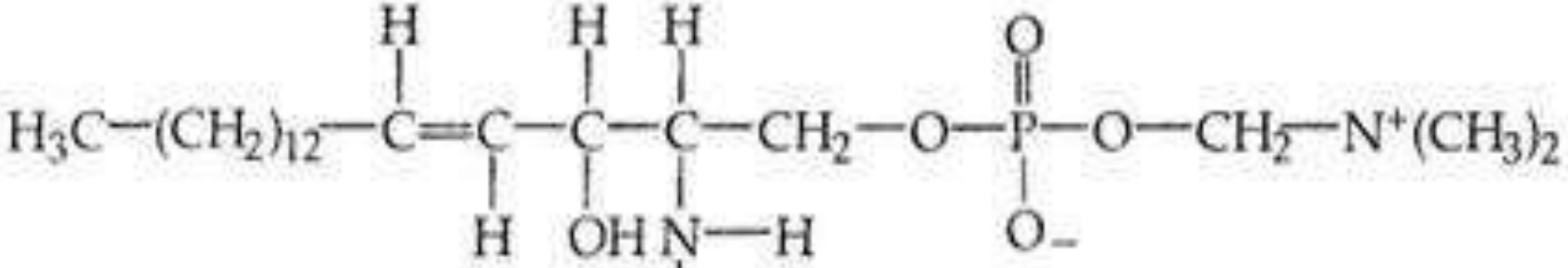
Sphingolipid



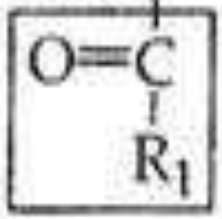
sphingolipid



Sphingosine



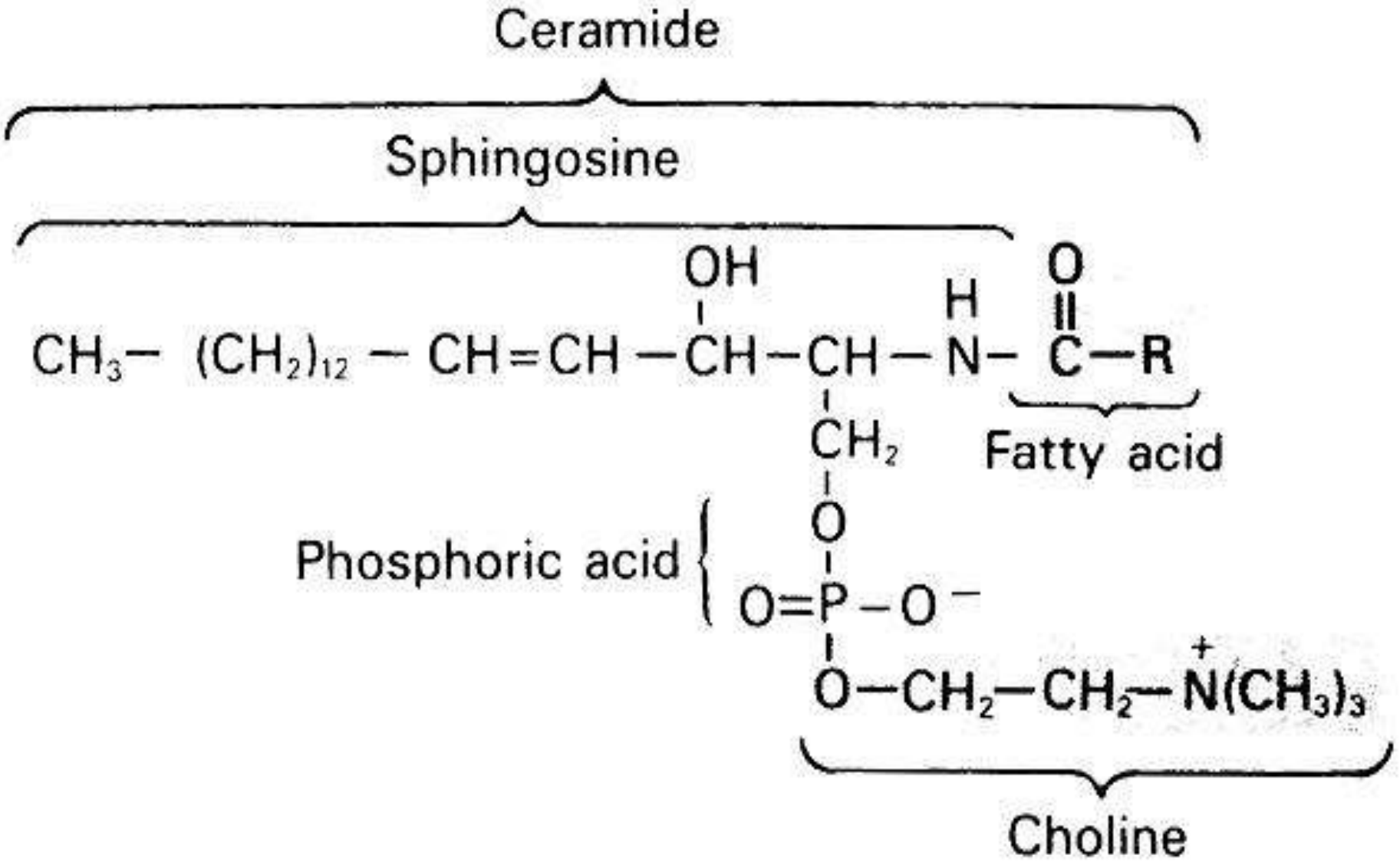
(Phosophoric acid) (Choline)



← Fatty acid unit

Sphingomyelin

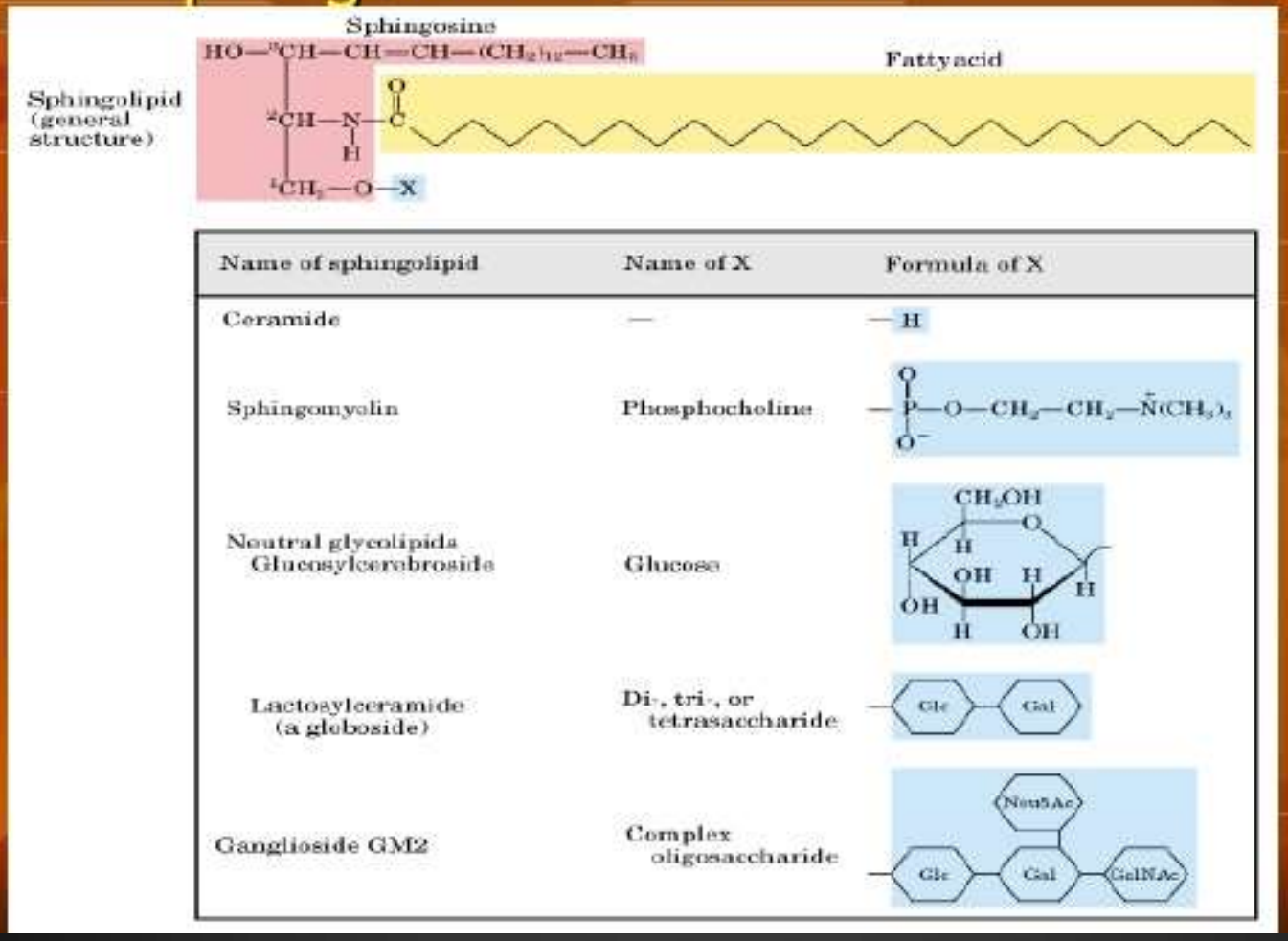
sphingolipid



4. Sphingolipids

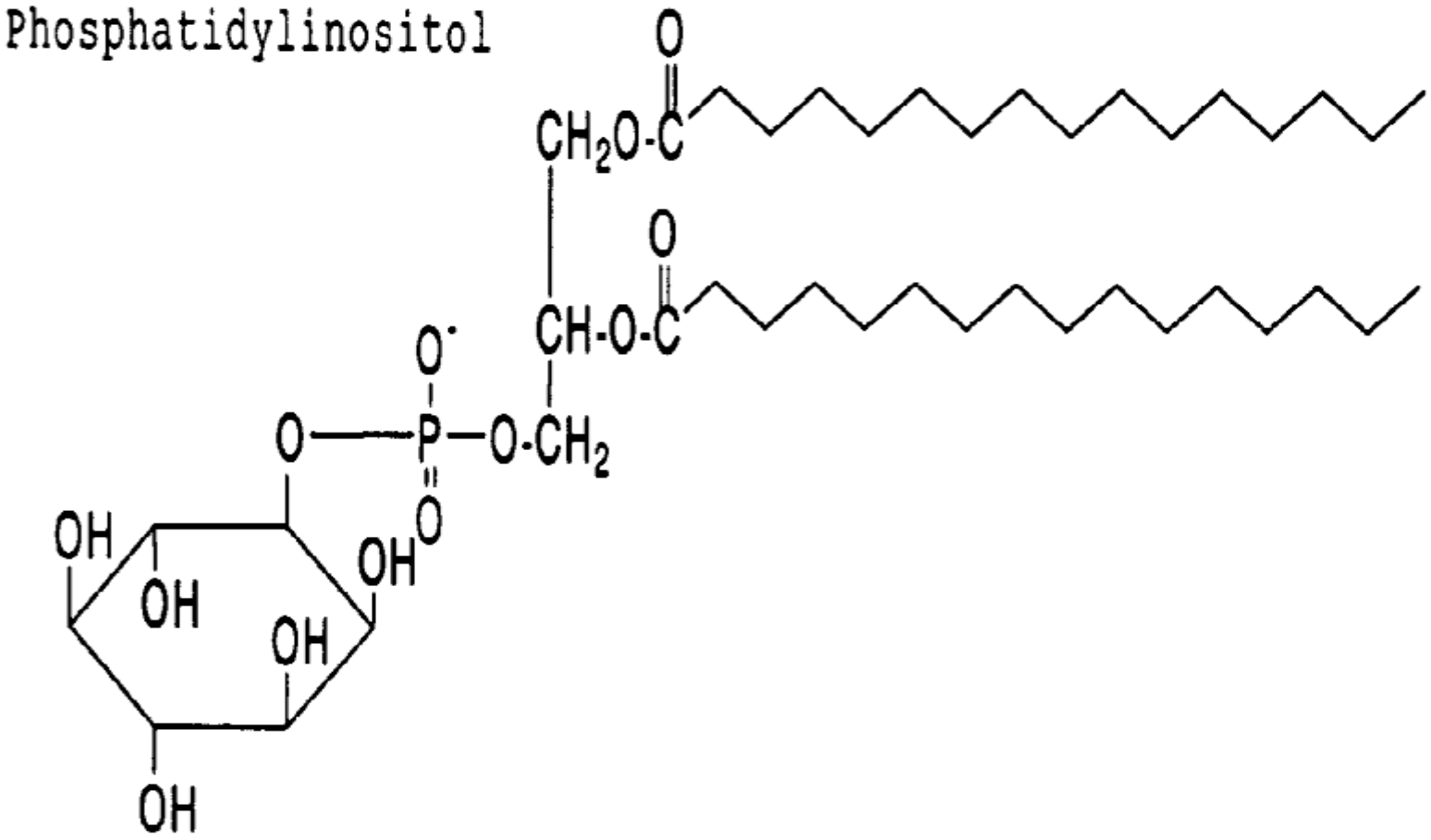
- are a complex family of compounds that share a common structural feature

- a sphingoid base backbone.



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	

Posphatidylinositol



Derived Lipids

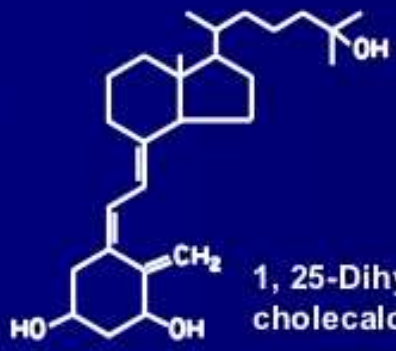
These substances are derived by hydrolysis from compound and simple lipids. These fatty acids include alcohols, mono- and diglycerides, carotenoids, steroids, and terpenes.

Derived Lipids:

- **Steroids** play many physiologically important roles.
- Cholesterol, in addition to its association with atherosclerosis, it is the precursor molecule of large number of biologically important steroids, including Vitamin D, steroid hormones, bile acids….etc.
- It contains the characteristic steroid nucleus.
- It is a major constituent of the cell membrane.

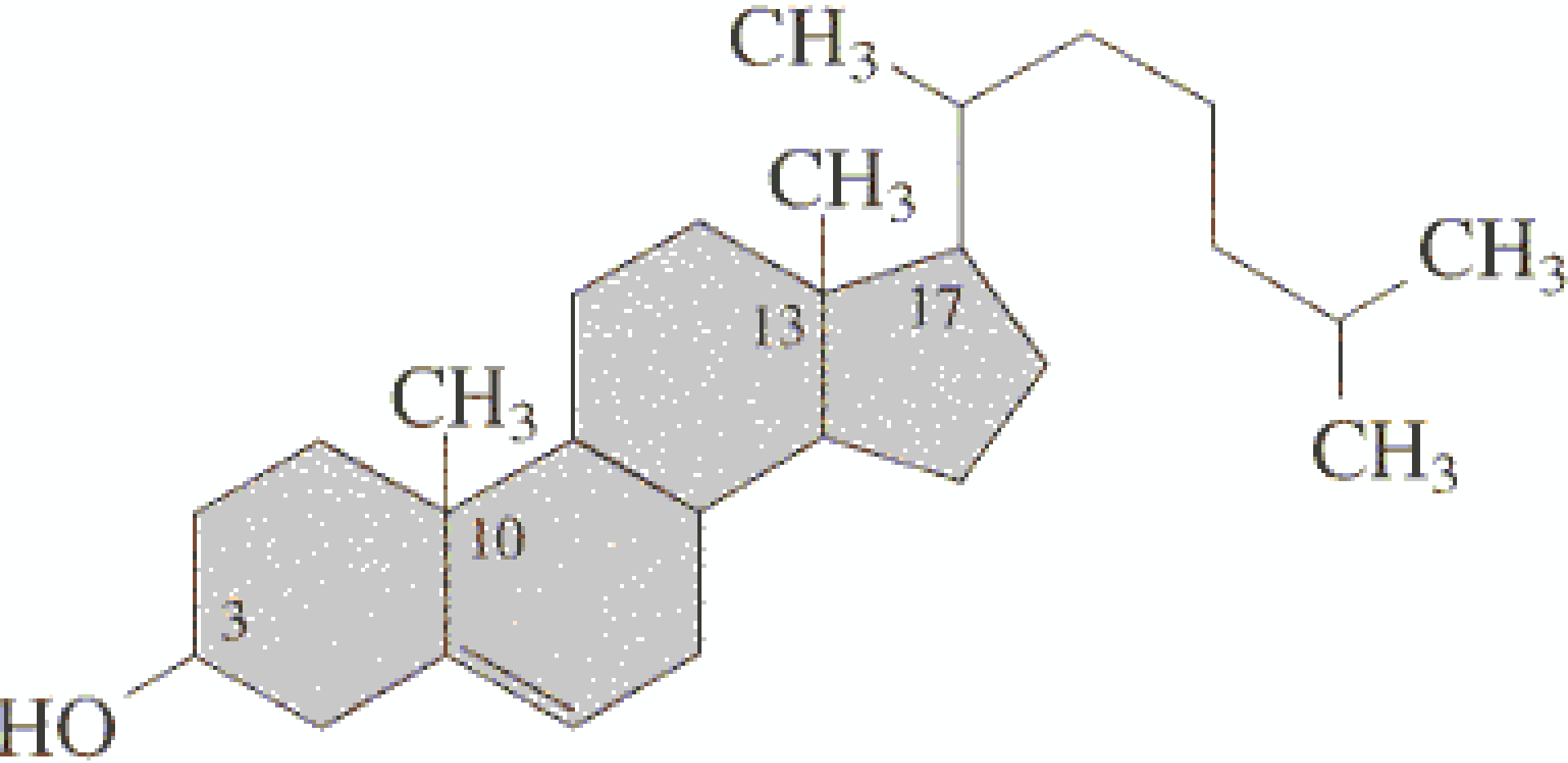
Steroid nucleus

Cholesterol

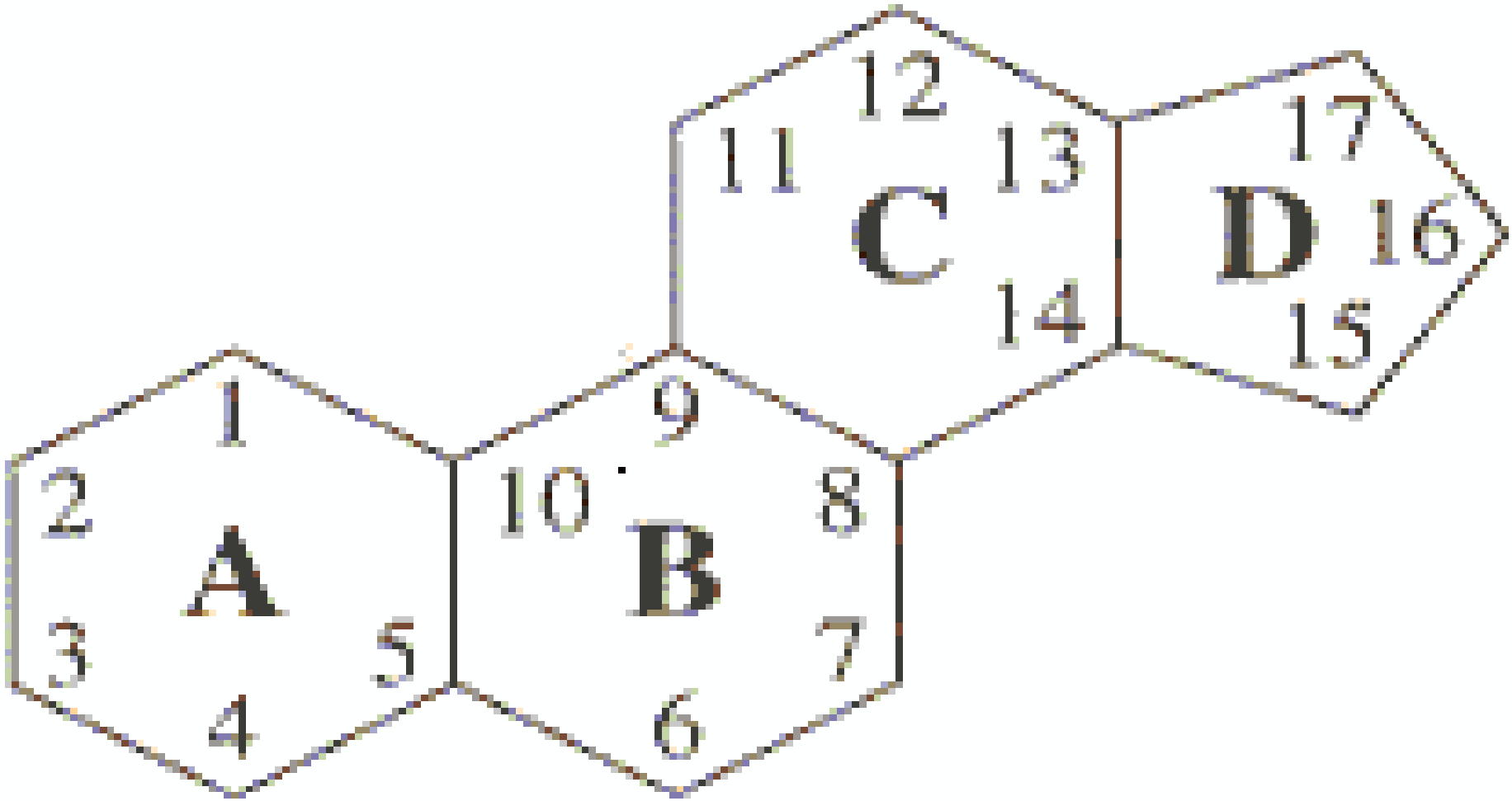


1, 25-Dihydroxy-cholecalciferol, Vitamin D

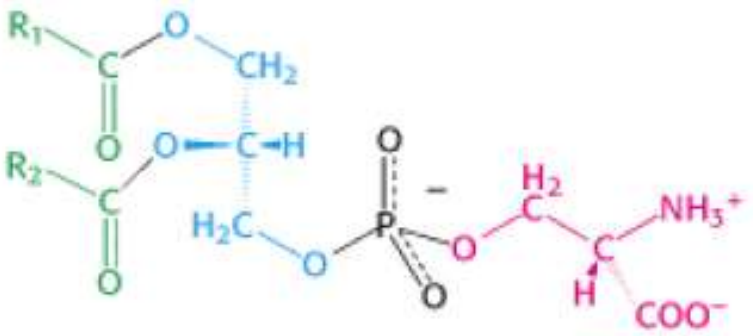
Cholesterol is the most abundant steroid in the human body



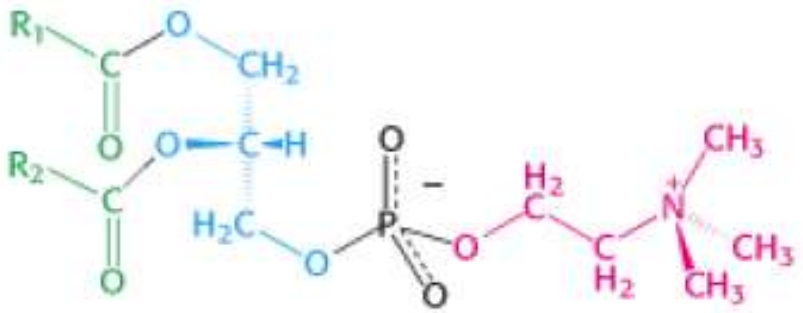
Pentahydrofenantrene (sterane)



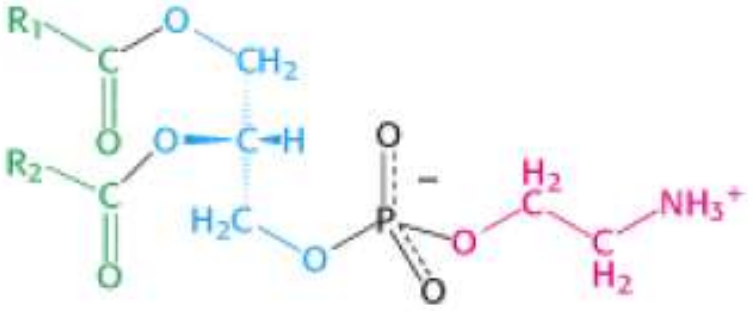
- Cholesterol, an unsaturated alcohol whose structure is the most abundant animal steroid. It has been estimated that a 60 kg person has a total of about 175 g of cholesterol distributed throughout the body. Much of this cholesterol is bonded through ester links to fatty acids, but some is found as the free alcohol. Gallstones, for example, are nearly purecholesterol.
- Cholesterol serves two important functions in the body. First, it is a minor component of cell membranes, where it helps to keep the membranes fluid. Second, it serves as the body's starting material for the synthesis of all other steroids, including the sex hormones.



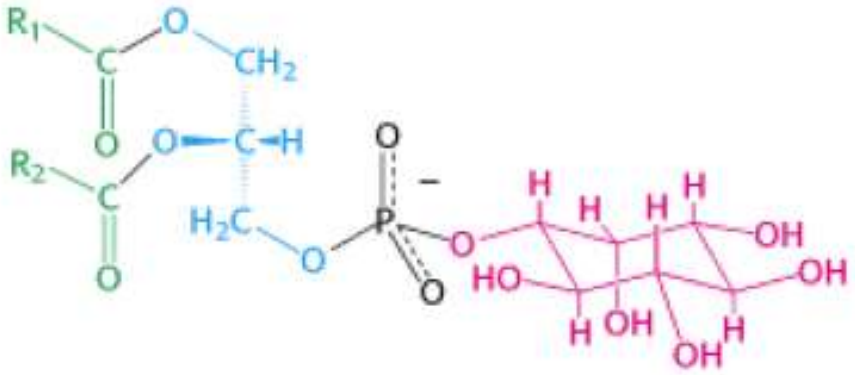
Phosphatidyl serine



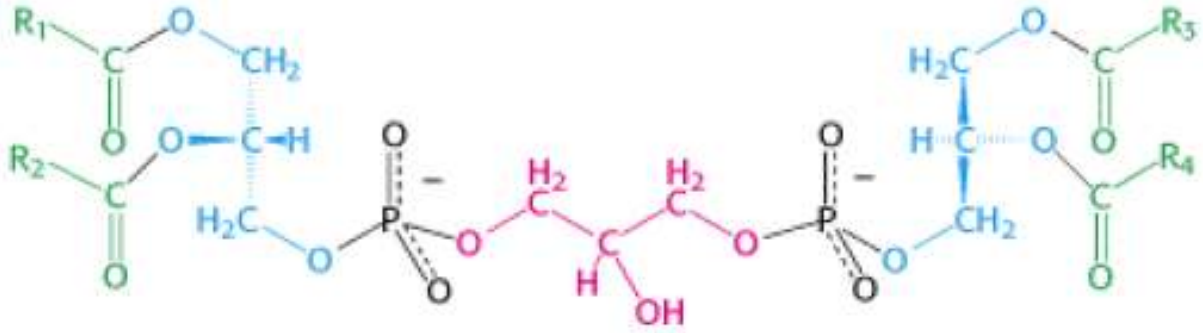
Phosphatidyl choline



Phosphatidyl ethanolamine

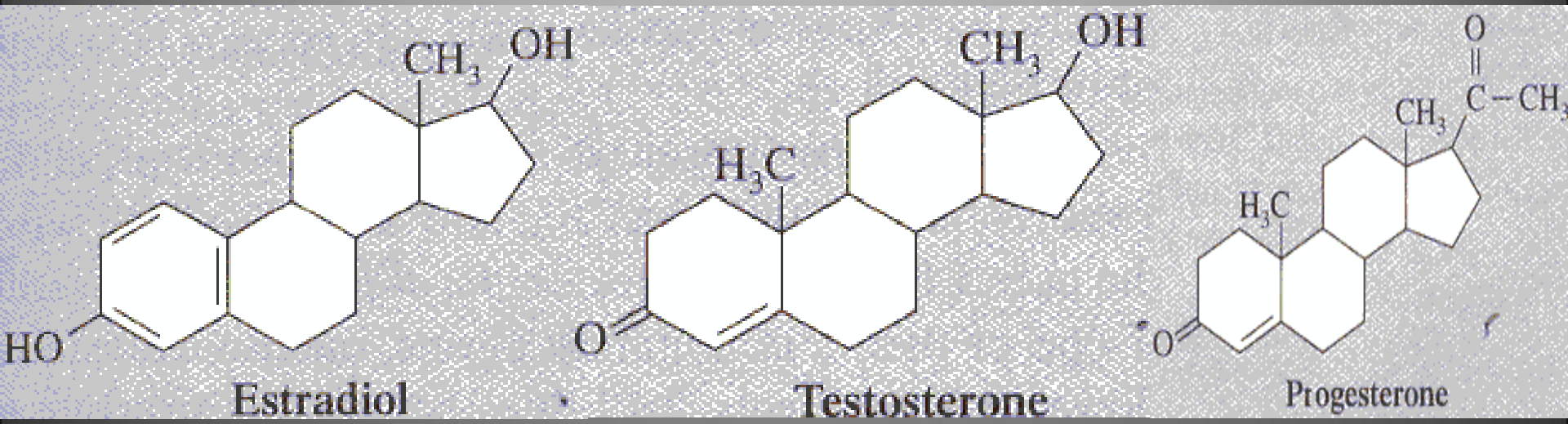


Phosphatidyl inositol



Diphosphatidyl glycerol (cardiolipin)

Steroids hormones.



Hormones are chemical messengers produced by ductless glands.

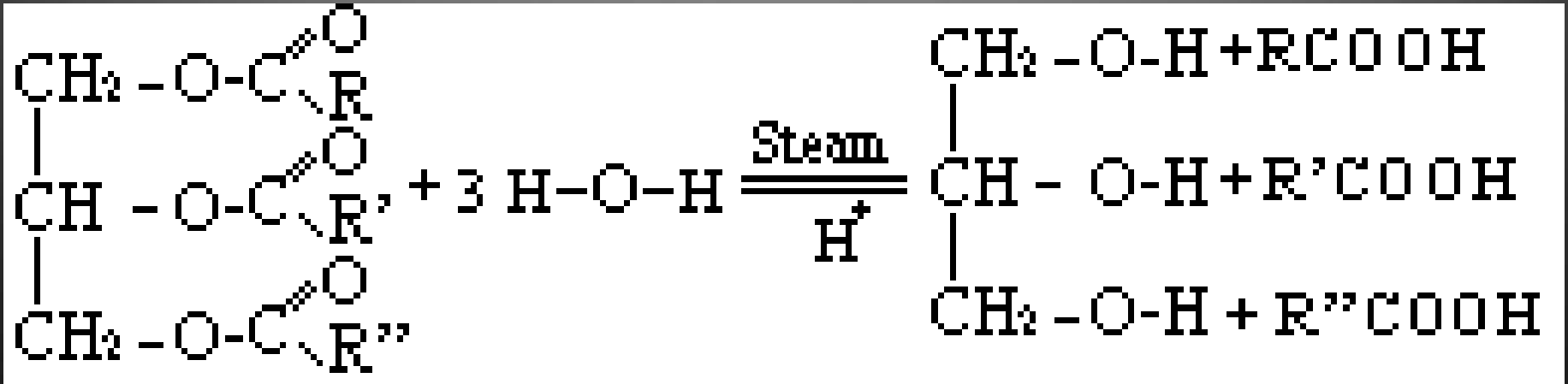
- The **isoprenoids** are a vast array of biomolecules that contain repeating fivecarbon structural units known as **isoprene units**.
- **Terpenes** are an enormous group of molecules that are found largely in the “essential oils” of plants. Steroids are derivatives of complex hydrocarbon ring system.
- Examples of these biomolecules, referred to as **mixed terpenoids**, include vitamin E (α-tocopherol), ubiquione, vitamin K, and some cytokinins (plant hormones).

Characterization of fats.

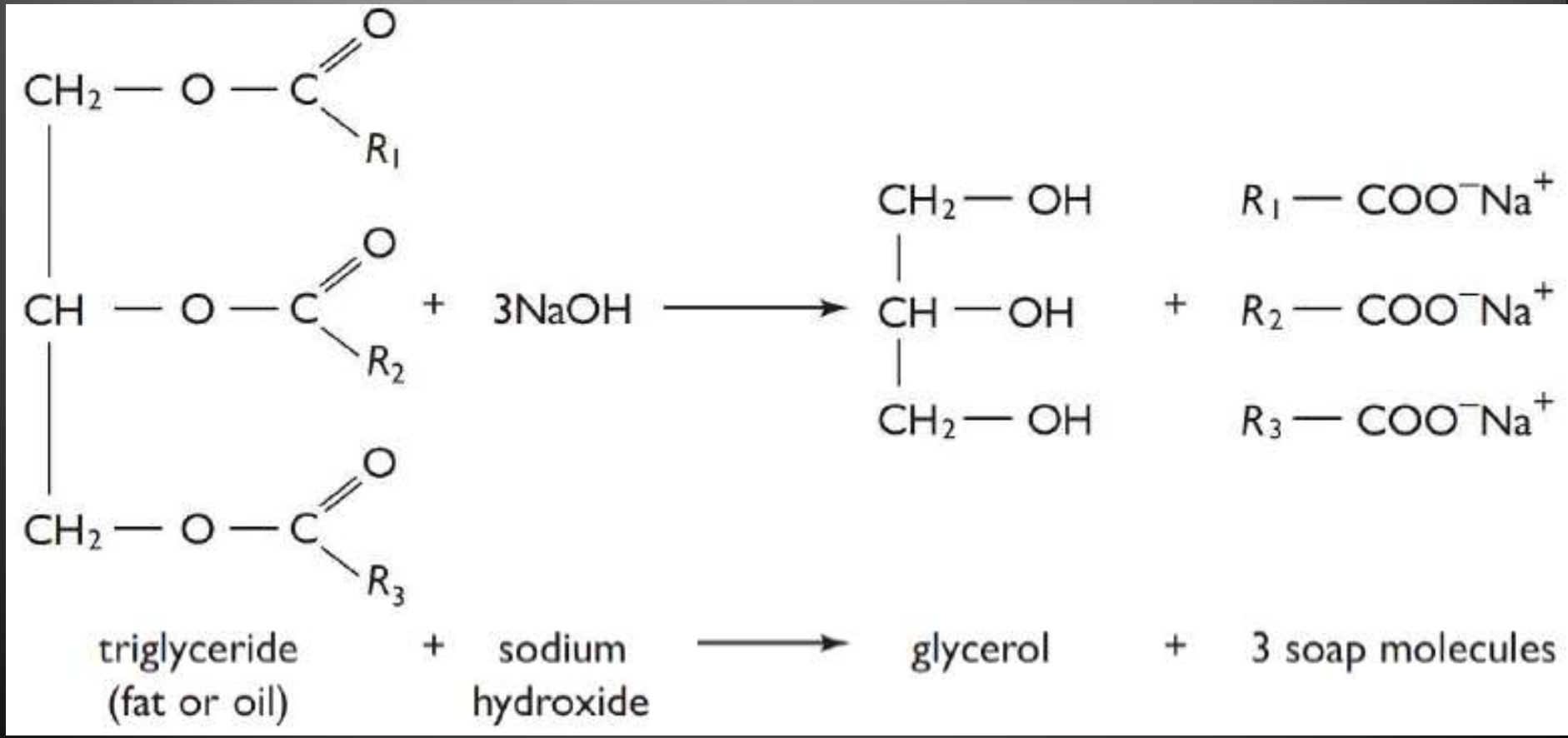
- **Acid number**. It is the number of milligrams of potassium hydroxide required to neutralise the free fatty acids in 1 g of the oil or fat.
- **Saponification number.** It is number of milligrams of potassium hydroxide required to completely saponify l00 g of the oil or fat.
- **Iodine number.** It is the number of grams of iodine that combine with 100 g of oil or fat. It is a measure of the degree of unsaturation of a fat or oil; a high iodine number indicates a high degree of unsaturation of the fatty acids of the fat.
- **Reichert -Meissl number**. (R. M. number). It is the number of millilitres of Cn=10 potassium hydroxide required to neutralise the distillate (obtained by saponification, acidification and steam distillation of the fat) of 5 g of the fat.

Chemical properties

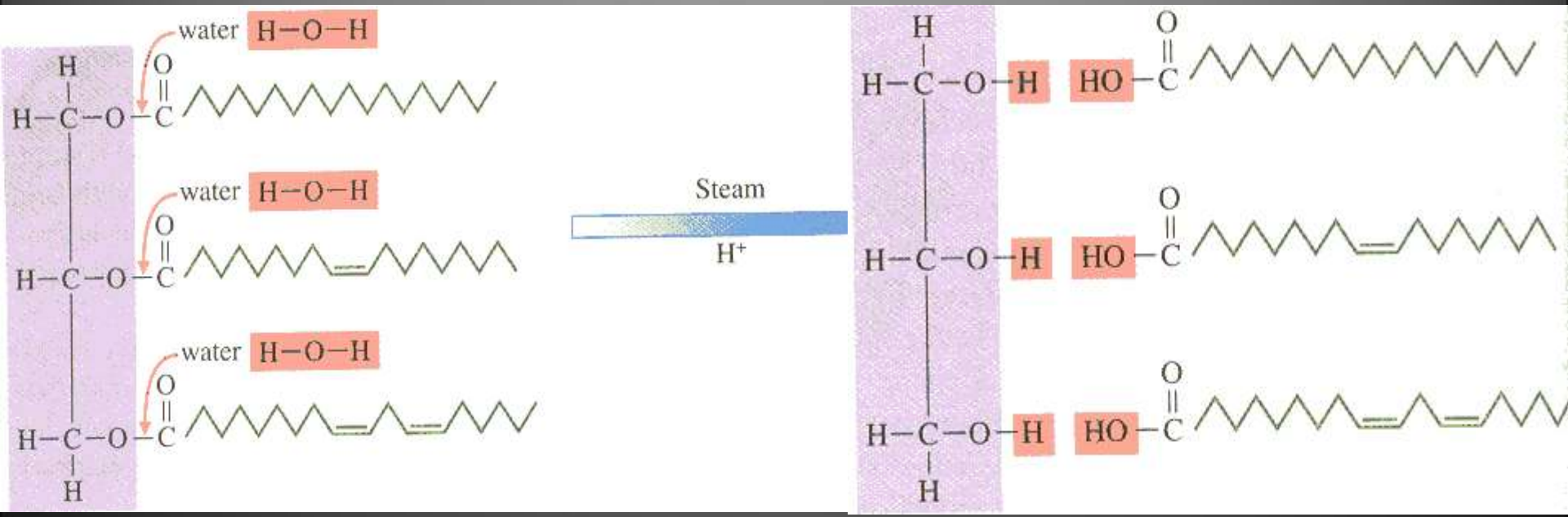
- **Hydrolysis.** There is acetic, basic and enzyme's hydrolysis.
- Acidic and enzyme:



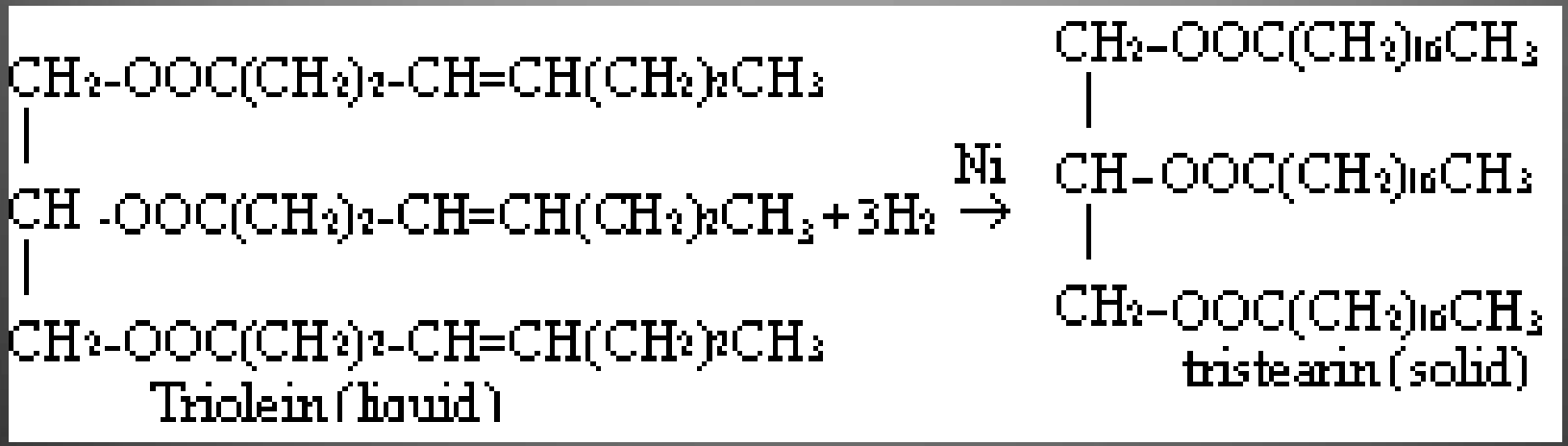
Saponification reaction



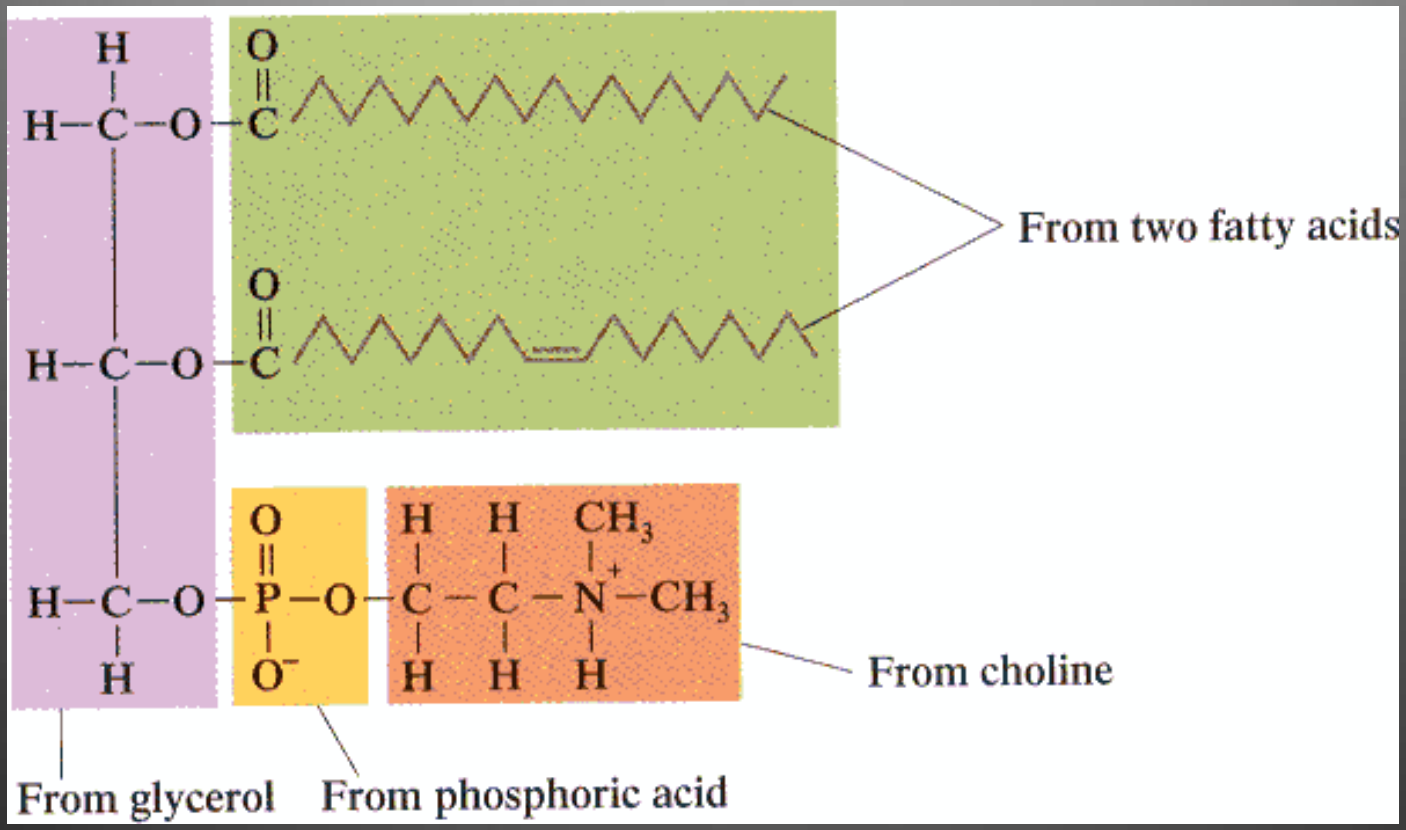
Saponification –basic hydrolysis



Hydrogenation.



Phosphatylcholine



Phosphatylcholine, structure of molecule

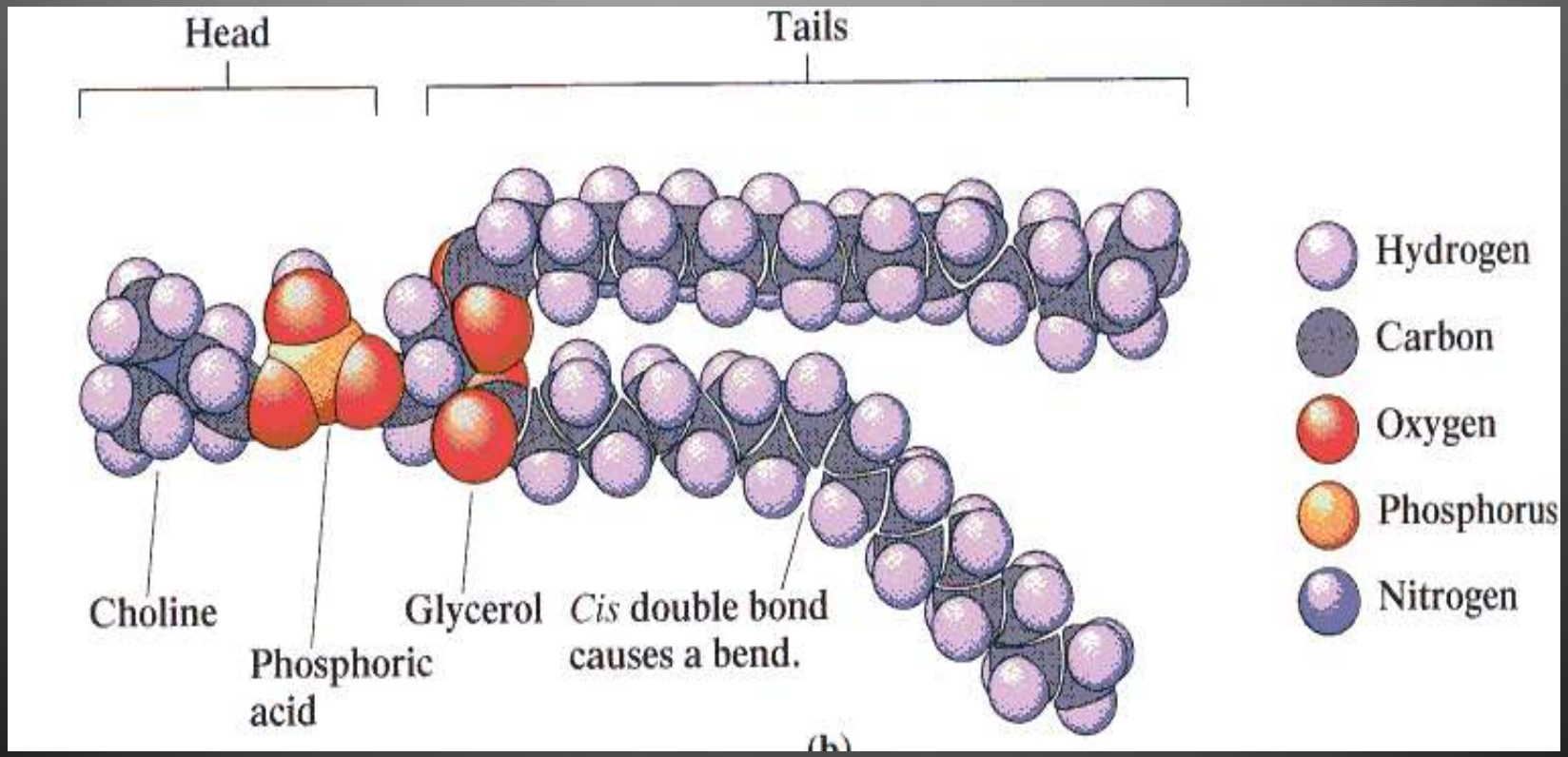
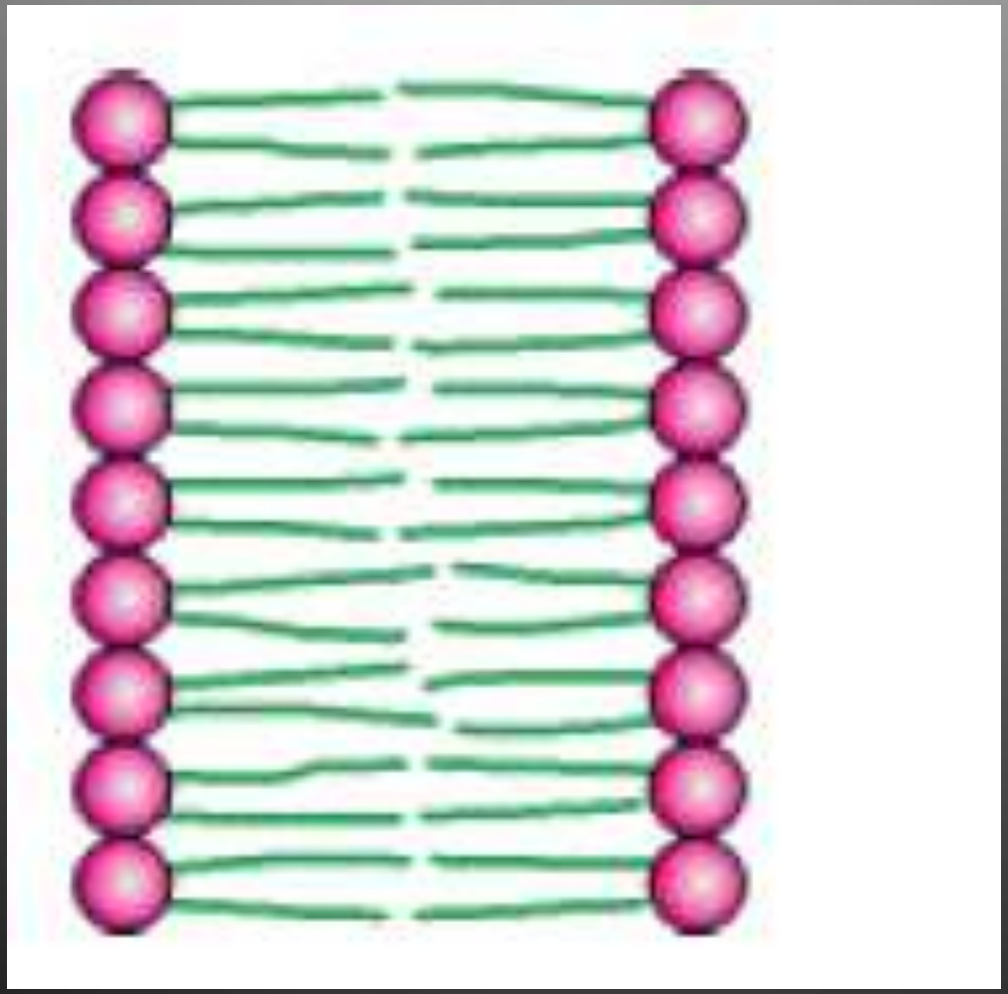
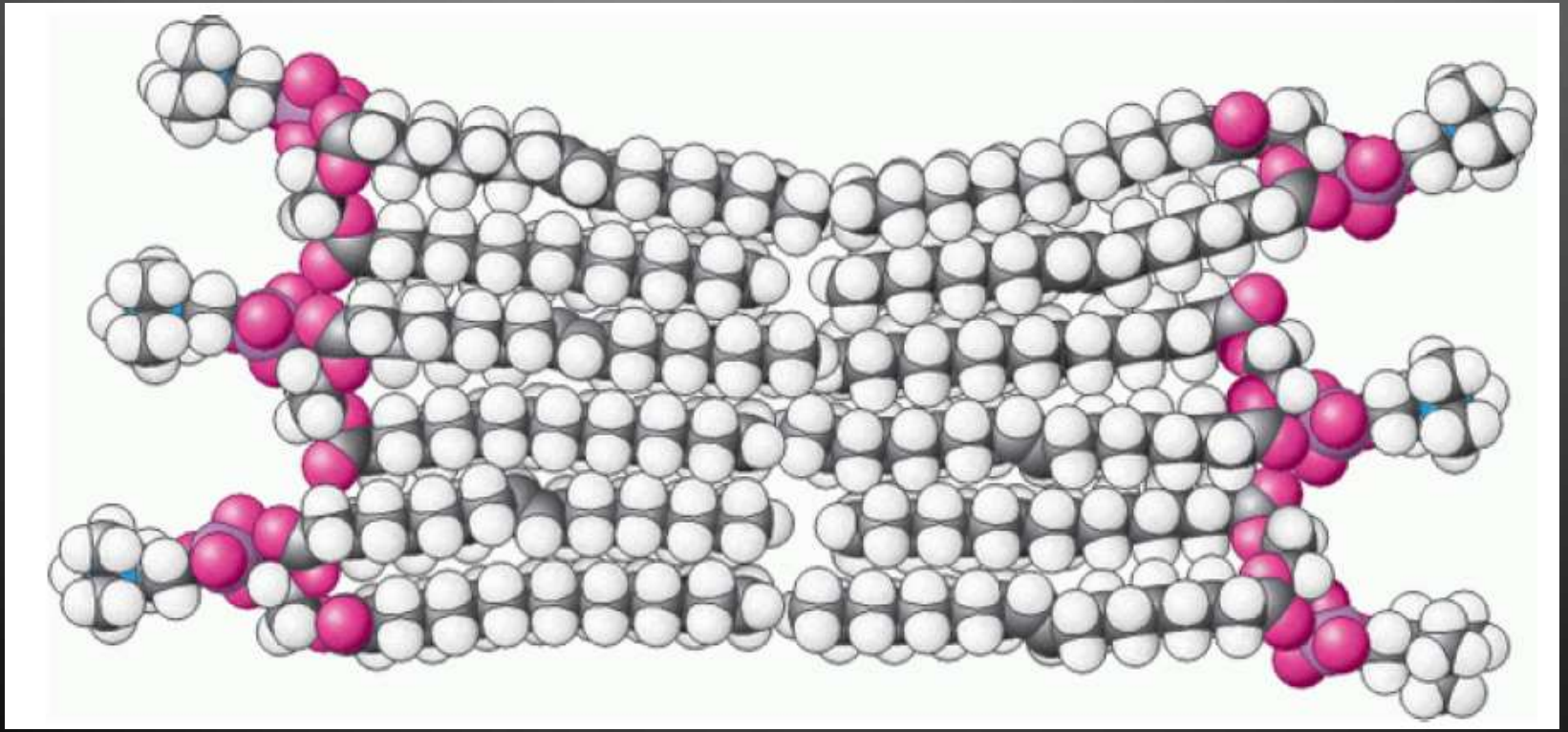


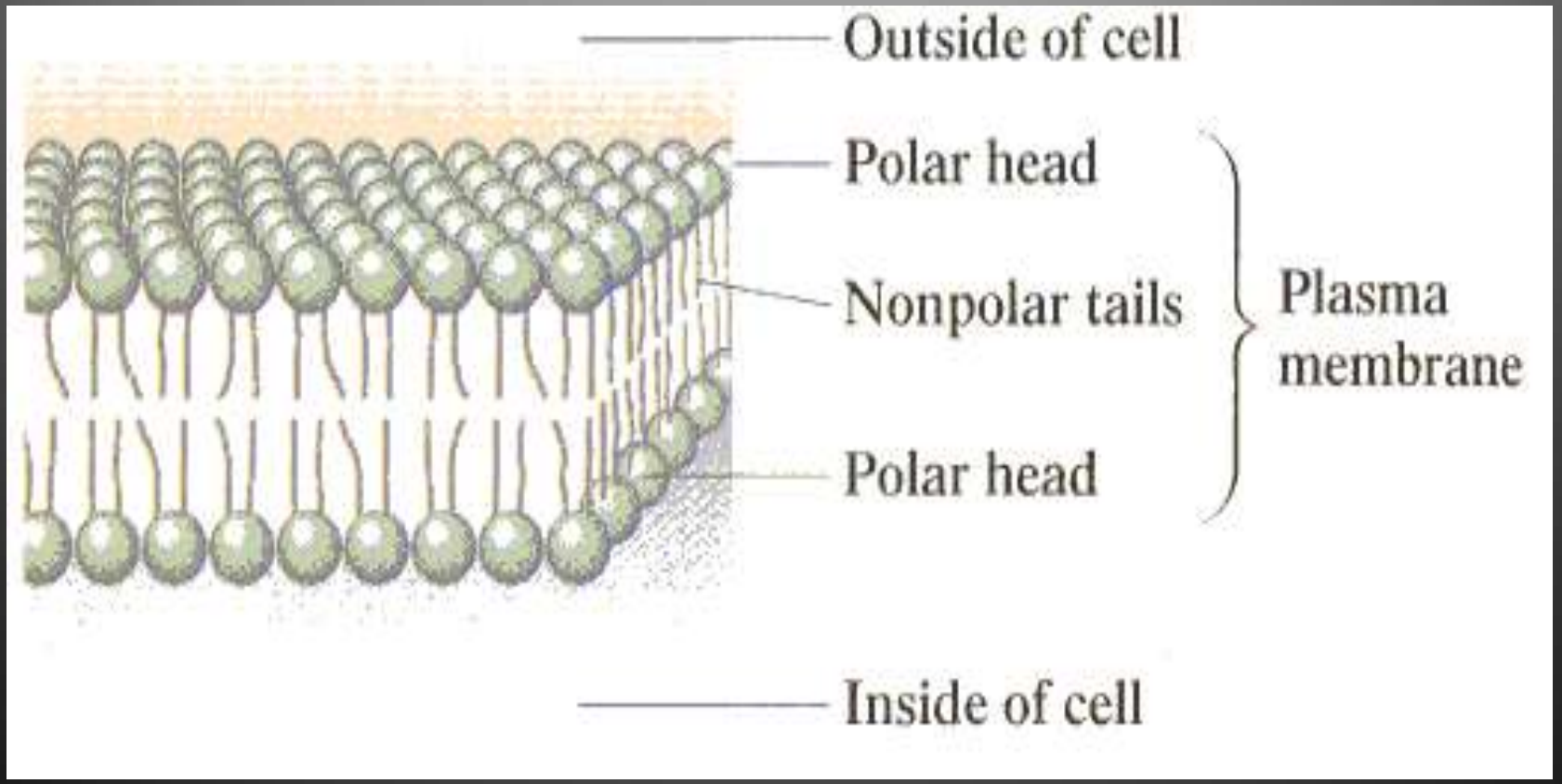
Diagram of a section of a bilayer membrane.



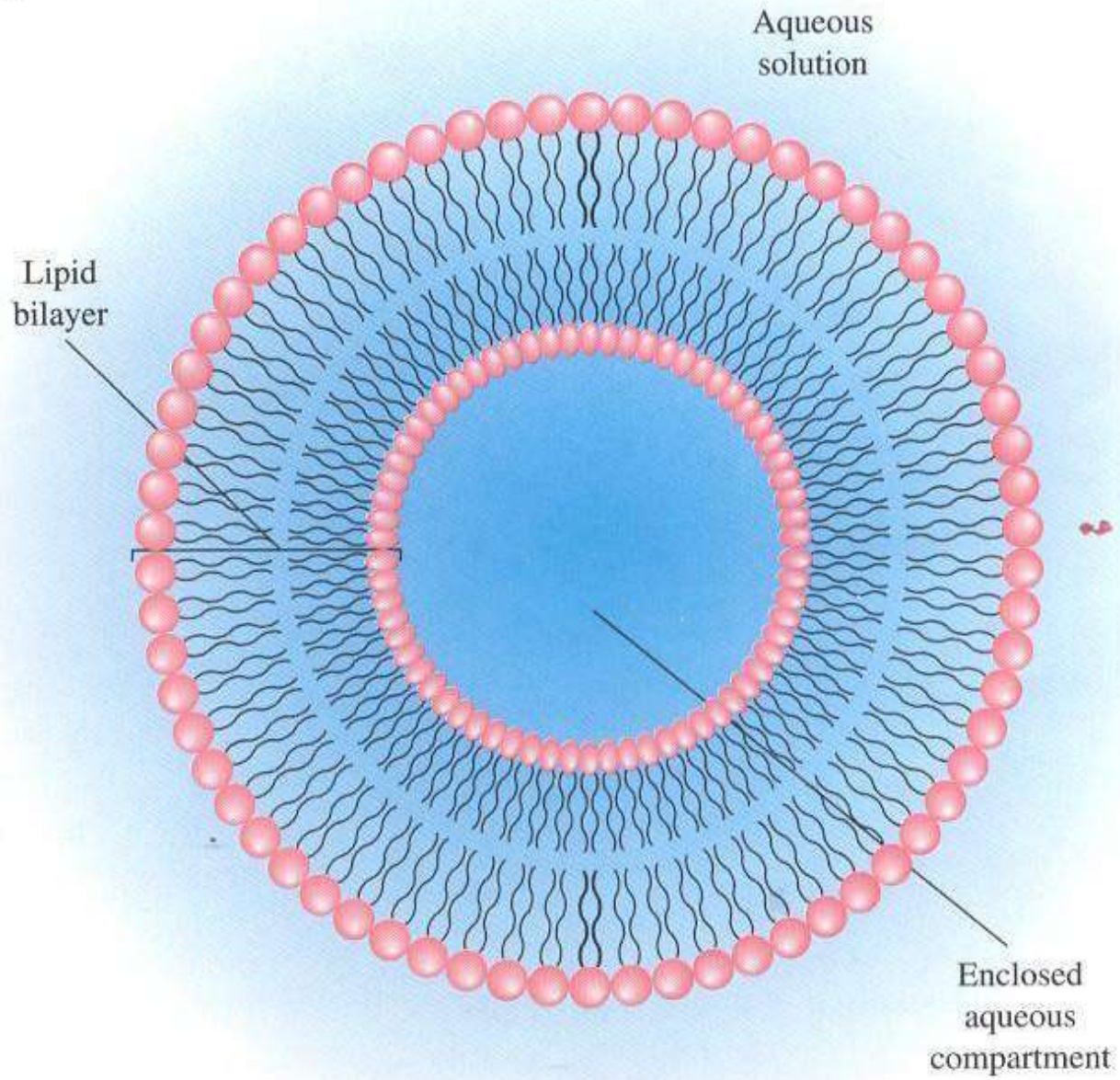
Space-filling model of a section of phospholipid bilayer membrane.

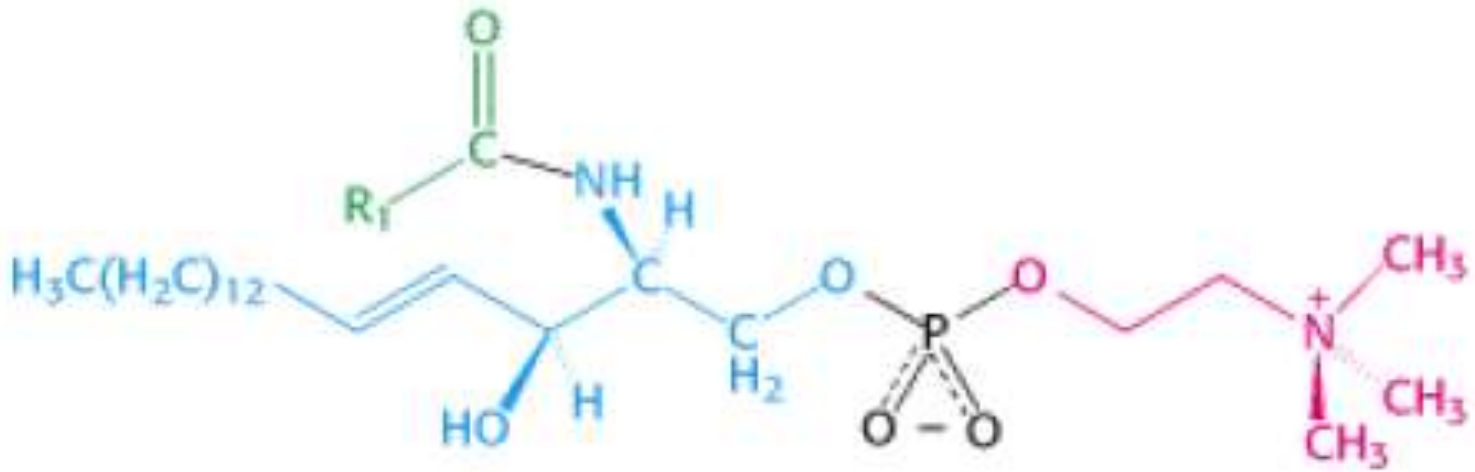


Lipid bilayer of plasma membrane

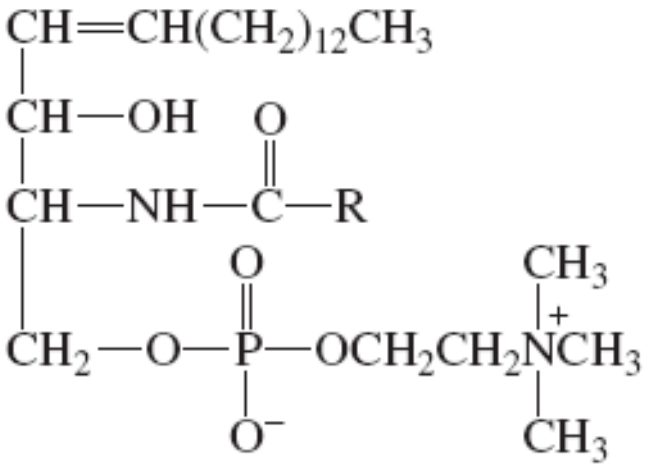


Liposome

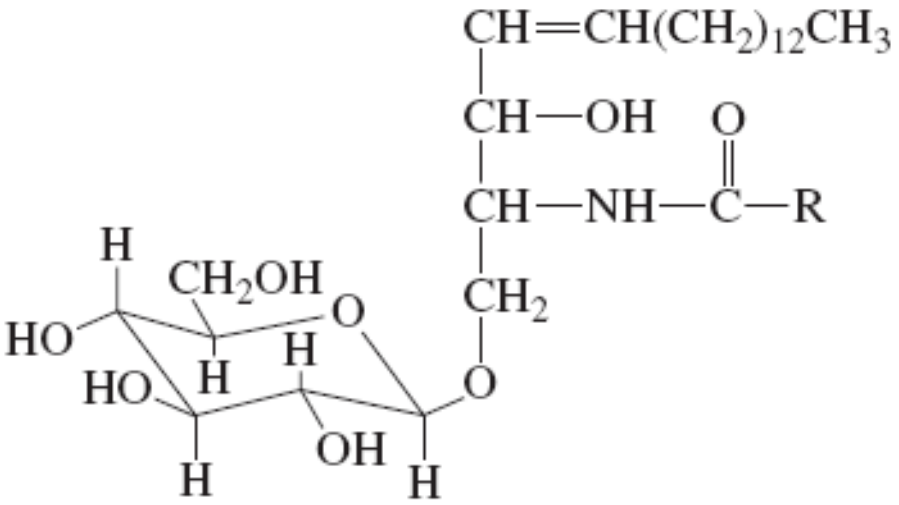

Aqueous solution
Lipid bilayer
Enclosed aqueous compartment



Sphingomyelin



a sphingomyelin

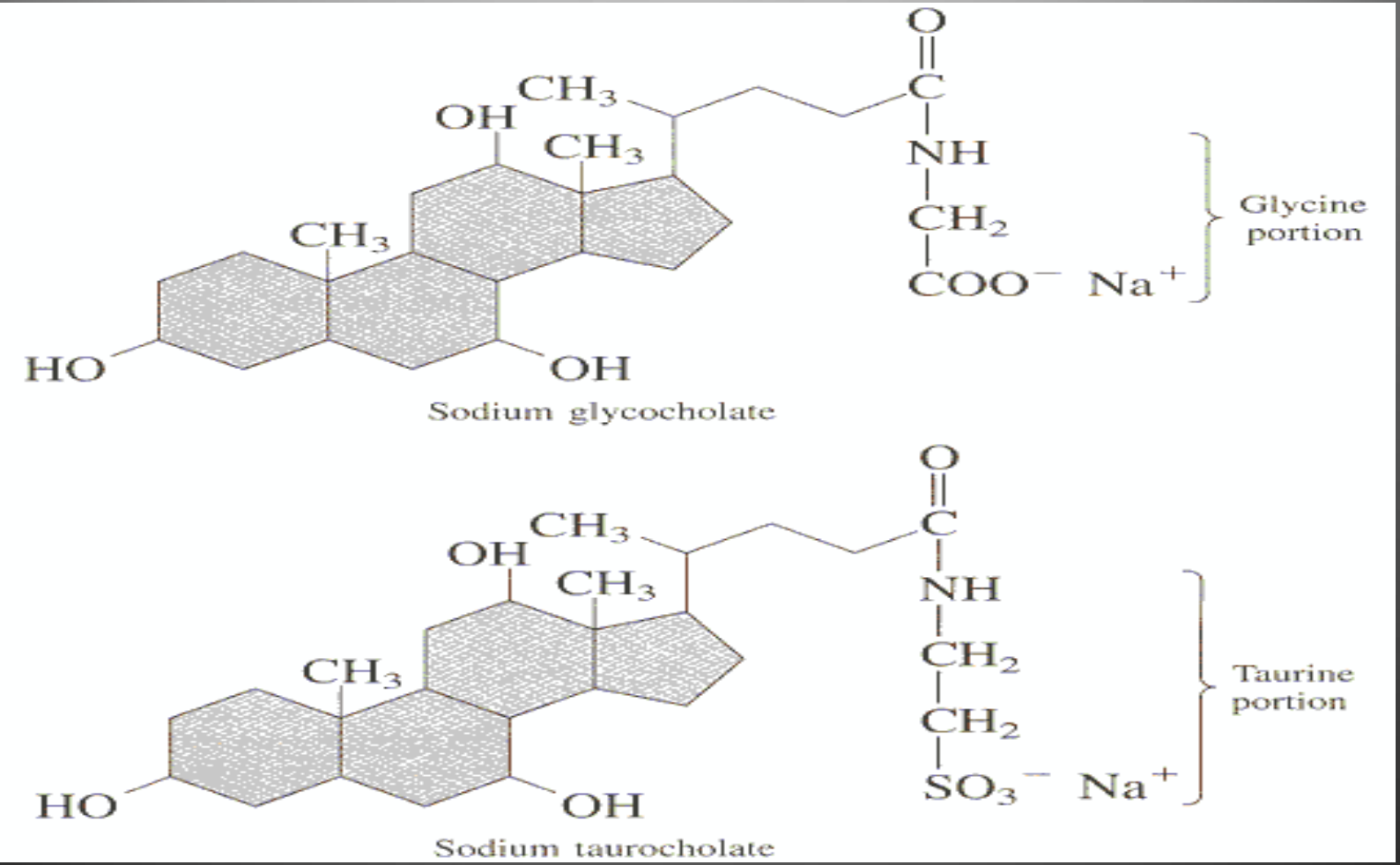


a glucocerebroside

Nonsaponifiable Lipids

- **Lipids** do not undergo hydrolysis in alkaline solution.
- **Nonsaponifiable** Lipids: steroids, eicosanoids, terpenes, pheromones, fat-soluble vitamins
- A **steroid** is a lipid whose structure is based on the tetracyclic (four-ring) system shown in the following examples. Three of the rings are six-membered, while the fourth is five-membered. Steroids have many diverse roles throughout both the plant and animal kingdoms.

Bile acids



The liver secretes a clear, golden-yellow, viscous fluid known as bile. It is stored in the gall bladder and is mainly useful for digestive system.

THANK YOU