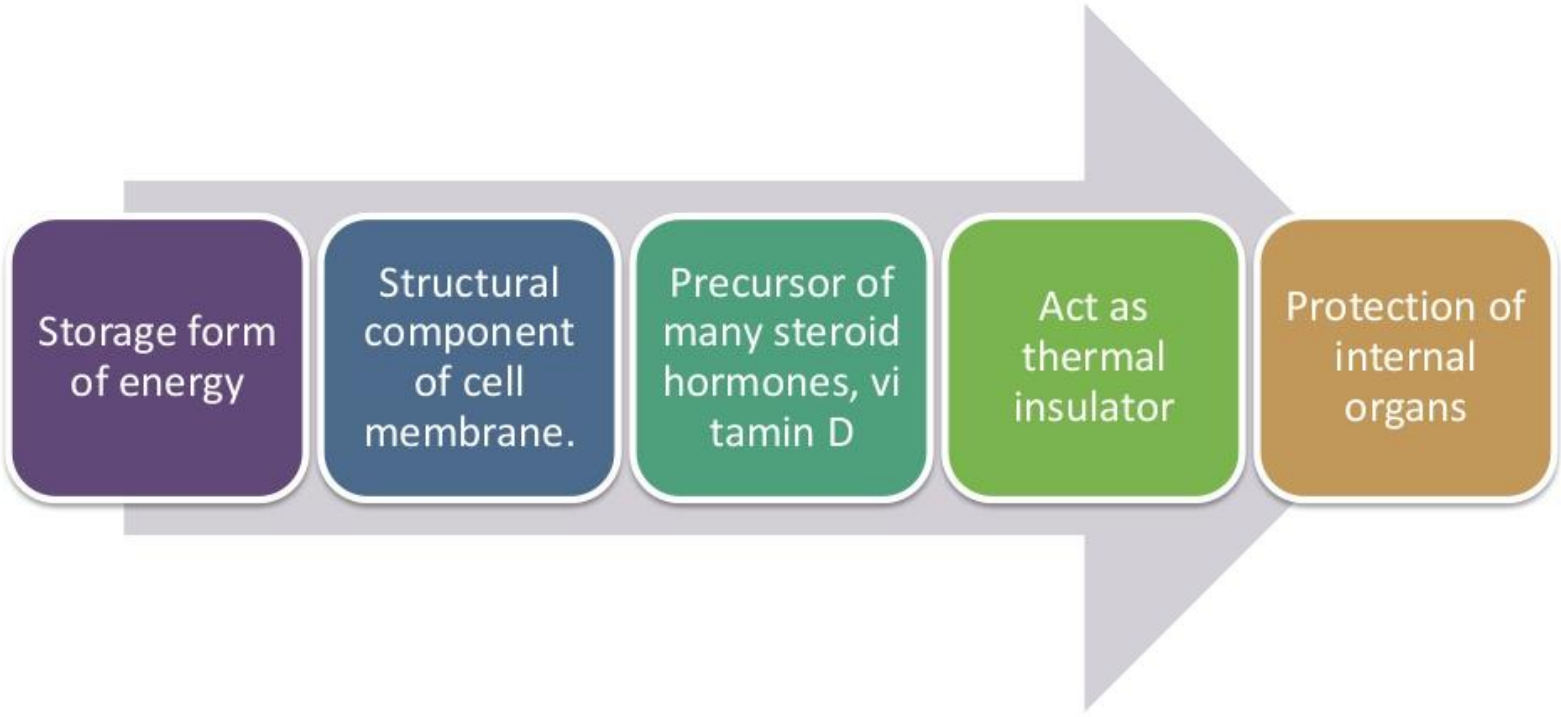
LIPIDS

LIPID CHEMISTRY

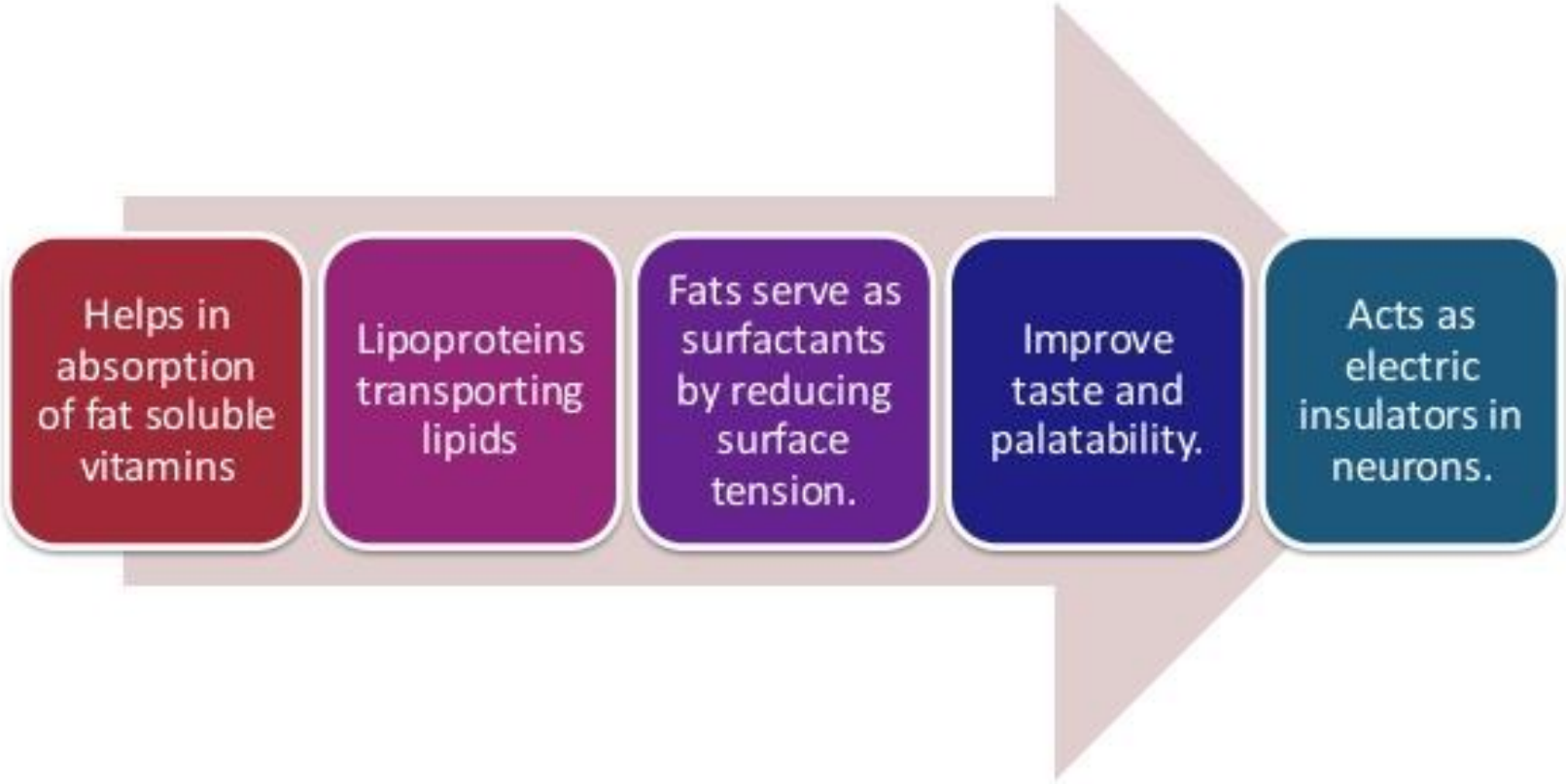
Definition

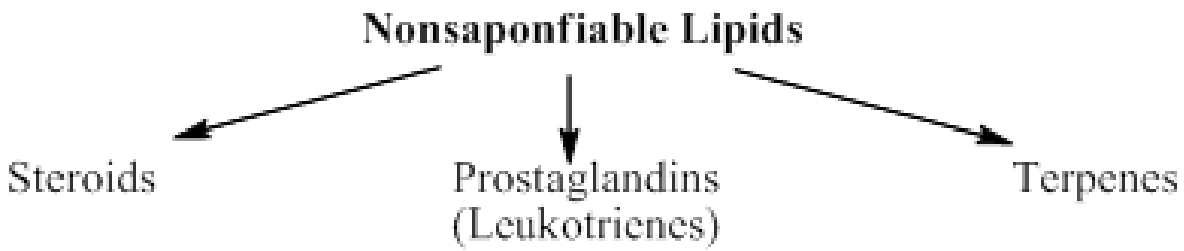
Organic substances relatively insoluble in water but soluble in organic solvents like chloroform, ether and benzene

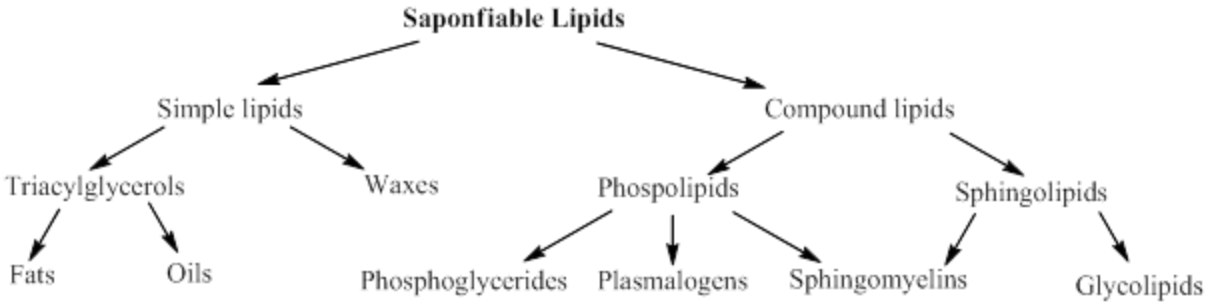
FUNCTIONS OF LIPIDS



FUNCTIONS OF LIPIDS




Nonsaponfiable Lipids
Steroids
Prostaglandins
(Leukotrienes)
Terpenes


Saponfiable Lipids
Simple lipids
Compound lipids
Triacylglycerols
Waxes
Phospolipids
Sphingolipids
Fats
Oils
Phosphoglycerides
Plasmalogens
Sphingomyelins
Glycolipids

Classification of lipids

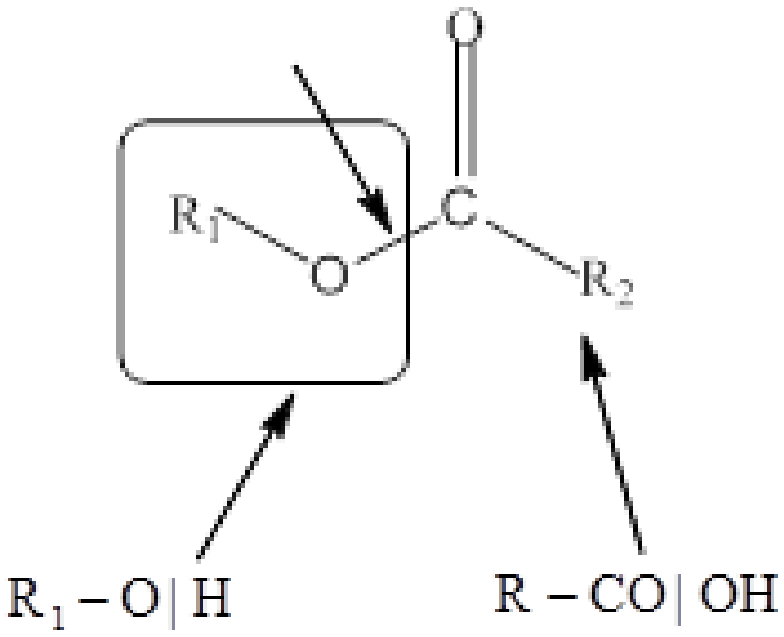
Saponifiable lipids

- contain at least one ester group, which undergoes hydrolysis in the presence of an acid, a base, or an enzyme.

Nonsaponifiable lipids

- do not undergo hydrolytic cleavage into smaller molecules.

Ester bond



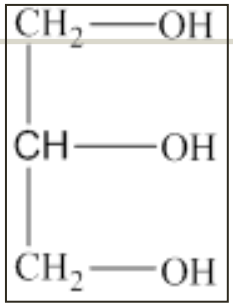
The main components of saponifiable lipids

alcohols

myricyl

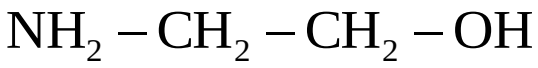
cetyl

glycerol

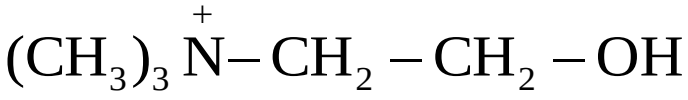


Amino compounds and orthophosphoric acid

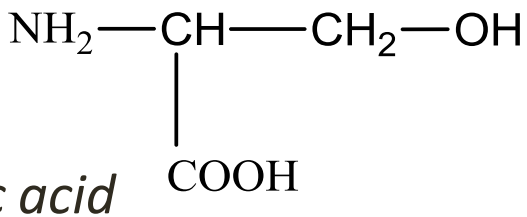
- *Colamine (ethanolamine)*



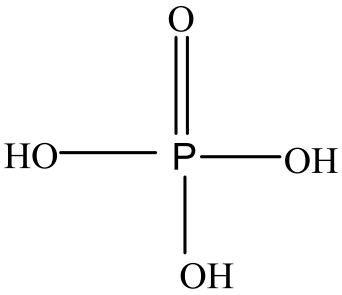
- *Choline*



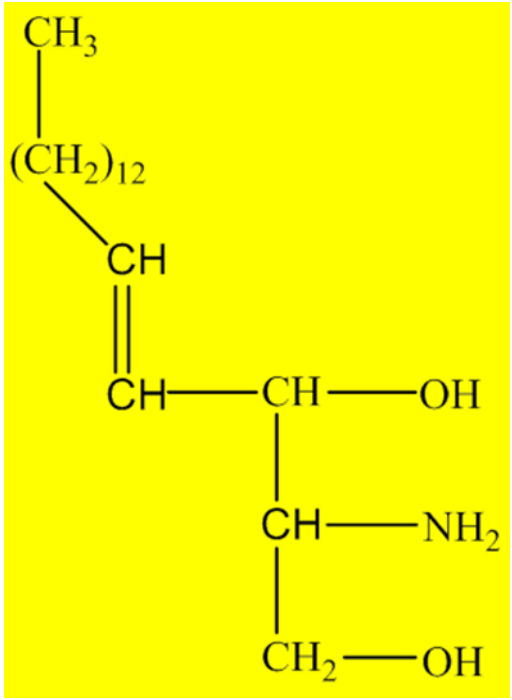
- *Serine*



- *Orthophosphoric acid*

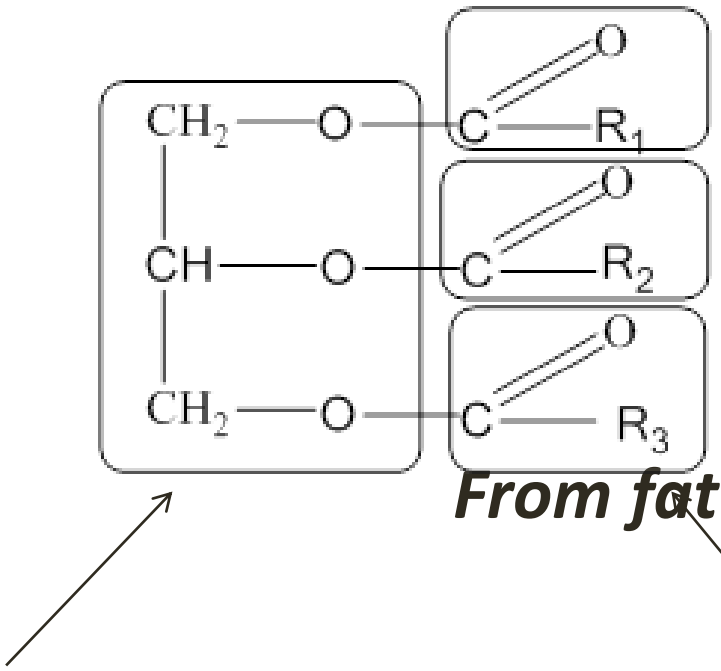


- sphingosine



Simple lipids-

- *are esters of fatty acids with various alcohols.*



From glycerol ***From fatty acids***

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.

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

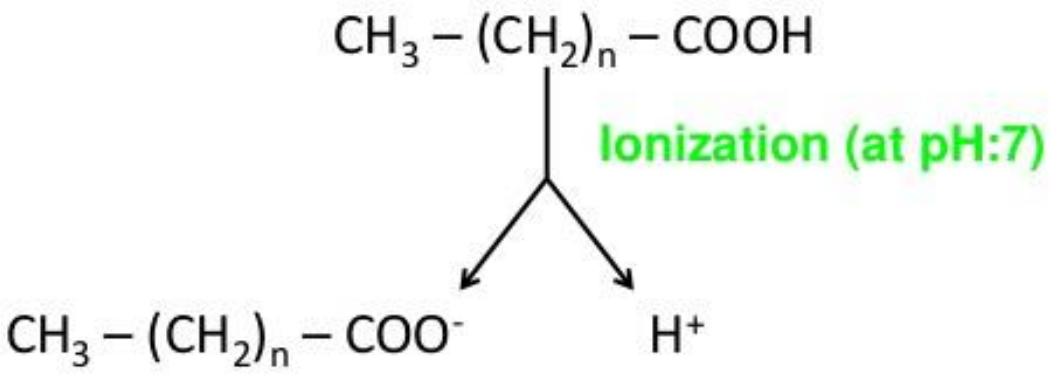
$CH_3 - CH_2 - CH_2 - COOH$ Butyric acid

4 3 2 1 *(Arabic numbers)*

γ β α *(Greek alphabetical numbers)*

1 2 3 4 *(Omega numbers)*

General Formula of Fatty Acids



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

H_2O-insoluble

polar

H_2O-soluble

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

Classification of fatty acids according to degree of saturation

- Saturated Fatty Acids
- **They do not contain double bonds**

- **Palmitic (16 C)**

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

[CH3-$(CH2)_{14}$-COOH]

- **Stearic acid (18 C)**

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

[CH3-$(CH2)_{16}$-COOH]

Unsaturated Fatty Acids

- They contain one or more double bonds
- They are named by adding suffix "enoic"
- Unsaturated fatty acids exhibit the geometrical isomerism at the double bonds.
- All naturally occurring fatty acids have the cis-configuration.

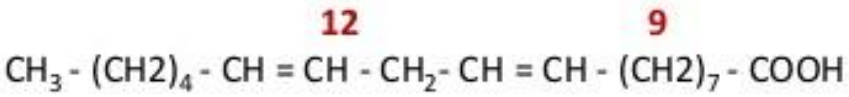
- e.g. Oleic acid (18: 1; 9) **ω**9

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

Polyunsaturated Fatty Acids

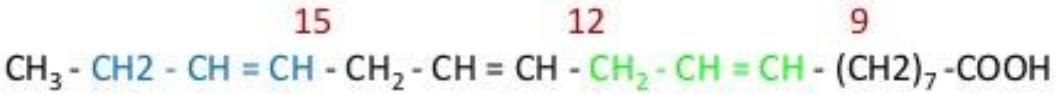
1. Dienoic fatty acids (contain 2 double bonds)

e.g. linoleic acid (18: 2 ; 9,12) ω6.



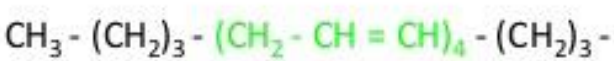
2. Trienoic fatty acids (contain 3 double bonds)

e.g. α-Linolenic (18: 3; 9,12, 15) ω3



3. Tetraenoic fatty acids (contain 4 double bonds)

e.g. Arachidonic (20: 4; 5, 8, 11, 14) ω 6



Classification of FA according to Biological Value

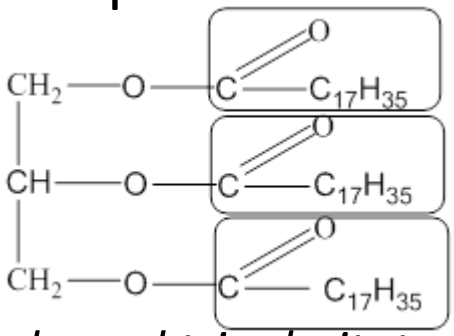
- Essential Fatty Acids:
- The FA that cannot be synthesized by the body, should be supplied through diet known as essential fatty acids.
- They are polyunsaturated fatty acids, linoleic acid and linolenic acid.

Some common *fatty acids*

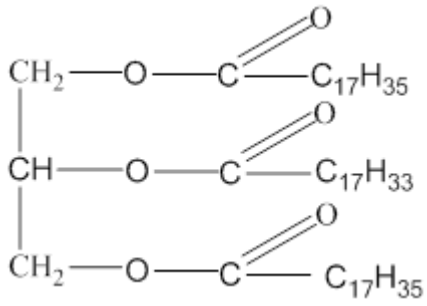
Some common ***fatty acids***

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

- **Fats** are triglycerides in which saturated fatty acids components predominate; they are solids at room temperature.
- **Oils** are triglycerides in which unsaturated fatty acids components predominate; they are liquids at room temperature.

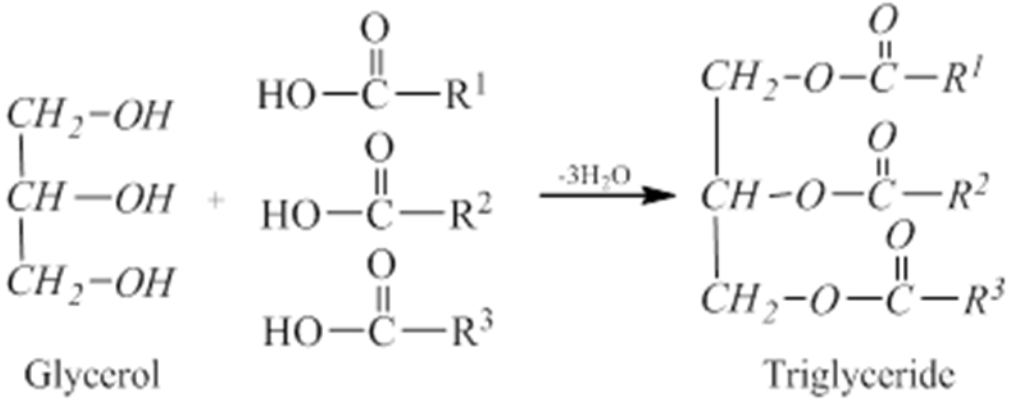


- *glyceryl tripalmitate*



2-oleoil-1,3-distearoilglycerol

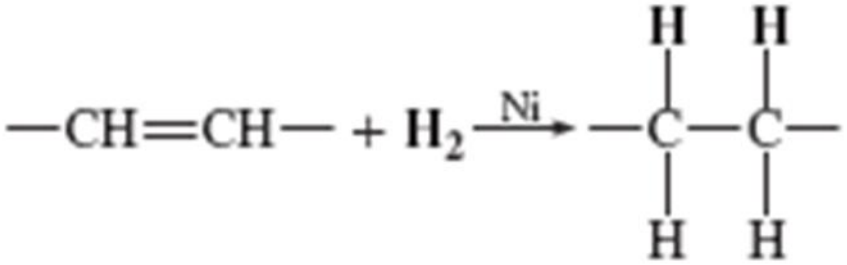
- Each of the three *OH* groups of glycerol forms an ester group by reaction with the *COOH* group of a fatty acid to form the triacylglycerol:



Chemical Properties of Triacylglycerols

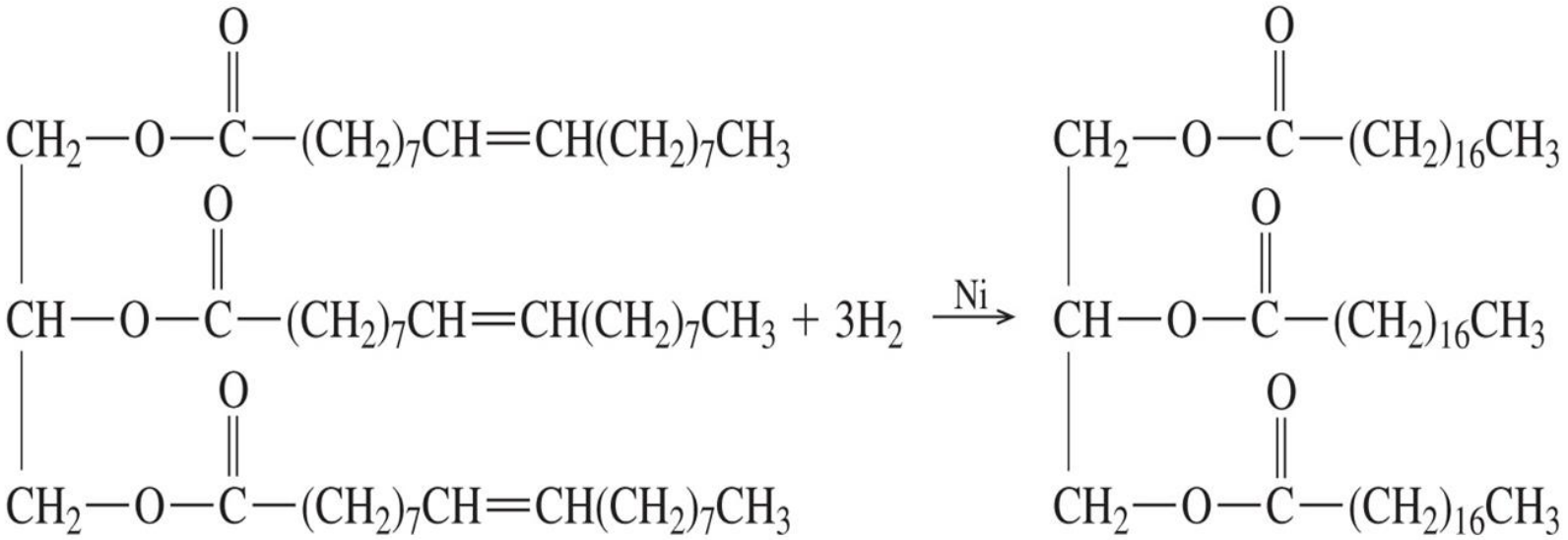
The chemical reactions of triacylglycerols are similar to those of alkenes and esters.

- In **hydrogenation**, double bonds in unsaturated fatty acids react with H_2 in the presence of a Ni or Pt catalyst.



- In **hydrolysis**, ester bonds are split by water in the presence of an acid, a base, or an enzyme.

Hydrogenation of Glyceryl Trioleate



Glyceryl trioleate (triolein)

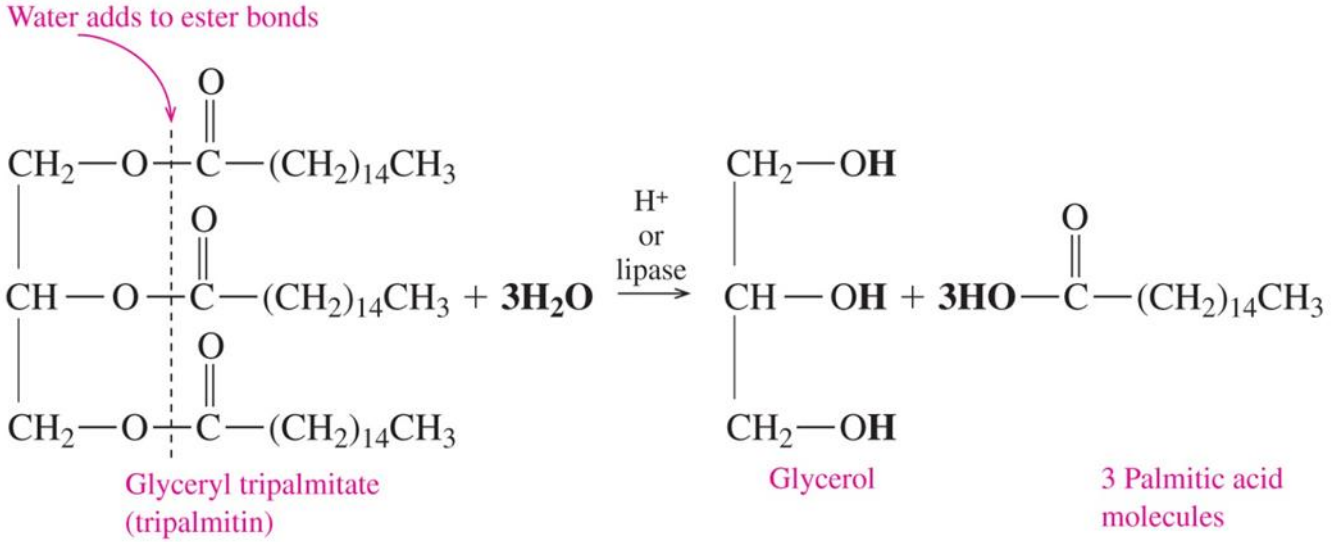
Glyceryl tristearate (tristearin)

© 2010 Pearson Education, Inc.

Hydrolysis

In **acid** or **enzyme hydrolysis**,

- water adds to the ester bonds
- triacylglycerols split into glycerol and three fatty acids
- an acid or enzyme catalyst is required



© 2010 Pearson Education, Inc.

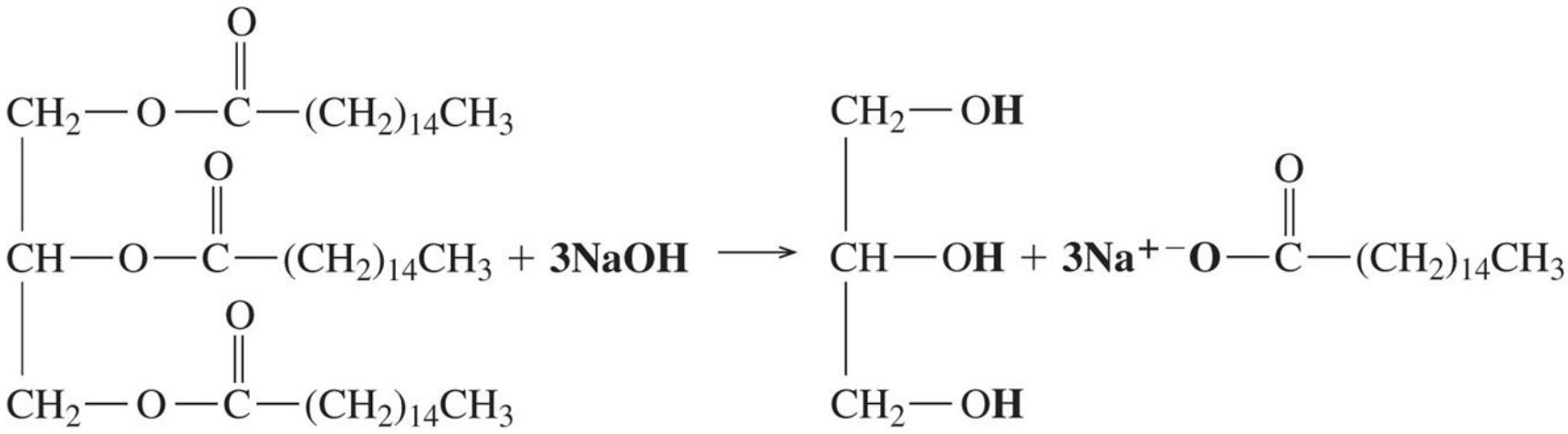
Base Hydrolysis (Saponification)

In **base hydrolysis (saponification)**,

- a triacylglycerol reacts with a strong base
- a triacylglycerol splits into glycerol and the salts of fatty acids
- soaps (salts of fatty acids) form

Saponification

Fat or oil + strong base ⟶ glycerol + salts of fatty acids (soaps)

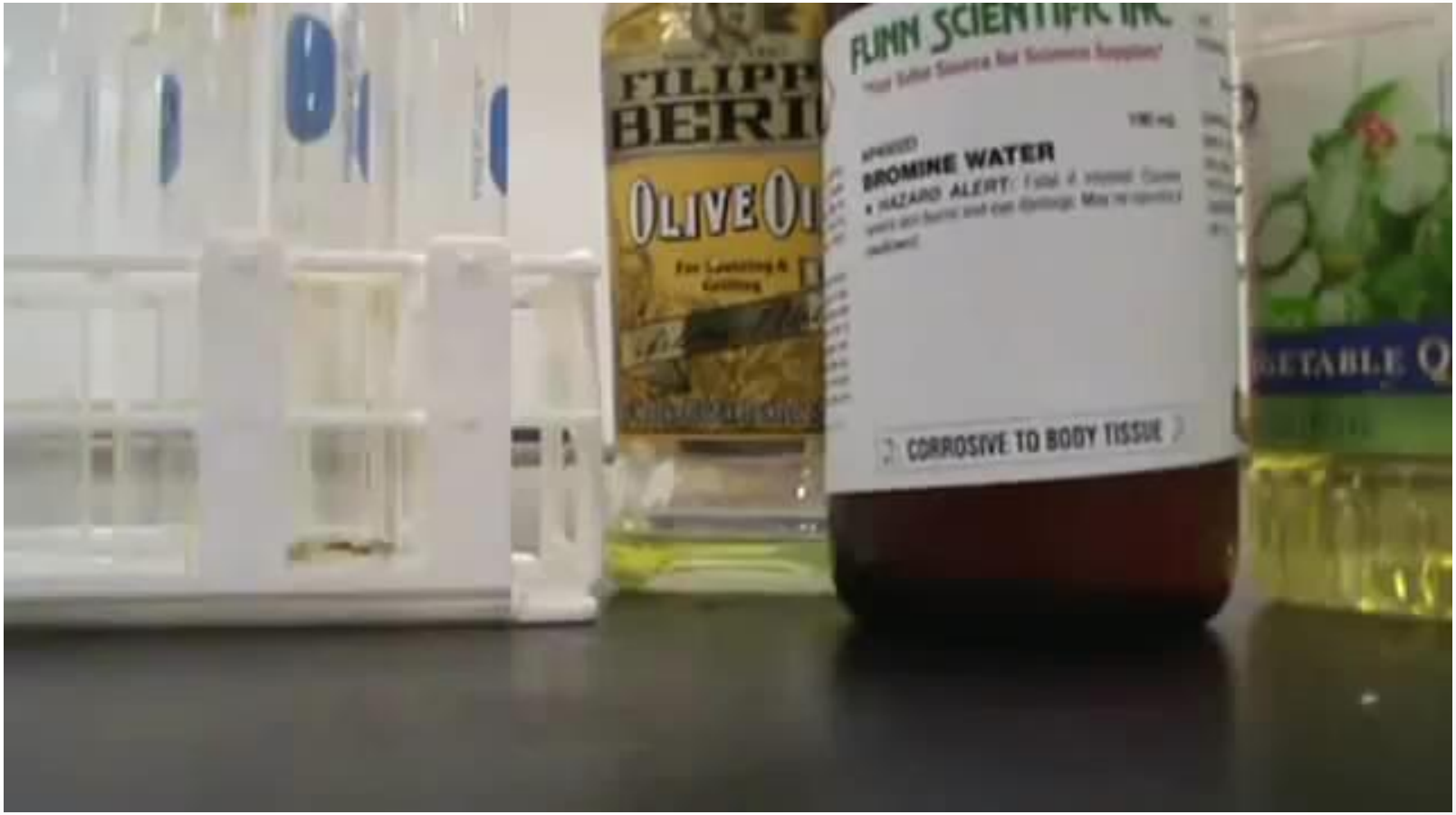


Glyceryl tripalmitate (tripalmitin)

Glycerol

3 Sodium palmitate (soap)

© 2010 Pearson Education, Inc.


FLINN SCIENTIFIC INC
BROMINE WATER
CORROSIVE TO BODY TISSUE

The **iodine number** of a triglyceride

- is the number of grams of iodine reacting with 100g of the triglyceride.
- The iodine number indicates the degree of unsaturation in the fatty acid components.

Saponification value

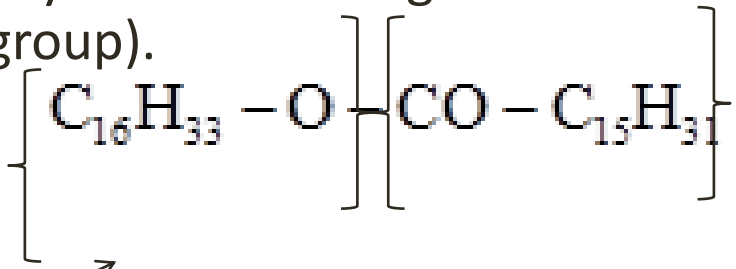
- The number of milligrams of KOH required to saponify 1.00 g of the glyceride
- Saponification reaction can be used in the laboratory to yield information about the structures of glycerides

Acid value (or "neutralization number" or "acid number" or "acidity")

The number of milligrams of potassium hydroxide required to neutralize the free fatty acid in one gram of a fat or oil.

Waxes

- are esters of fatty acids with long chain monohydric alcohols (one hydroxyl group).



Spermaceti

From cetyl alcohol

From palmitic acid

Beeswax

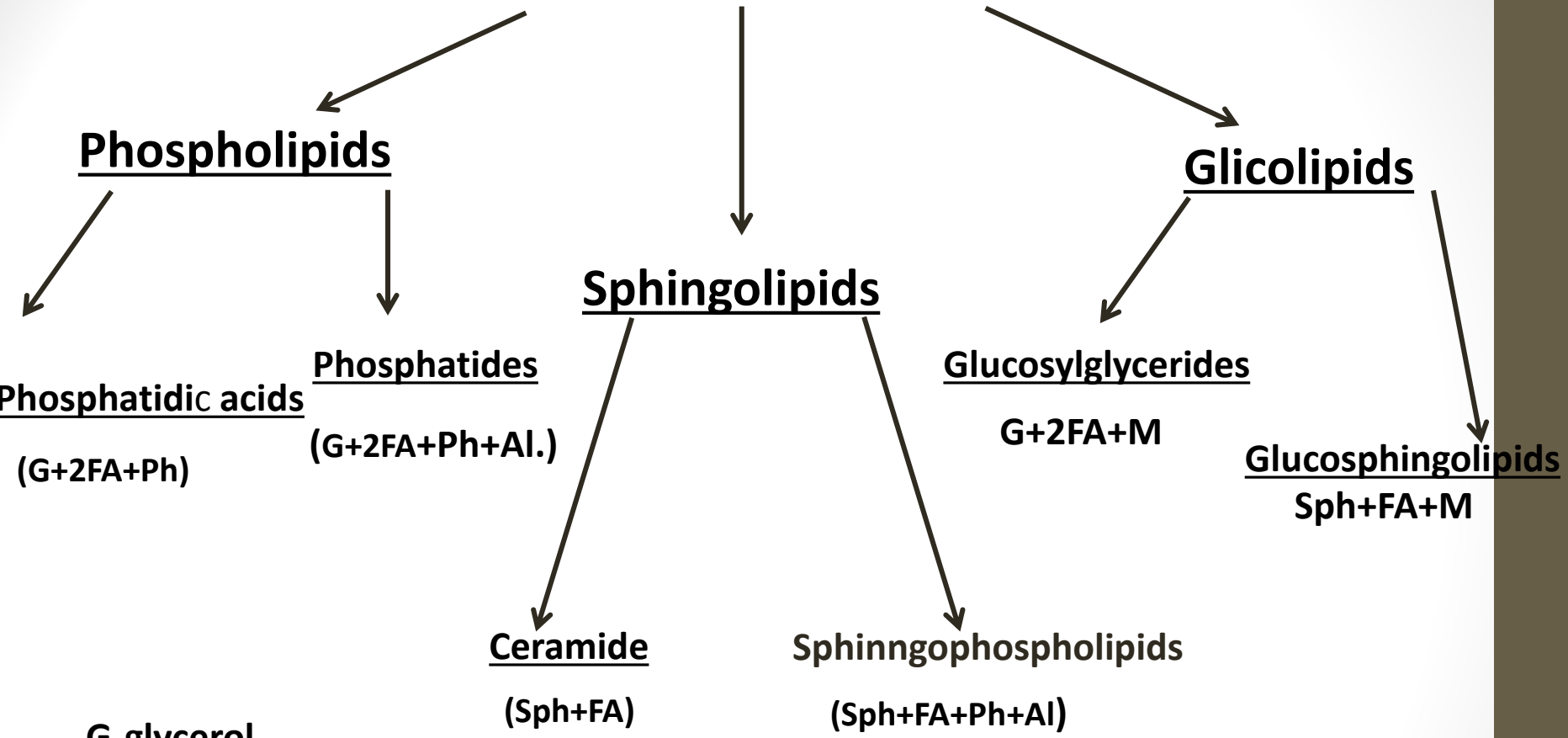
From miricyl alcohol

From palmitic acid

Compound lipids

- Lipids, which are hydrolyzed to generate an alcohol, fatty acids , phosphoric acid, amino compounds, carbohydrates are called compound.

Compound lipids



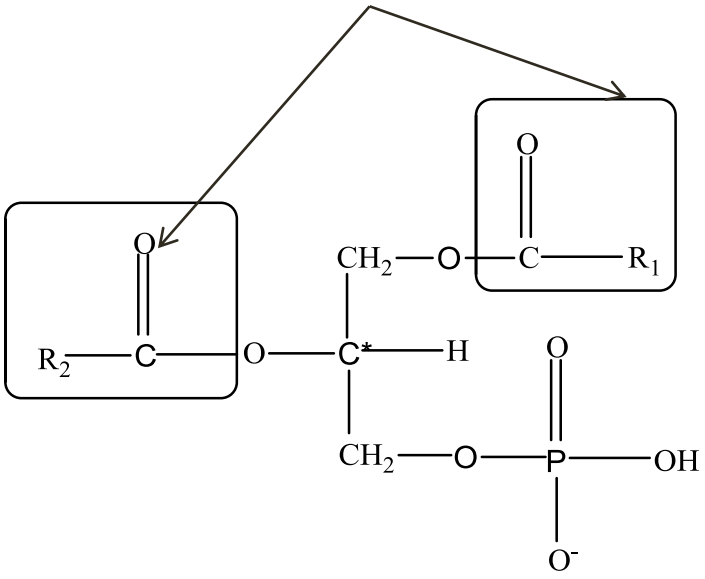
G-glycerol
FA-fatty acids
Ph- Phosphate
Al- alcohol
Sph-sphingosine
M.-monosaccharide

Phospholipids

- They are hydrolased to form phosphoric acid

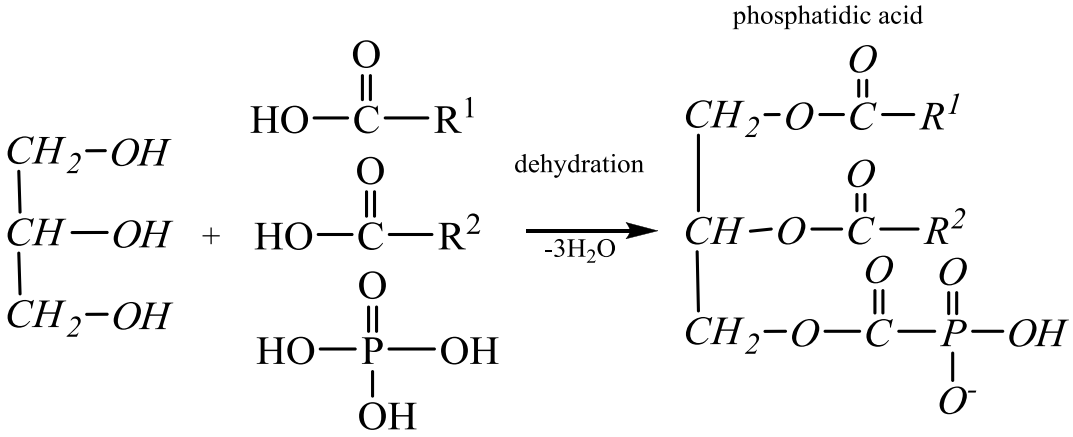
Phosphatidic acids

From fatty acids

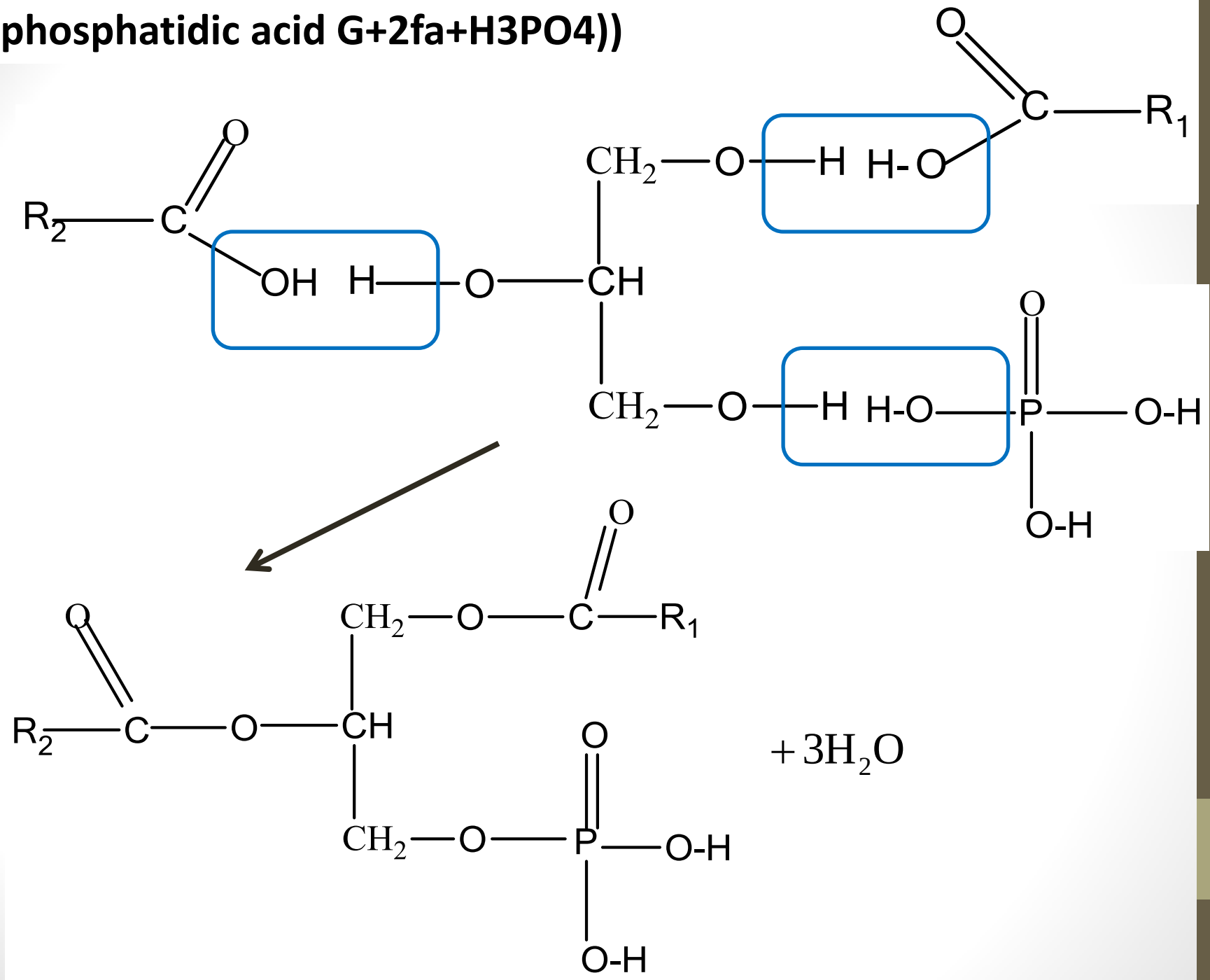


Phosphatidic acid

- A phosphoglyceride forms by reaction of glycerol with two fatty acids and one phosphoric acid to form phosphatidic acid

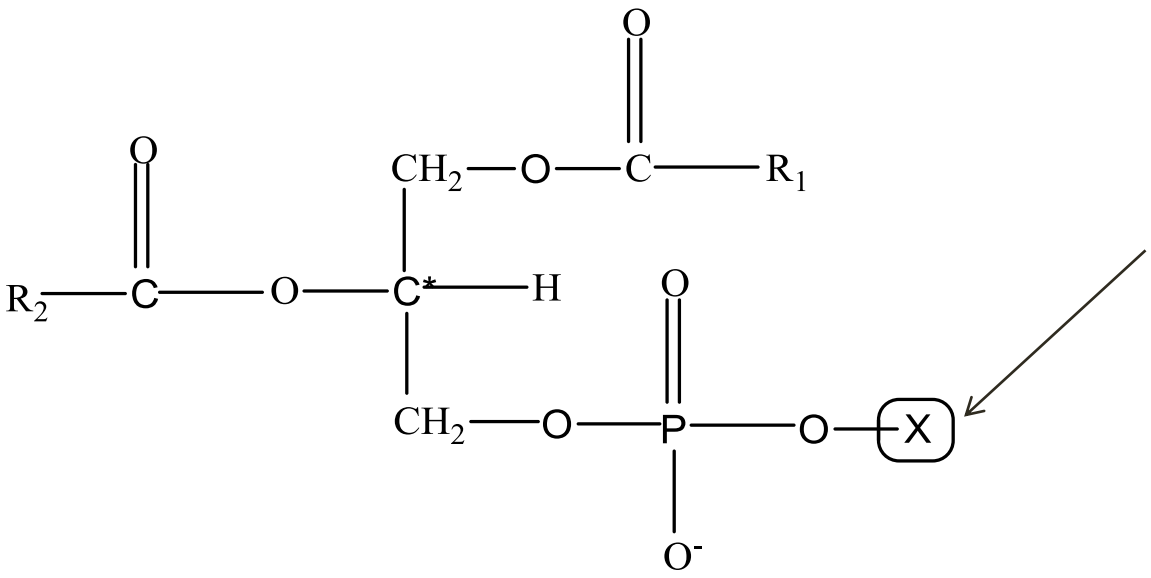


(phosphatidic acid G+2fa+H3PO4))



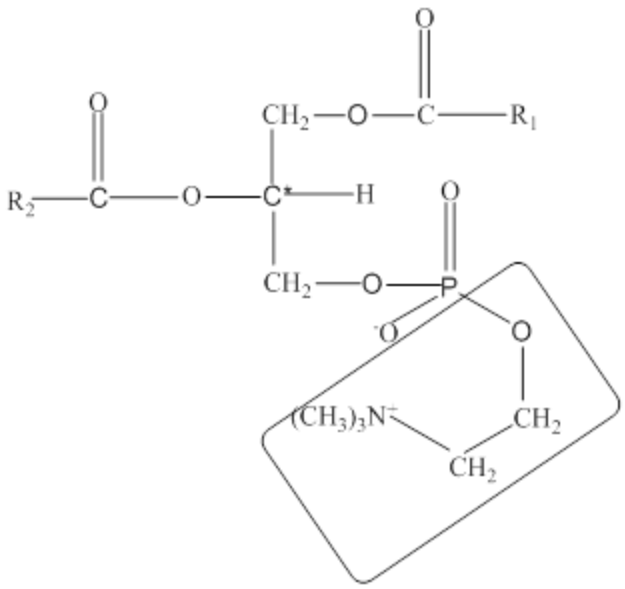
Phosphatides

- are ester derivatives of phosphatidic acid



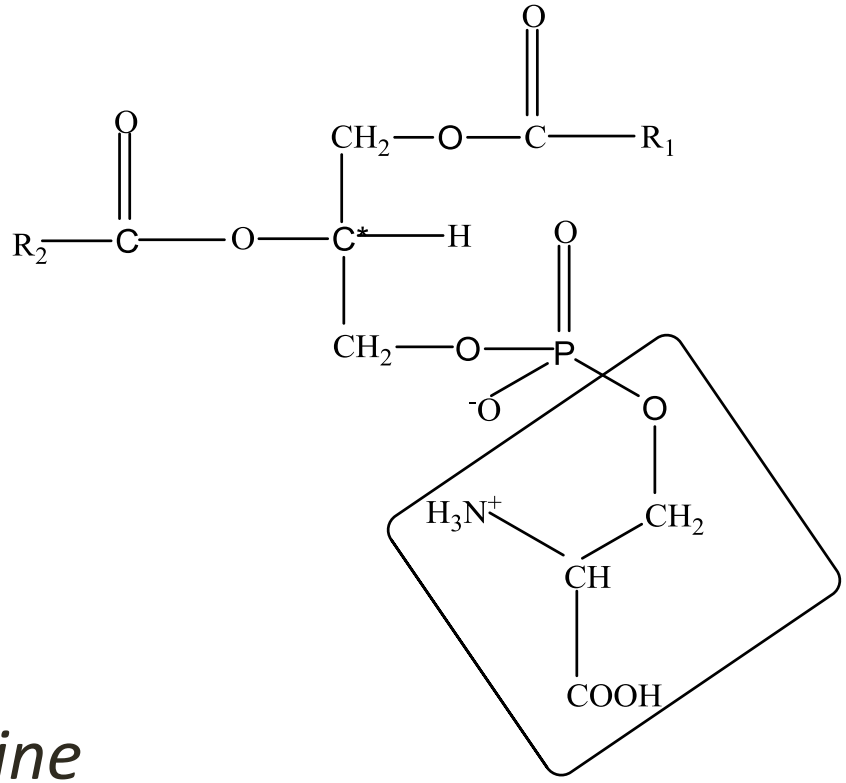
Colamine (ethanolamine)
Choline
Serine

X is *choline*



lecithin

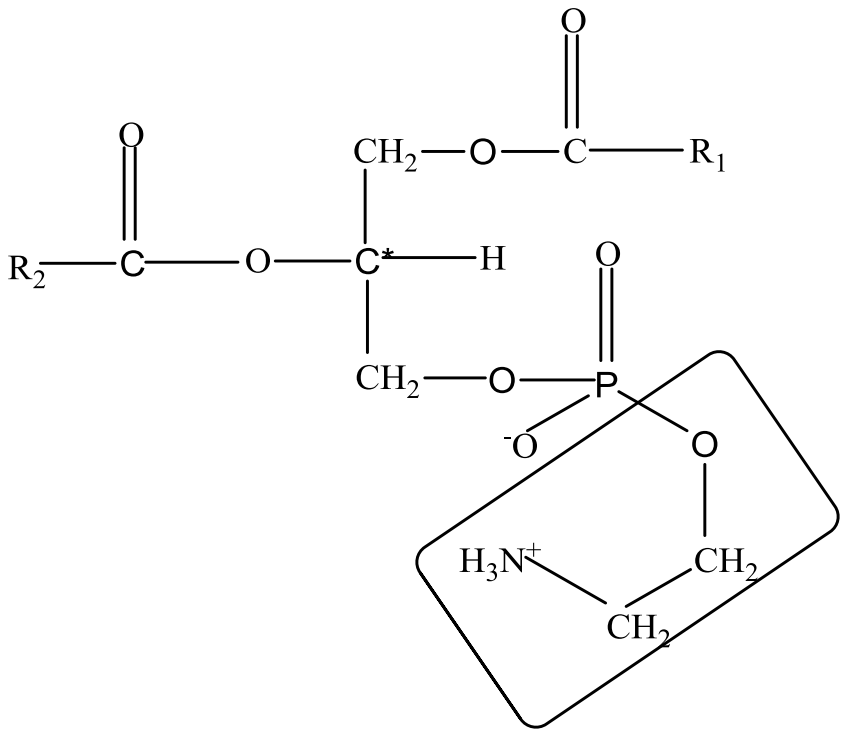
X is serine



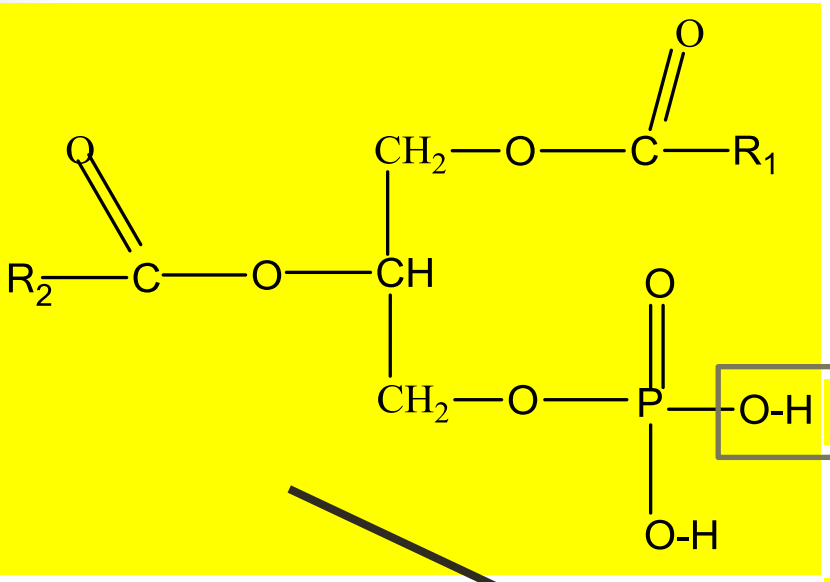
phosphatidyl serine

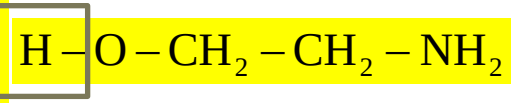
X is *colamine (ethanolamine)*

- *Phosphatidyl Colamine*



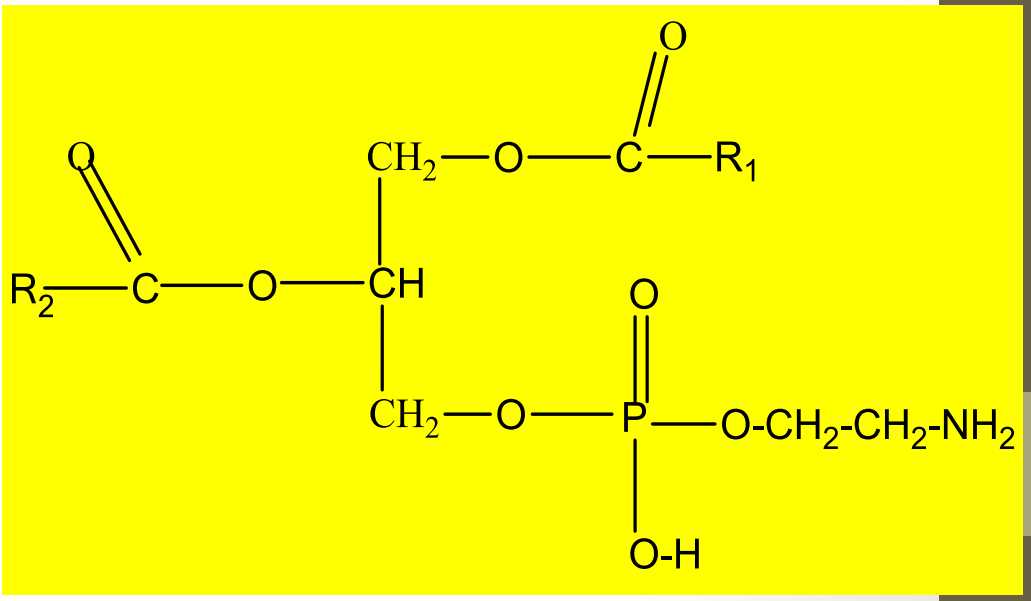
Phosphatides (G+2FA+Ph+Al)= Phosphatidic acid+aminoalcogol)





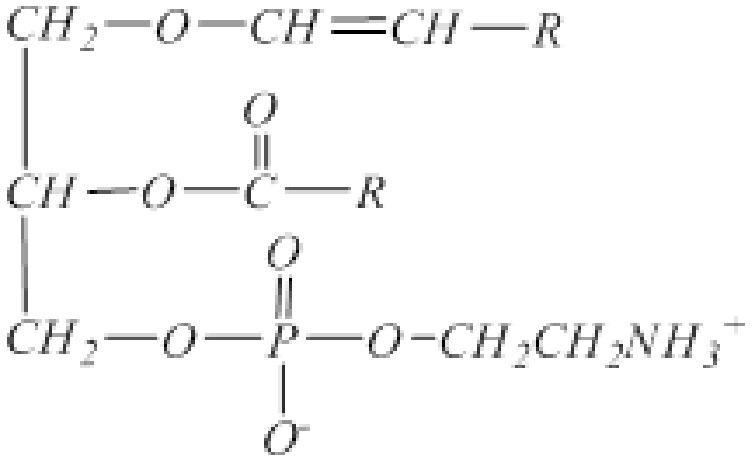
colamine (ethanolamine)

$-H_2O$



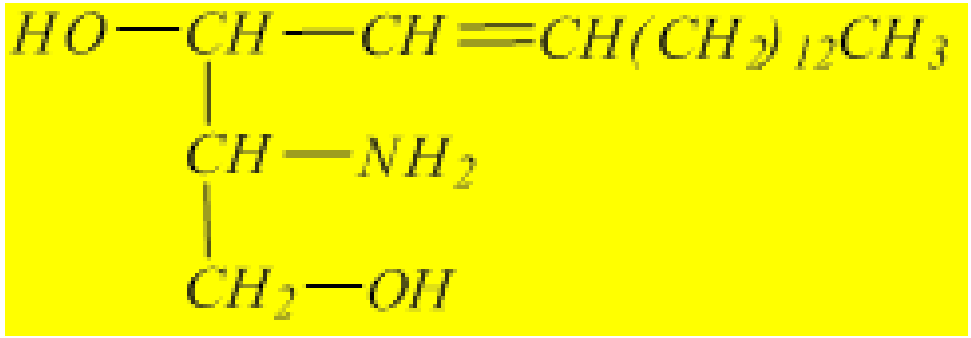
Plasmalogen

- are similar to phosphoglycerides except that the fatty ester unit at C-1 is replaced by a fatty vinyl ether unit (-O-CH=CH-R)

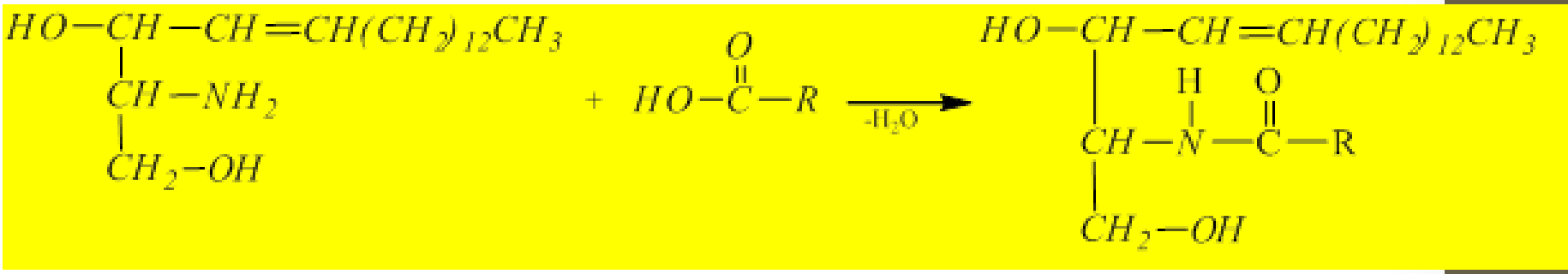


Sphingolipids

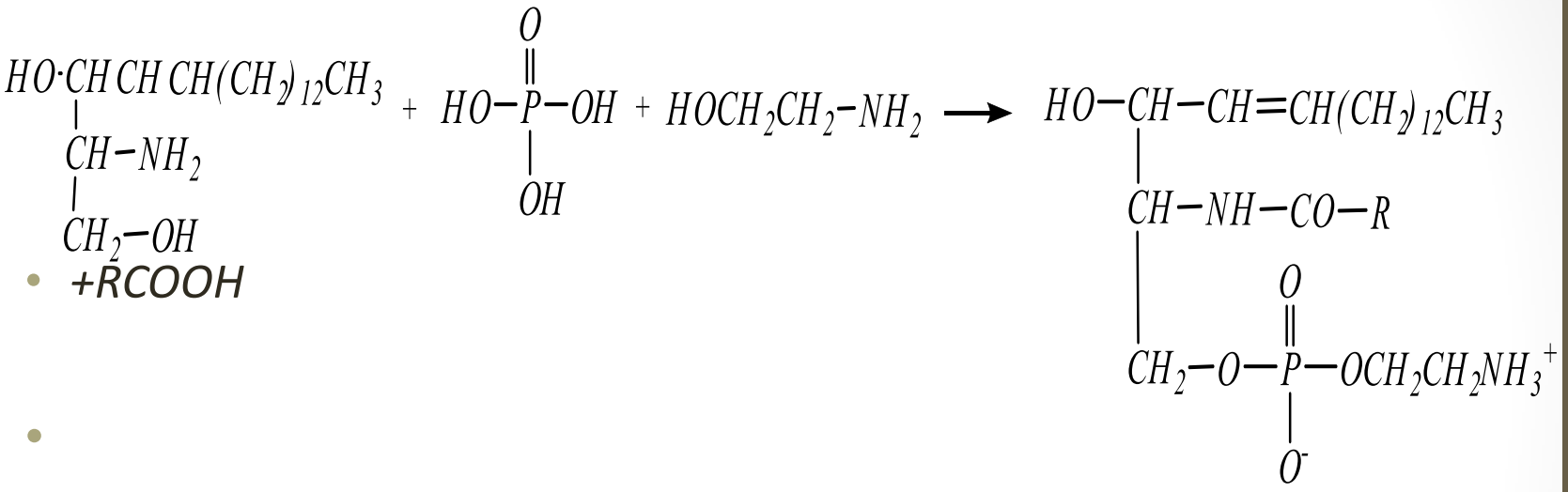
- are based on sphingosine instead of glycerol:



Ceramide


HO–CH–CH=CH(CH2)12CH3
CH–NH2
CH2–OH
+
HO–C–R
O
-H2O
HO–CH–CH=CH(CH2)12CH3
CH–N–C–R
H
O
CH2–OH

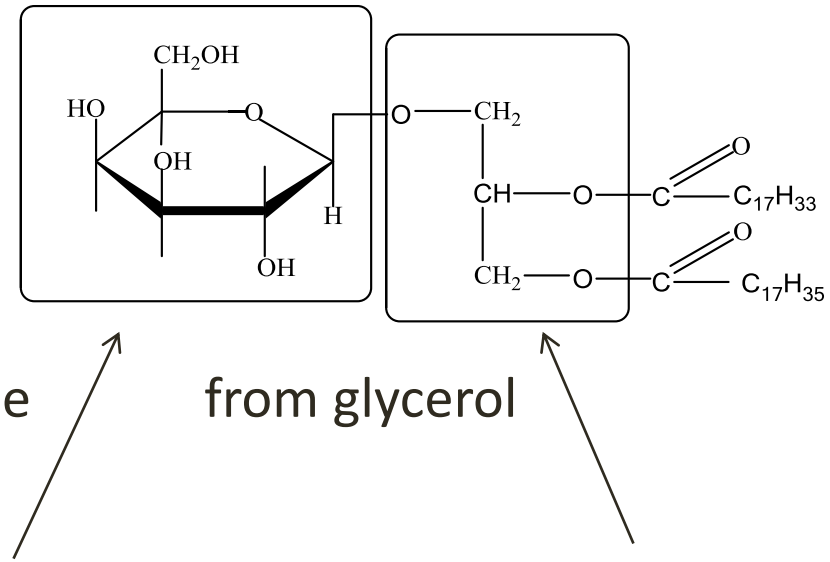
Sphingophospholipids



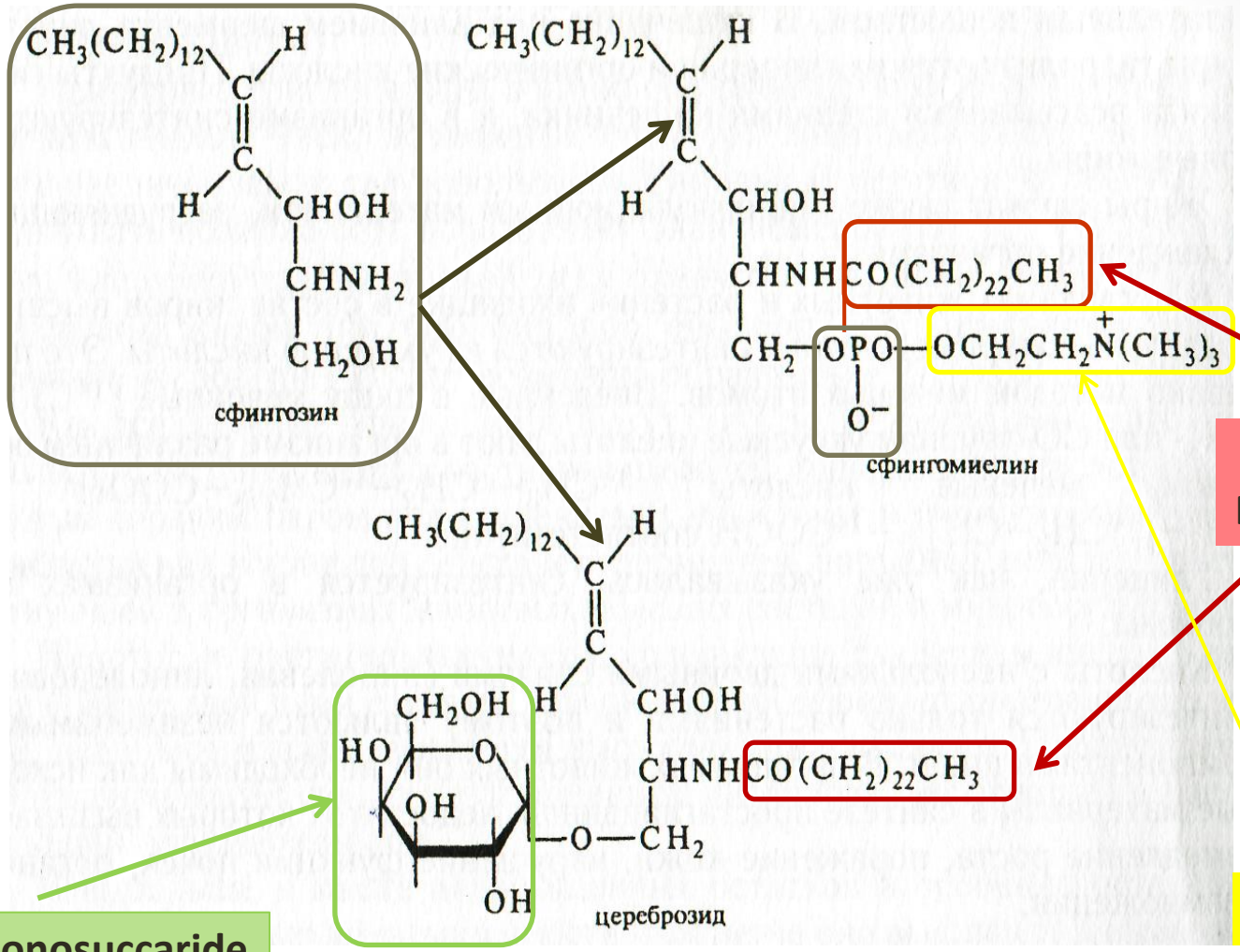
- +RCOOH

Glycolipids

- Glycolipids - esters of fatty acids, glycerol or Sphingosine which also contains: carbohydrate components (glucose, galactose, etc.).



- from galactose from glycerol



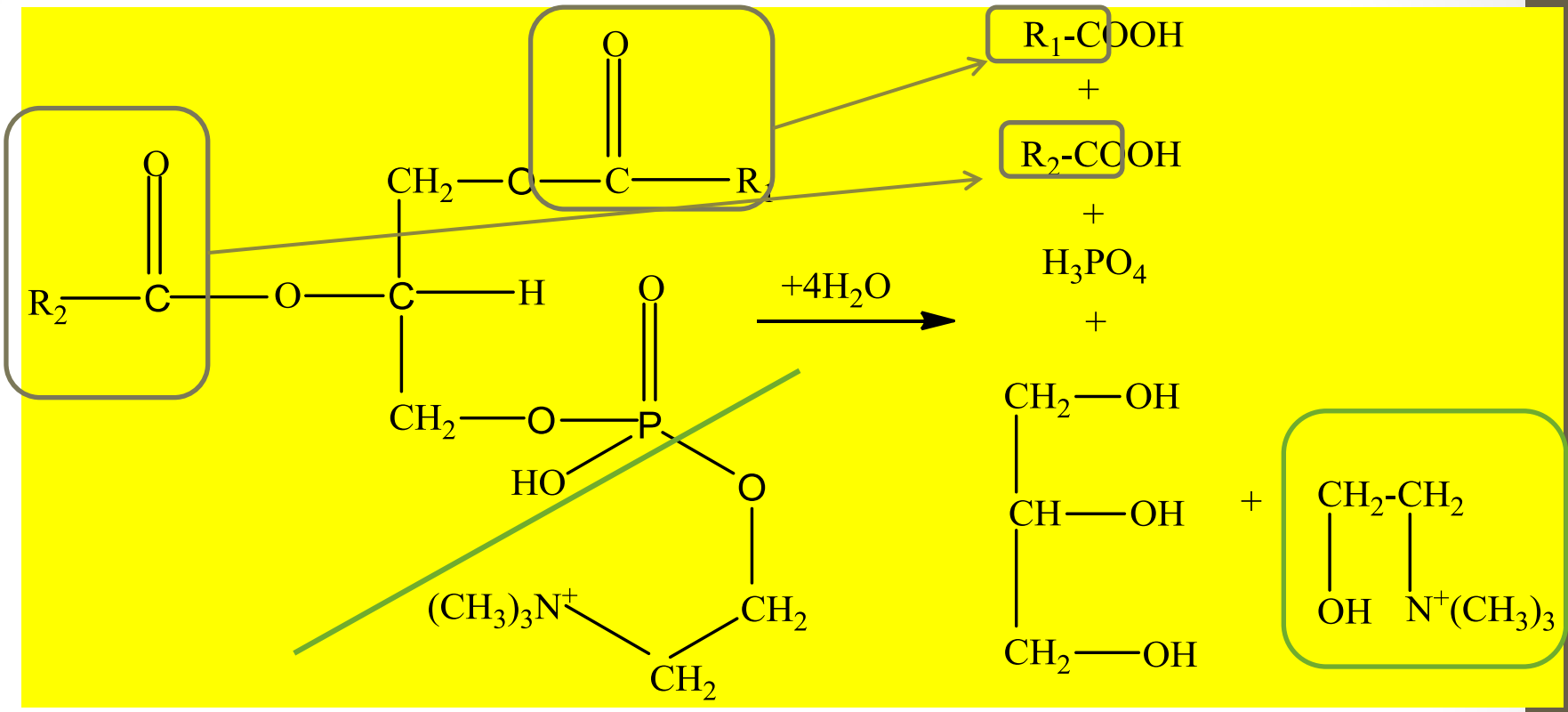
From fatty acid

From choline

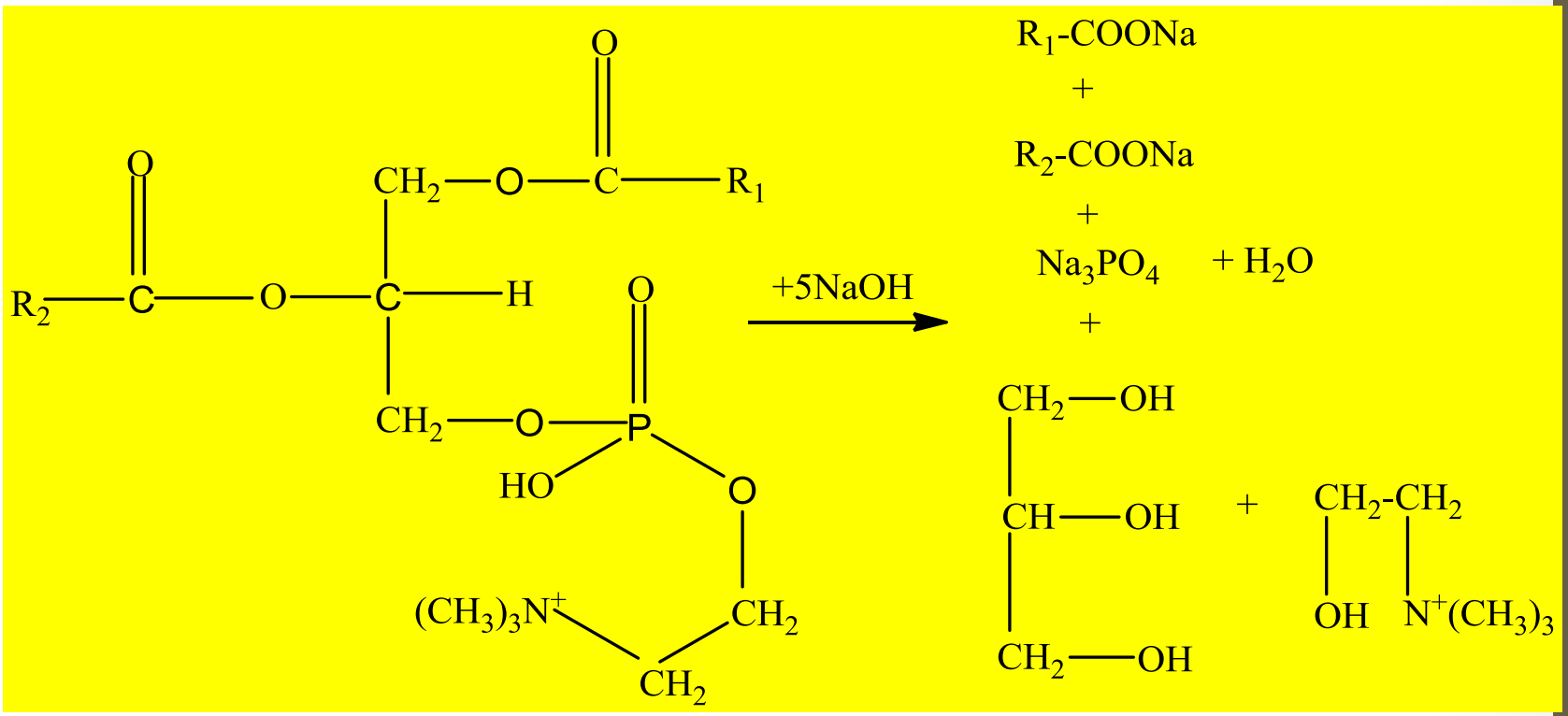
From monosuccaride

glucophospholipid

Acidic hydrolysis of compound lipids



Saponification of compound lipids

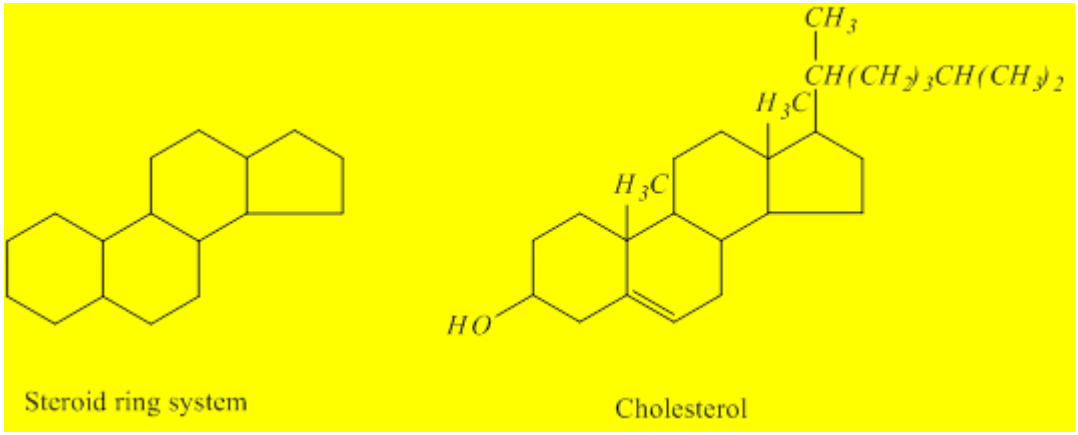


NONSAPONIFIABLE LIPIDS

- **Nonsaponifiable** lipids are not cleaved into smaller molecules by hydrolysis because of the absent of ester groups.

Steroids

- contain a four-ring system of three 6-membered rings and one 5-membered ring:



Steroid ring system

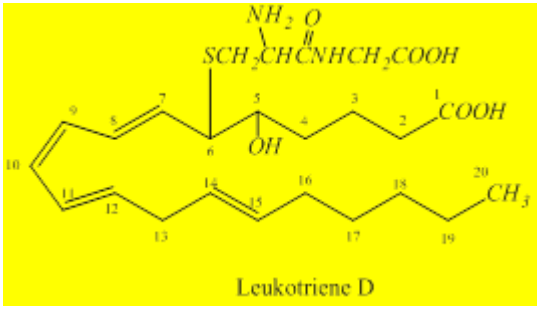
Cholesterol

Cholesterol

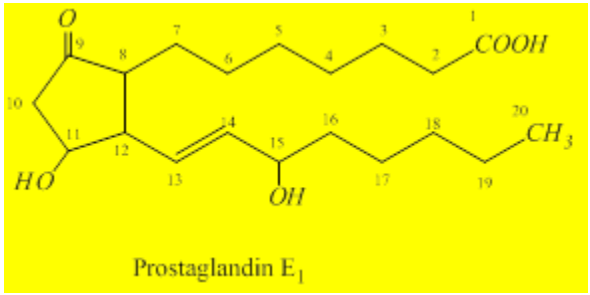
- Cholesterol, the most abundant steroid, is an important constituent of cell membranes and the starting material for biosynthesis of the steroids.
- This includes the sex hormones, such as progesterone, estradiol, testosterone, and androsterone, adrenocortical hormones such as aldosterone and cortisone, bile salts, and vitamin D.

Leukotrines

- contain 20 carbons in a continuous chain with a *COOH* group at one end.
- Prostaglandins are similar to the leukotrienes except that there is a 5-membered ring as part of the 20-carbon chain.



Leukotriene D



Prostaglandin E_1

Terpenes

- contain multiples of five carbons since they are synthesized by linking together isoprene units.
- The isoprene unit is a branched C 5 unit. Vitamines A (trans-retinol), D, and E are terpenes.

The isoprene unit is a branched C 5 unit. Vitamines A (trans-retinol), D, and E are terpenes.