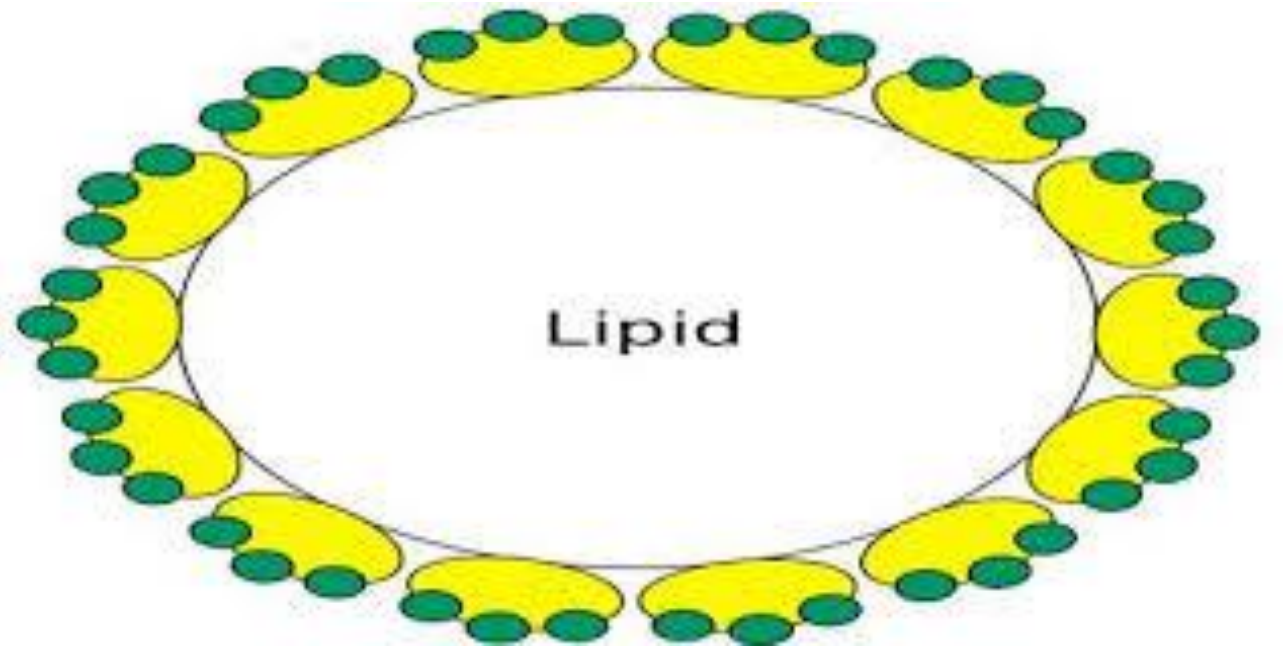
Biochemistry
Lipids



Dr. Sura Mohsin

Learning Objectives

- Definition and classification
- Fatty acids
- Triglycerides neutral fats and oils
- Triglycerides reactions
- Waxes
- Phospholipids
- Sphingolipids
- Biological membrane
- Isoprenoids
- Terpenes
- Steroids
- Prostaglandines

Lipids

Definition

Lipids are organic compounds that are found in living organisms. They have variety of structures and functions, and soluble in organic solvents due to their hydrocarbon component.

These organic compounds are insoluble in water but soluble in organic solvents like chloroform, ether and benzene.

Lipid Properties

- Lipids are oily or greasy nonpolar molecules, stored in the adipose tissue of the body.
- Lipids are energy-rich organic molecules, which provide energy for different life processes.
- Lipids are a class of compounds characterized by their solubility in nonpolar solvents and insolubility in water.
- Lipids are significant in biological systems as they form a mechanical barrier dividing a cell from the external environment known as the cell membrane.

• Lipids are the waxy, greasy, or oily compounds found in plants and animals.

– wax coating that protects plants

– structural components (cell membranes)

– insulation against cold

Classification of Lipids

Lipids are divided into:

Saponifiable lipids : contain esters, which can undergo saponification (hydrolysis under basic conditions) (waxes, triglycerides, phosphoglycerides, sphingolipids)

Nonsaponifiable lipids: do not contain ester groups, and cannot be saponified (steroids, prostaglandins. Isoprenoids)

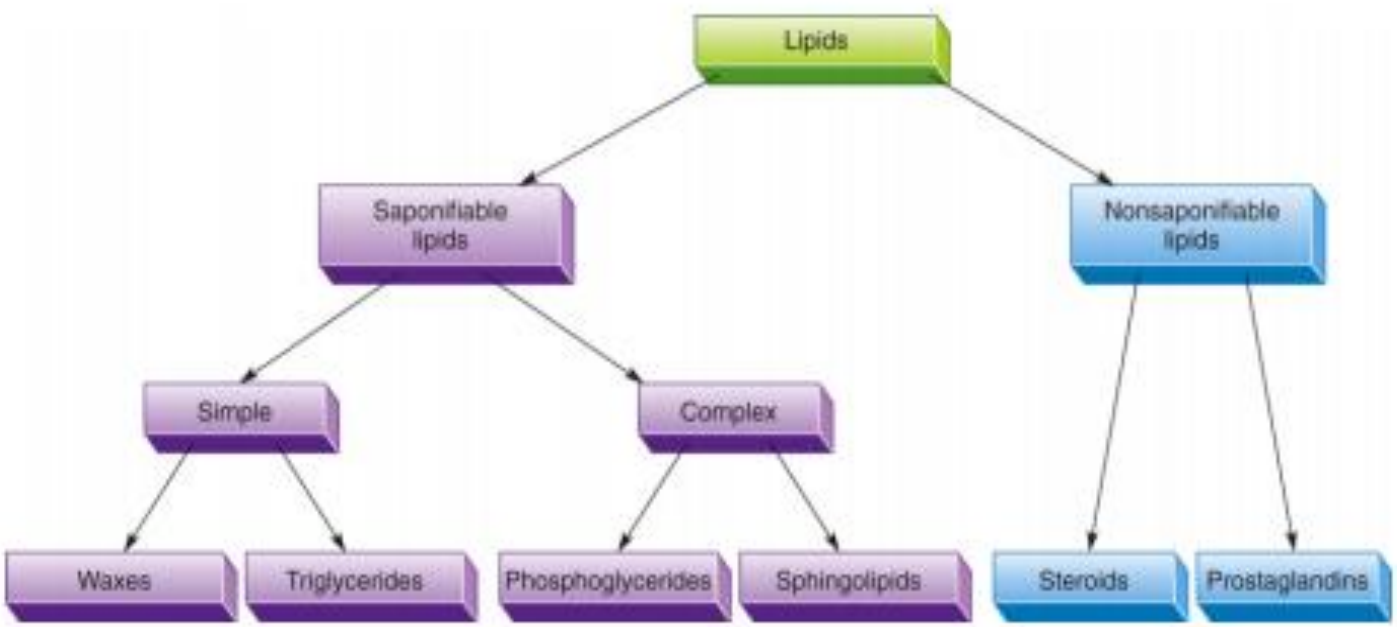
Saponification: the process in which esters are hydrolyzed under basic conditions (NaOH,KOH).

Saponifiable Lipids

Saponifiable lipids can also be divided into groups:

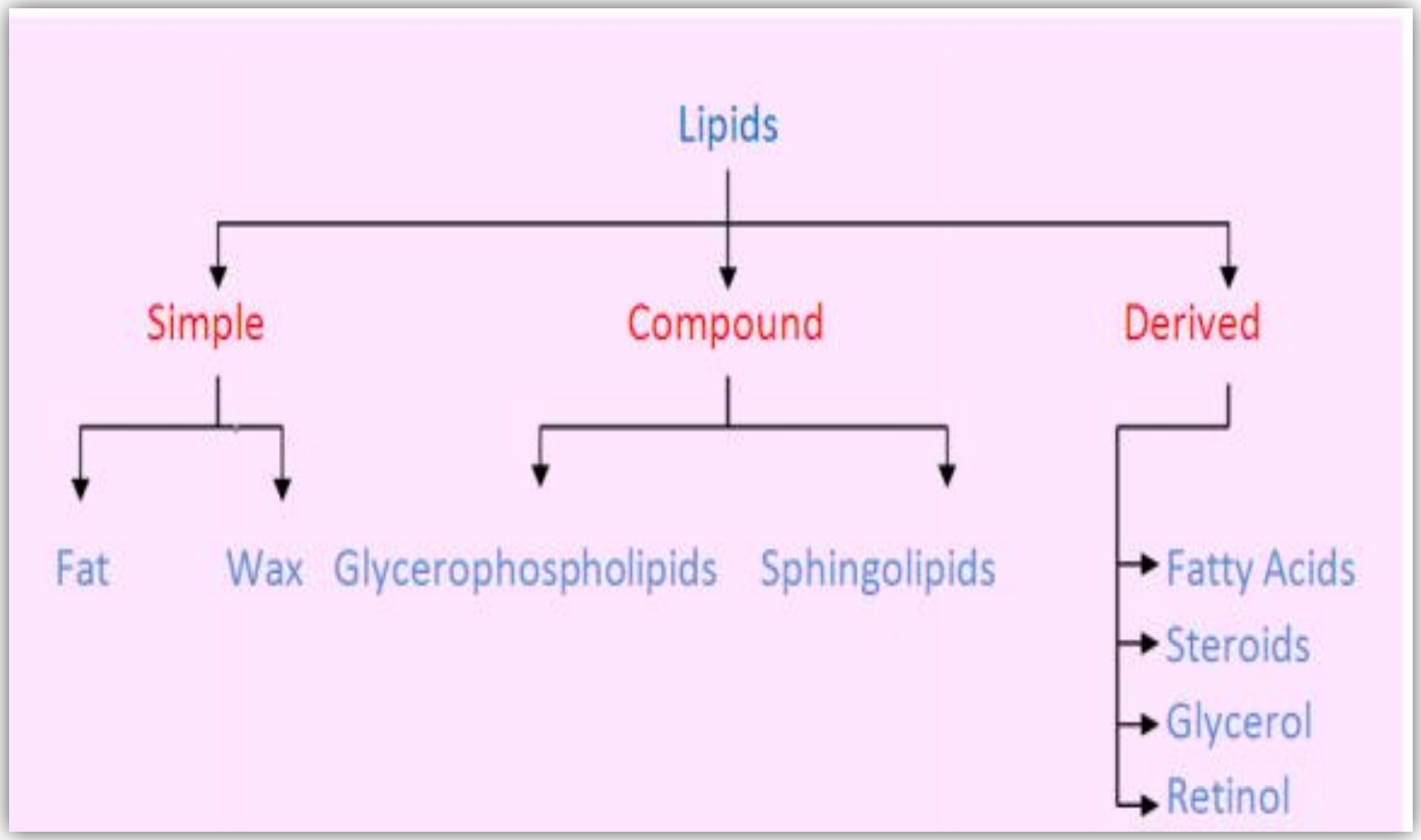
Simple lipids (fatty acid+ alcohol) and includes waxes and triglyceride.

Complex lipids (fatty acid + alcohol + other compounds) and includes phosphoglycerides and sphingolipids.



Classification of Lipids

- Based on the composition of lipids are classified as

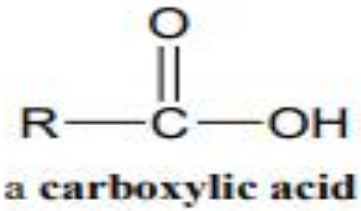


Fatty Acids

Definition: Fatty acids are long chain carboxylic acid and The fundamental building blocks of many lipids

Properties of fatty acids:

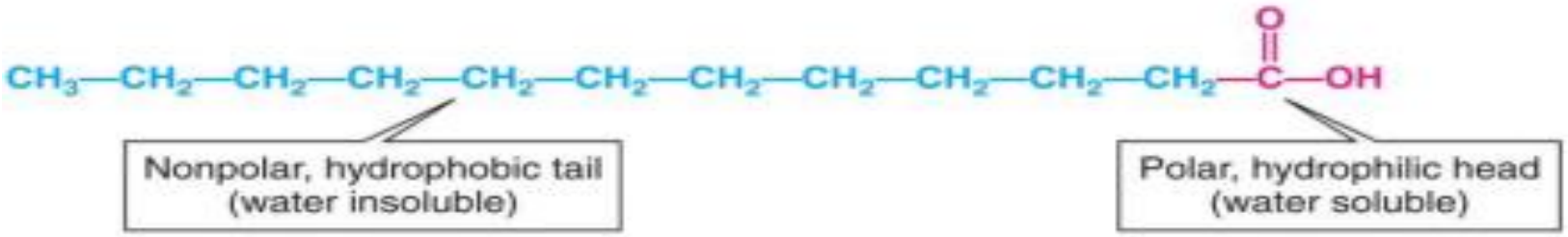
- The long nonpolar tail of F.A. that are responsible for most of the fatty or oily characteristics of fats
- Carboxylic group, polar head of F.A is very hydrophilic under conditions of physiological pH and it exists as the carboxylate anion COO^-.



a carboxylic acid

RCOOH RCO$_2$H

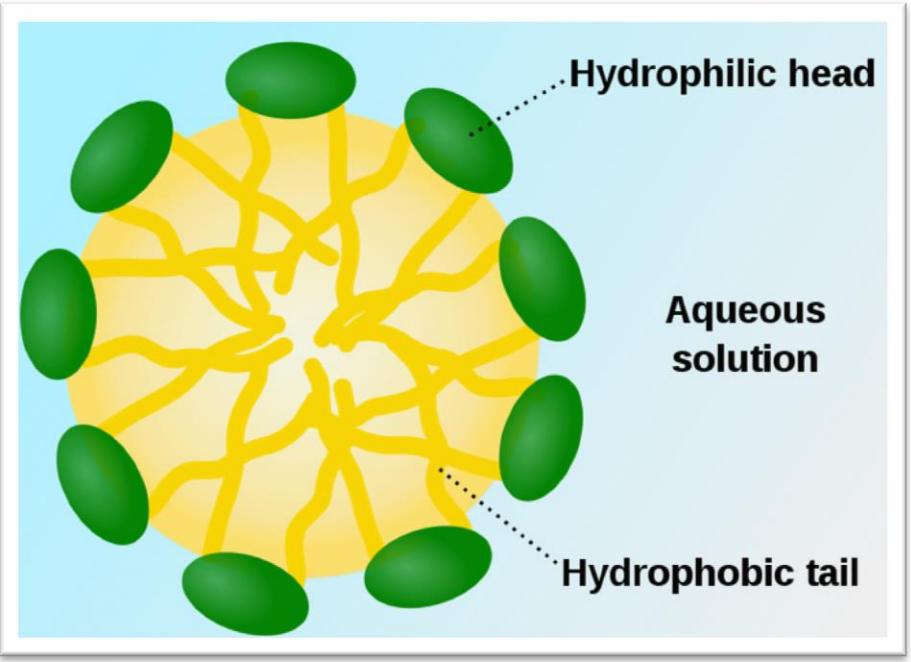
condensed ways of writing the carboxyl group

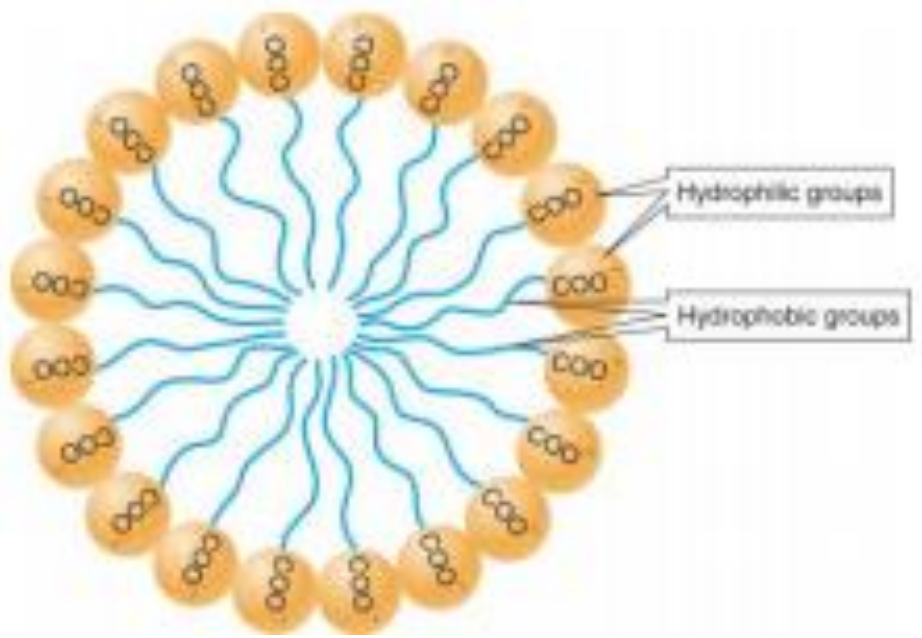


Fatty Acid Micelles

- In aqueous solutions, fatty acids associate with each other in spherical clusters called micelles, : in which the non polar chain extend toward the interior of the structure a way from water and the polar carboxylate groups face outward in contact with the water (some time contain hundreds or thousands of F.As).

F.As held together by weak dispersion forces. Micelle is important in transport of insoluble lipids in the blood.

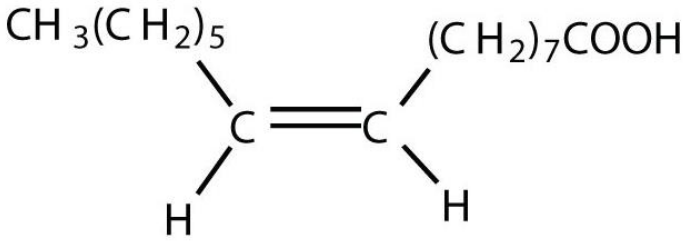




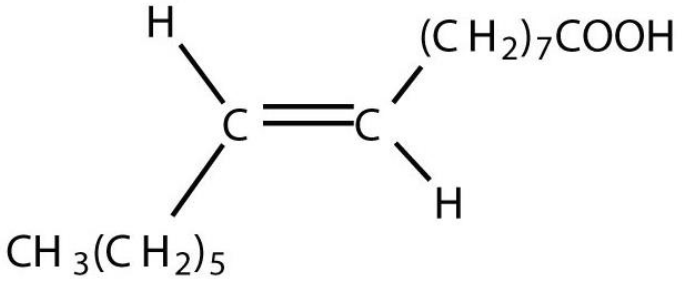
Characteristics of Fatty Acids

The F.As found in natural lipids have several characteristics:

- They are usually have straight chains (no branches).
- They are about 10 to 20 carbon atoms in length.
- They usually have an even number of carbon atoms including the carboxyl carbon.
- The carbon chains may be saturated (all single bonds) or unsaturated (containing double bonds or more).
- There are usually have two functional groups including the carboxyl group and the double bonds.
- Shorter fatty acids usually have lower melting points than longer ones (stearic acid [18C] = 70ºC, palmitic acid [16C] = 63ºC).
- The double bonds are usual in Cis configurations



cis fatty acid

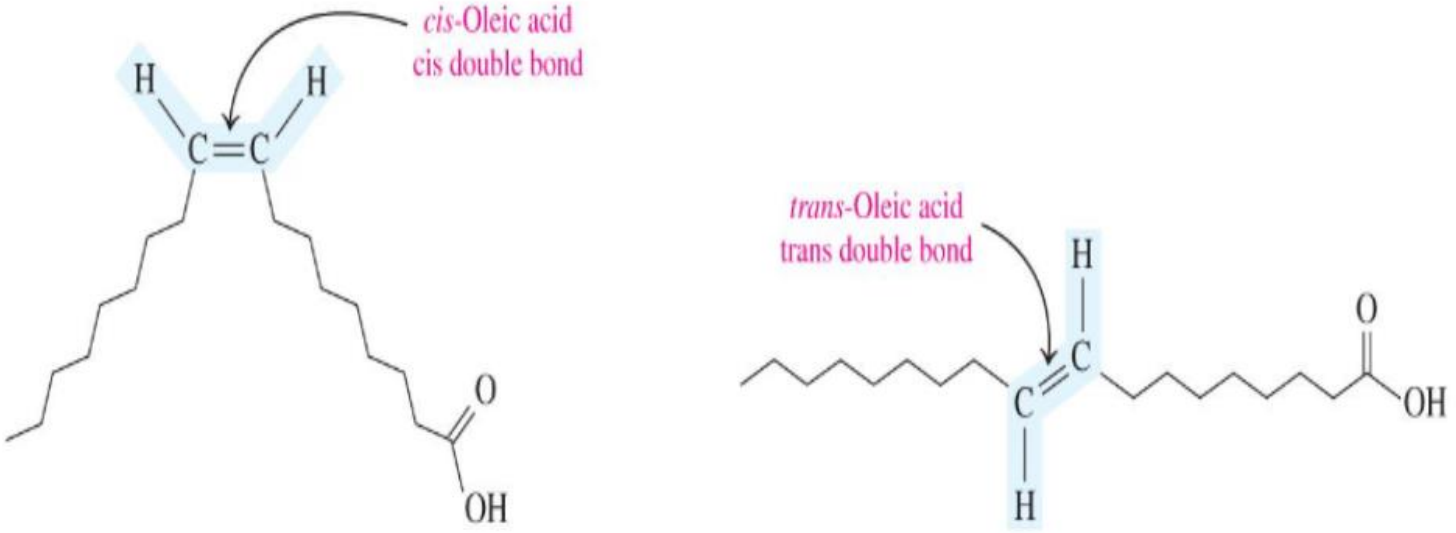


trans fatty acid

Cis and Trans Unsaturation Fatty Acid

Unsaturated fatty acids can be drawn as Cis and trans isomers

- Oleic acid is a monounsaturated fatty acid found in olives, with one double bond at carbon 9.

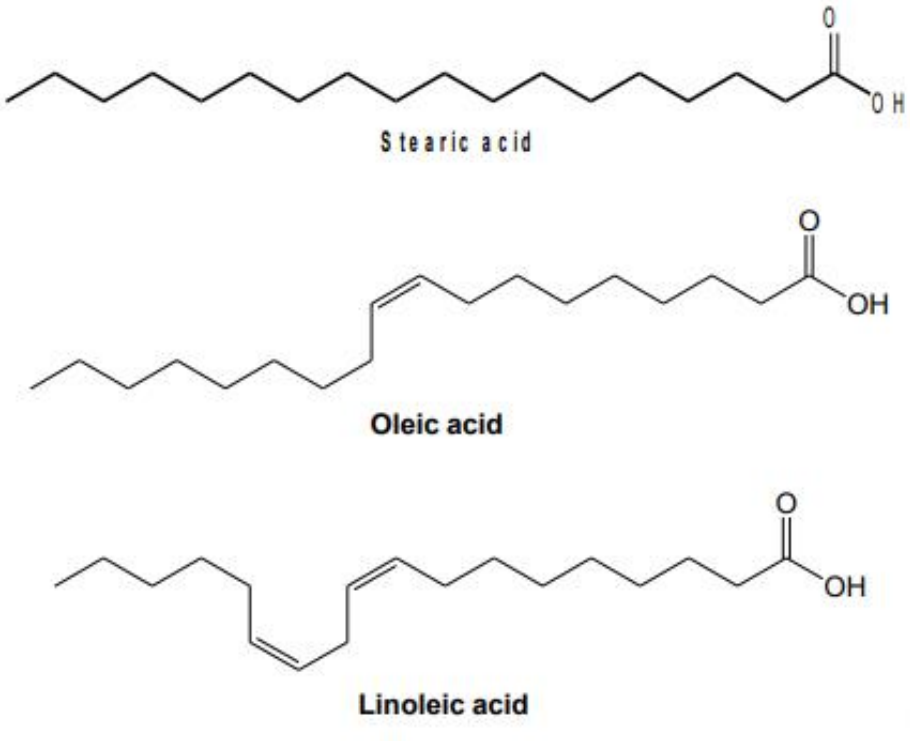


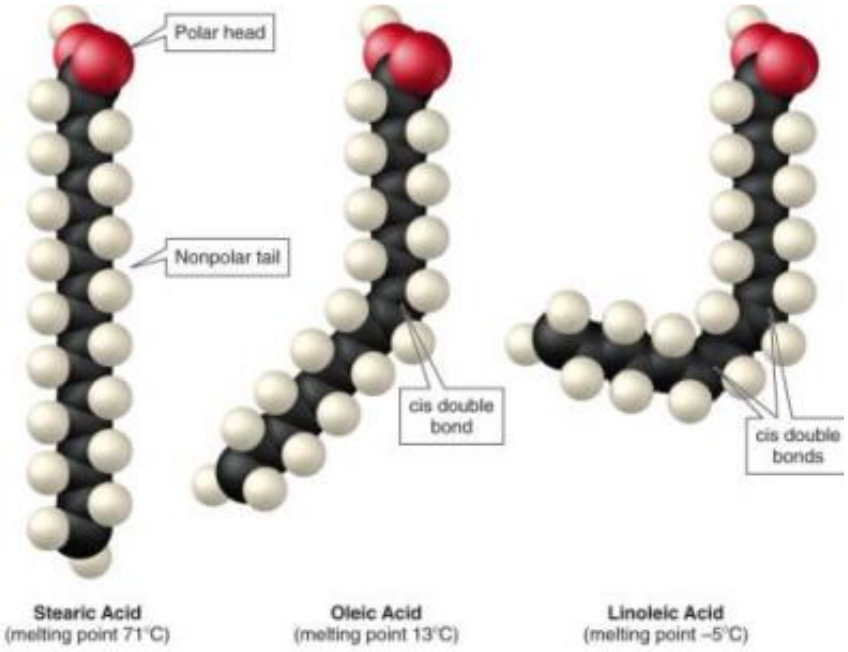
Almost all naturally occurring unsaturated fatty acids have one or more cis double bonds.

The presence of double bond and the length of F.A chain in membrane lipids partly explain the fluidity of biological membranes.

Saturated and Unsaturated Fatty Acids

- The Cis-double bonds in unsaturated fatty acids put an inflexible “kink” in the carbon chain, preventing the molecules from packing together as tightly as saturated fatty acids do. As a result, the intermolecular forces are weaker and unsaturated F.As have lower melting points and are usually liquids at room temperature.
- For example, stearic acid (saturated), oleic acid (one doublebond), and linoleic acid (two double bonds) all have 18 carbons in the chain, but their melting points are drastically different:





Saturated fatty acid

Saturated fatty acid structure are straight. Straight structures are tightly packed together .

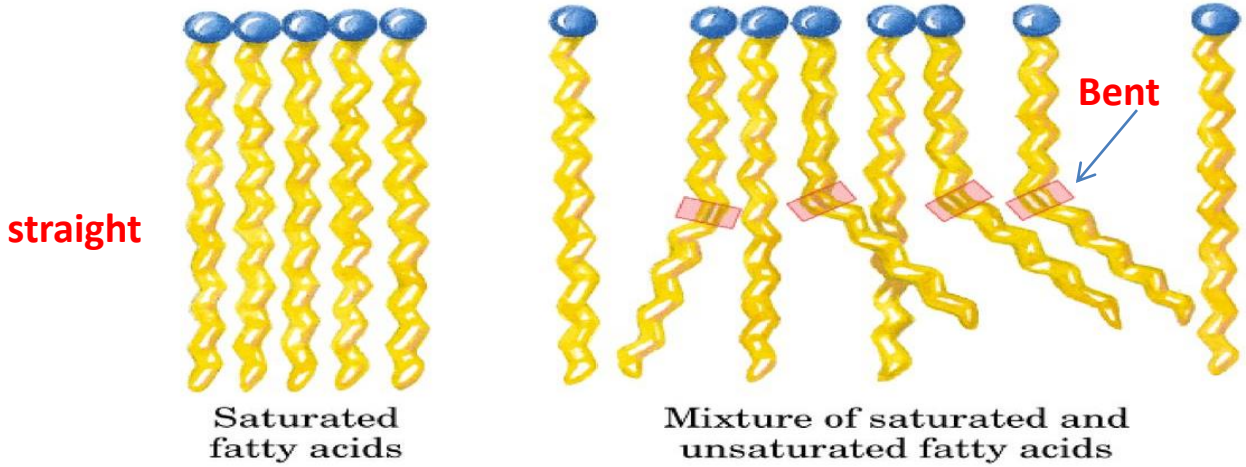
Unsaturated fatty acid

Double bond

Weaker/unstable bond

Easy to cleavage /metabolized

Unsaturated fatty acid structure are bent (kink). Bent structures are not compact and has no tight packed



Structures and Melting Points of Saturated Fatty Acids

Table 18.1 Structures and Melting Points of Common Fatty Acids

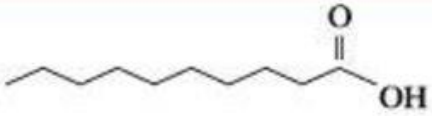
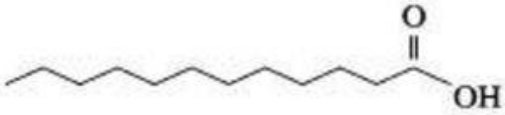
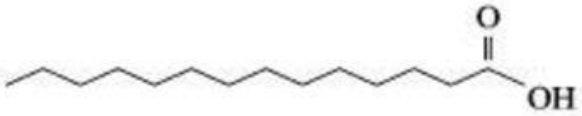
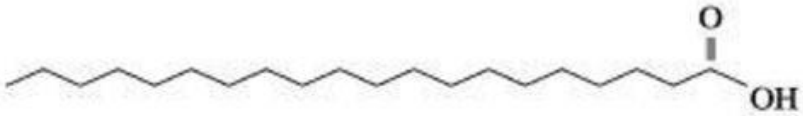
Name	Carbon Atoms	Structure	Melting Point (°C)	Source
Saturated Fatty Acids				
Capric acid	10		32	Saw palmetto
Lauric acid	12		43	Coconut
Myristic acid	14		54	Nutmeg
Palmitic acid	16		62	Palm
Stearic acid	18		69	Animal fat
Arachidic acid	20		76	Peanut oil, vegetable and fish oils

Table 17.2 Structures and Melting Points of Common Fatty Acids

Name	Carbon Atoms	Double Bonds	Structure	Melting Point (°C)	Source
Saturated					
Lauric acid	12	0	$CH_3-(CH_2)_{10}-COOH$	43	Coconut
Myristic acid	14	0	$CH_3-(CH_2)_{12}-COOH$	54	Nutmeg
Palmitic acid	16	0	$CH_3-(CH_2)_{14}-COOH$	62	Palm
Stearic acid	18	0	$CH_3-(CH_2)_{16}-COOH$	69	Animal fat
Unsaturated					
Palmitoleic acid	16	1	$CH_3-(CH_2)_5-CH=CH-(CH_2)_7-COOH$	0	Butter
Oleic acid	18	1	$CH_3-(CH_2)_7-CH=CH-(CH_2)_7-COOH$	13	Olives, corn
Linoleic acid	18	2	$CH_3-(CH_2)_4-CH=CH-CH_2-CH=CH-(CH_2)_7-COOH$	−9	Soybean, safflower, sunflower
Linolenic acid	18	3	$CH_3-CH_2-CH=CH-CH_2-CH=CH-CH_2-CH=CH-(CH_2)_7-COOH$	−17	Corn

Fatty Acids Naming

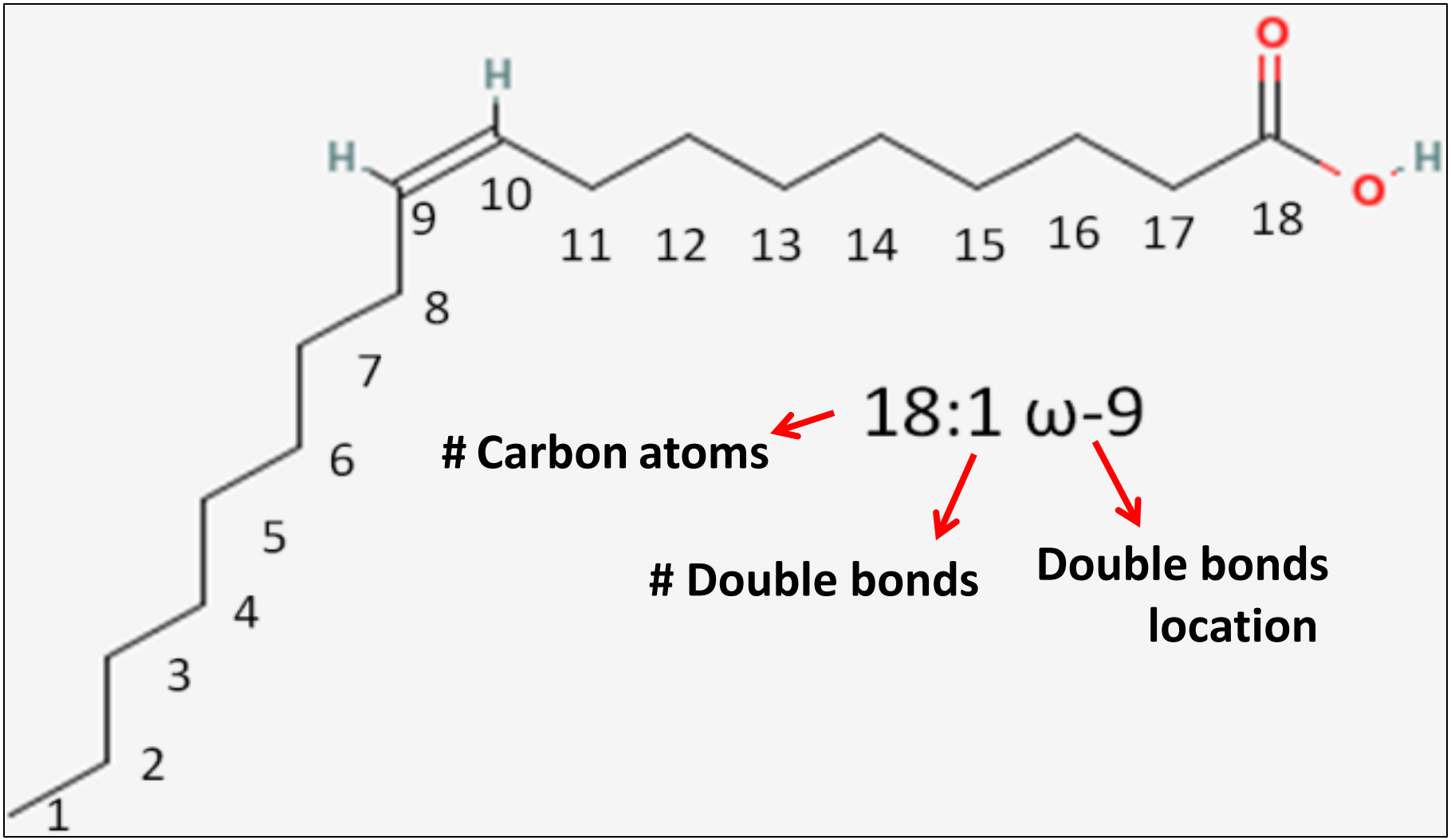
There are three naming systems used for fatty acids:

- **Delta nomenclature**
- **Omega nomenclature**
- **Common names**

The Omega Nomenclature and common names are mainly used in the nutrition field while the delta nomenclature is used when describing specific fatty acids.

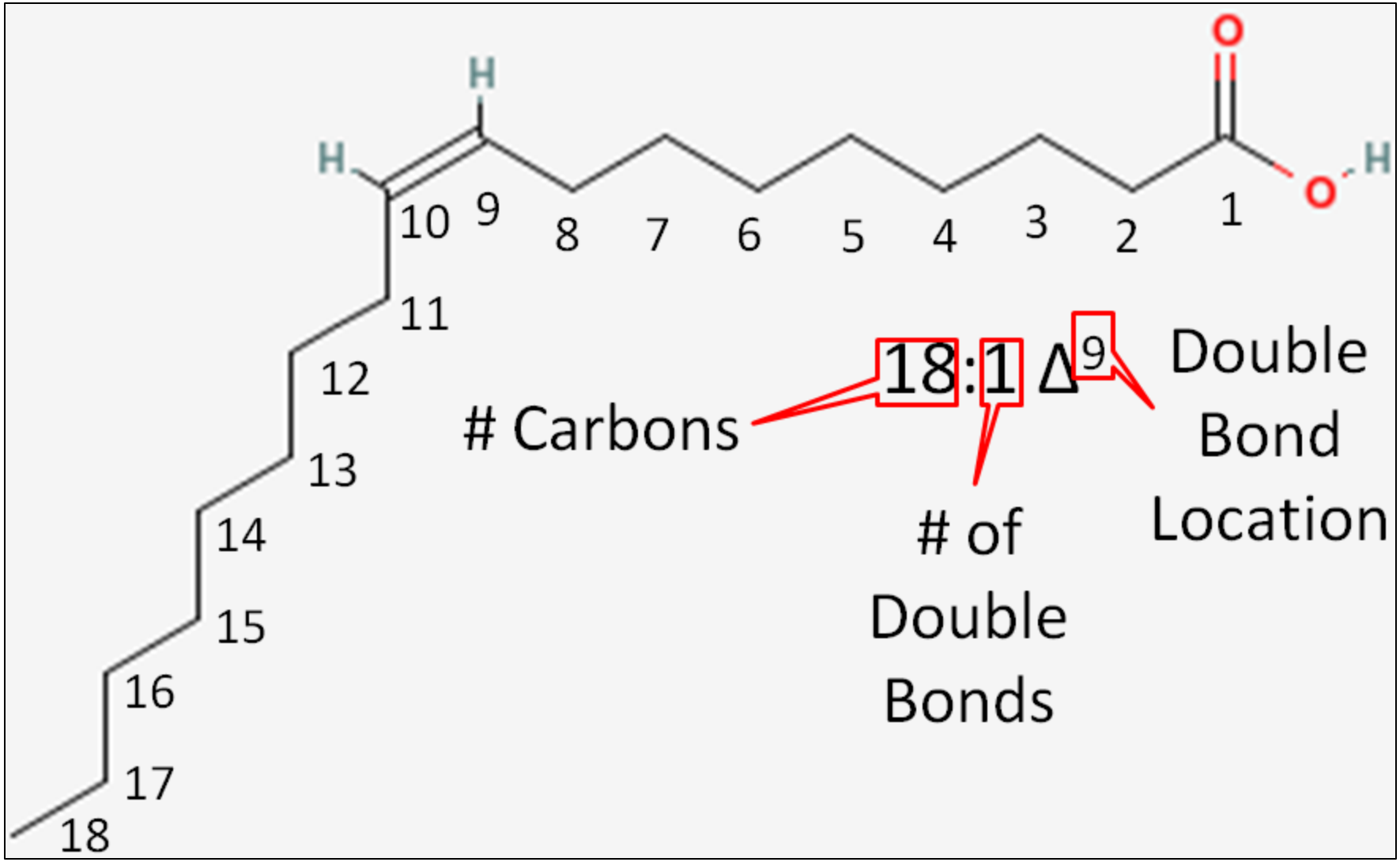
Omega Nomenclature

Number of carbon atoms from the methyl (aka omega) end to the first carbon in the double bond closest to the methyl end = 9



Delta Nomenclature

Number of carbon atoms from the carboxylic acid (alpha) end



Common Names

S.N	Common Name	Systematic Name
1	Palmitic Acid	Hexadec**anoic** Acid
2	Stearic Acid	Octadec**anoic** Acid
3	Oleic acid	Octadeca**enoic** acid
4	Linoleic Acid	Octadeca**dienoic** acid
5	Linolenic Acid	Octadeca**trienoic** acid
6	Arachidonic acid	Eicosa**tetraenoic** acid

Essential Fatty Acids

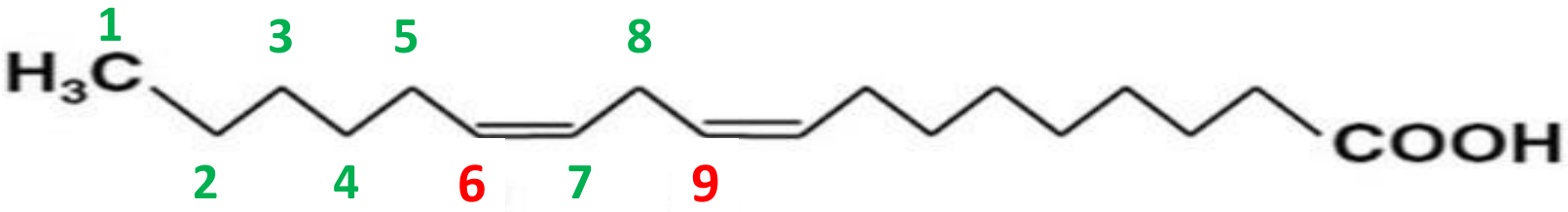
Essential fatty acids are fatty acid needed by the body but not synthesized within the body.

- Human body can synthesis all F.As except two (linoleic acid , linolenic acid) both polyunsaturated fatty acids with 18-carbon chains, cannot be synthesized in the body and must be obtained from the diet. These are essential fatty acids.

Linoleic acid and Linolenic acid

- Both acids are found in plants and fish oils.
- In the body, both acids used to produce hormone like substances that regulate a wide range of functions and characteristic including blood pressure, blood clotting ,blood lipid level ,immune response to injury and infections.

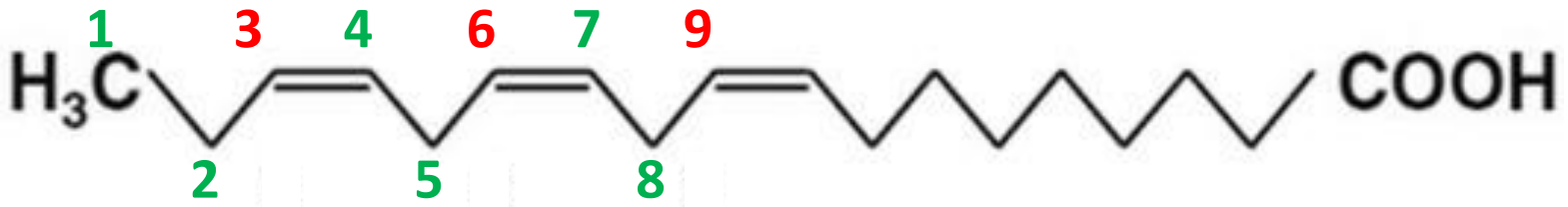
- **Linoleic Acid (vegetable oil)**



An omega-6 polyunsaturated fatty acid

Linoleic acid (18:2 n-6)
Omega-6 fatty acid with double bonds at positions 6 and 9 counting from the methyl group

- **Linolenic Acid (Fish oil)**



An omega-3 polyunsaturated fatty acid

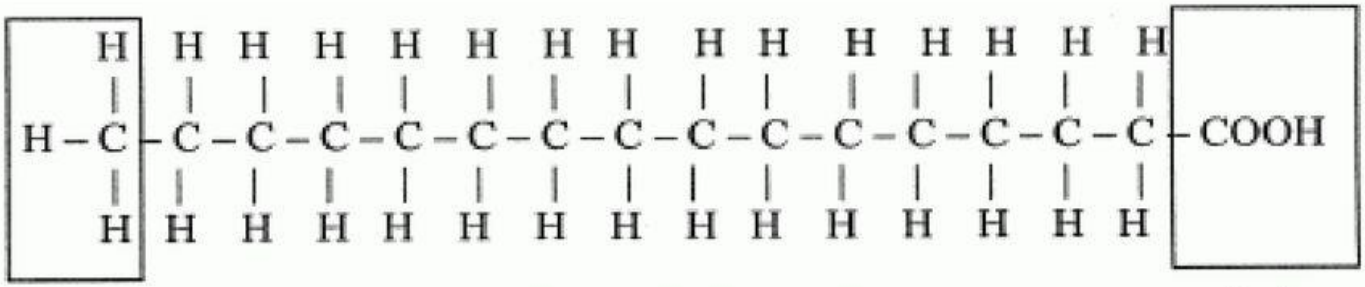
α-linolenic acid (18:3 n-3)
Omega-3 fatty acid with double bonds at positions 3, 6, and 9 counting from the methyl group

Both acids can be converted to other omega-3 and -6 F.As.

Examples of Fatty Acids

- Some fatty acids and their common names:
  - 14:0 myristic acid; 16:0 palmitic acid; 18:0 stearic acid;
  - 18:1 cisΔ^{9} oleic acid
  - 18:2 cis$\Delta^{9,12}$ linoleic acid
  - 18:3 cis$\Delta^{9,12,15}$ α-linonenic acid
  - 20:4 cis$\Delta^{5,8,11,14}$ arachidonic acid
  - 20:5 cis$\Delta^{5,8,11,14,17}$ eicosapentaenoic acid (an omega-3)

Carboxylic Acid Functional Group Of Fatty Acid



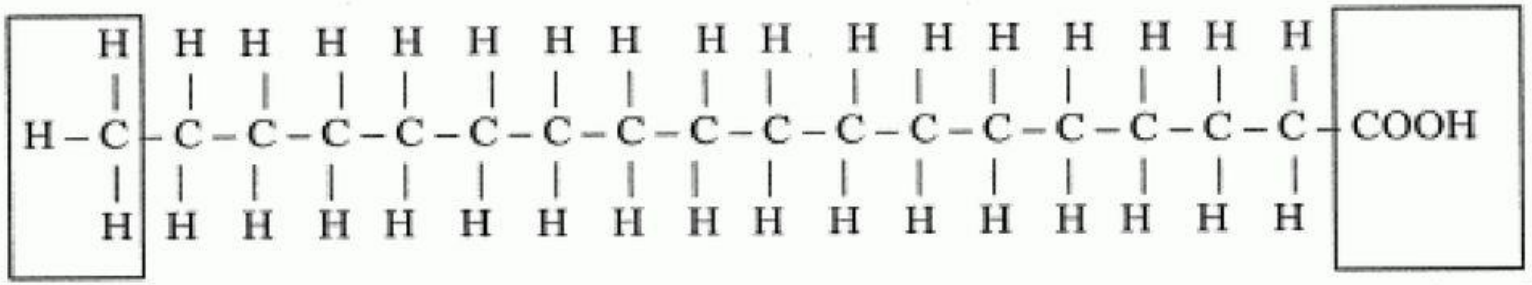
Methyl
Oil-Soluble

OMEGA (ω) END

PALMITIC ACID
16 carbons

Carboxyl
Water-Soluble

DELTA (Δ) END



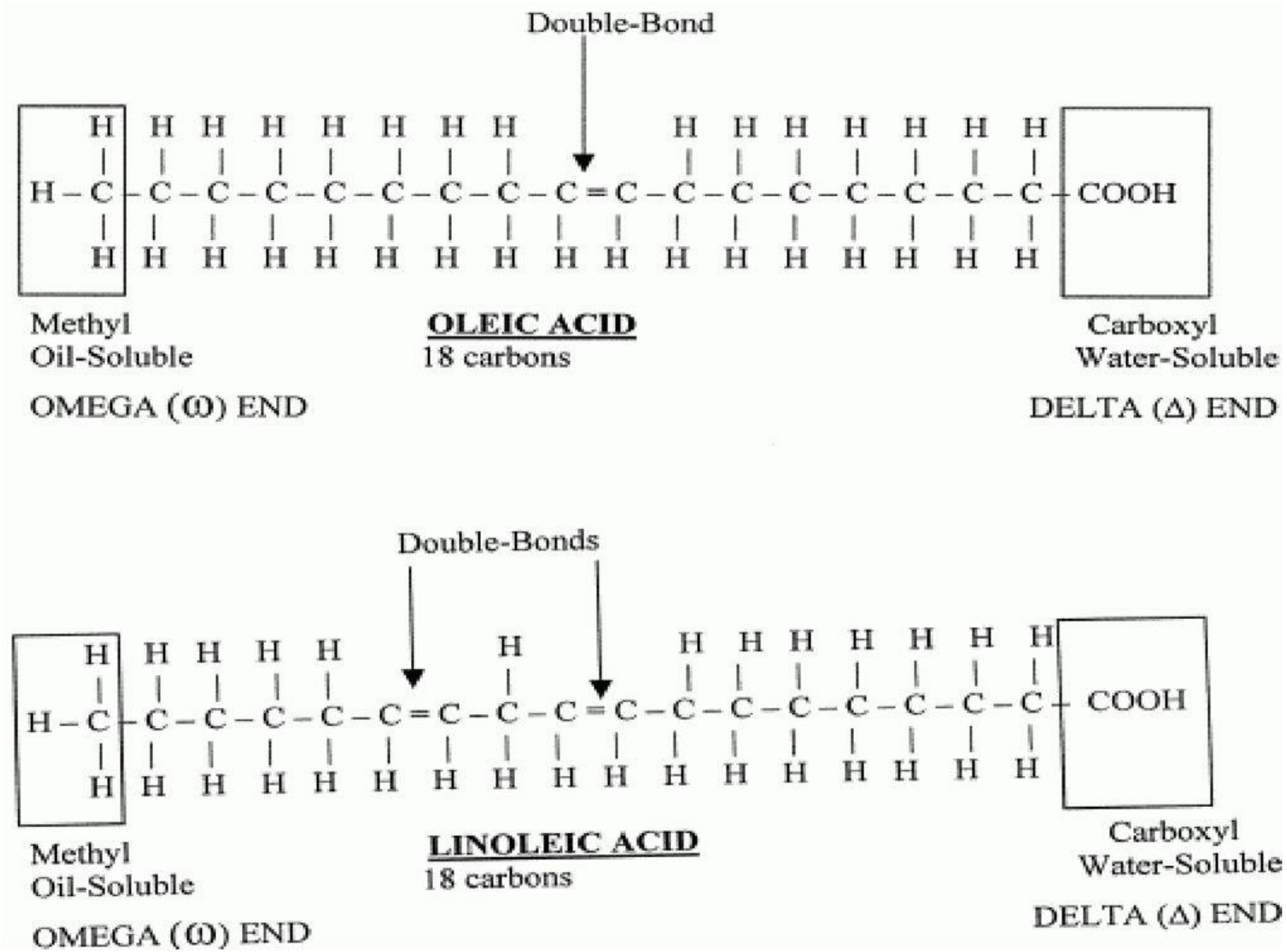
Methyl
Oil-Soluble

OMEGA (ω) END

STEARIC ACID
18 carbons

Carboxyl
Water-Soluble

DELTA (Δ) END



Numbering of carbon atoms of fatty acid is done from both ends, ω end & Δ end/ α end

Examples: Saturated and Unsaturated Fatty Acids

Indicate whether the following fatty acids are saturated or unsaturated. Which of them are solids and which are liquids at room temperature?

CH3 (CH2)14COOH

CH3 (CH2)4CH=CHCH2CH=CH(CH2)7COOH

CH3 (C14H24)COOH

CH3 (C10H20)COOH

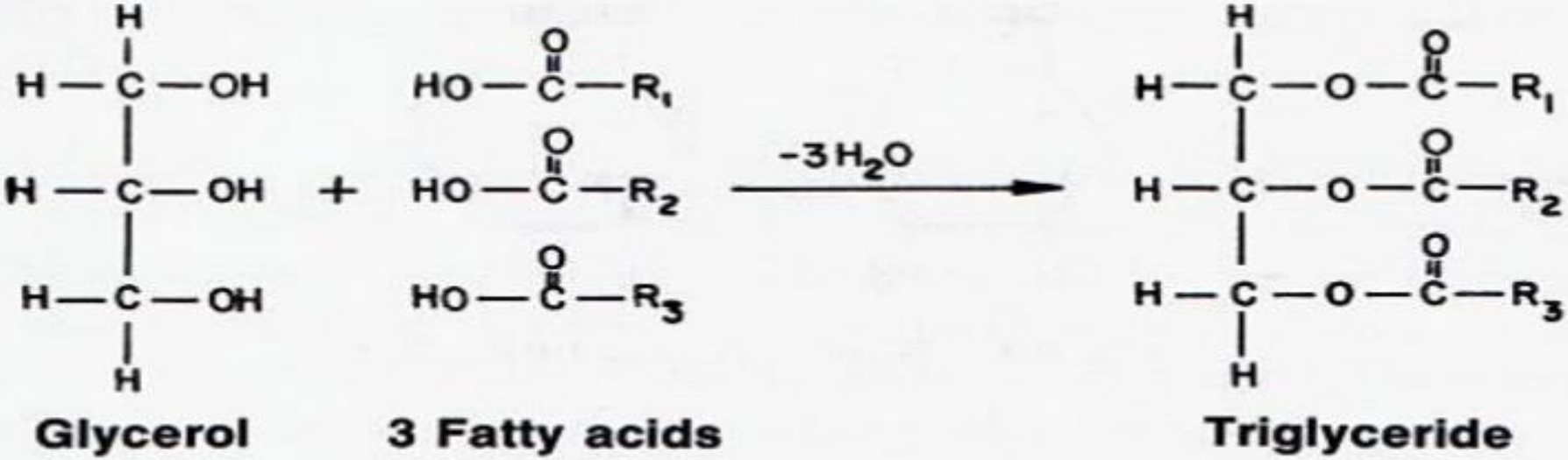
Chemical Reaction of Fatty Acid

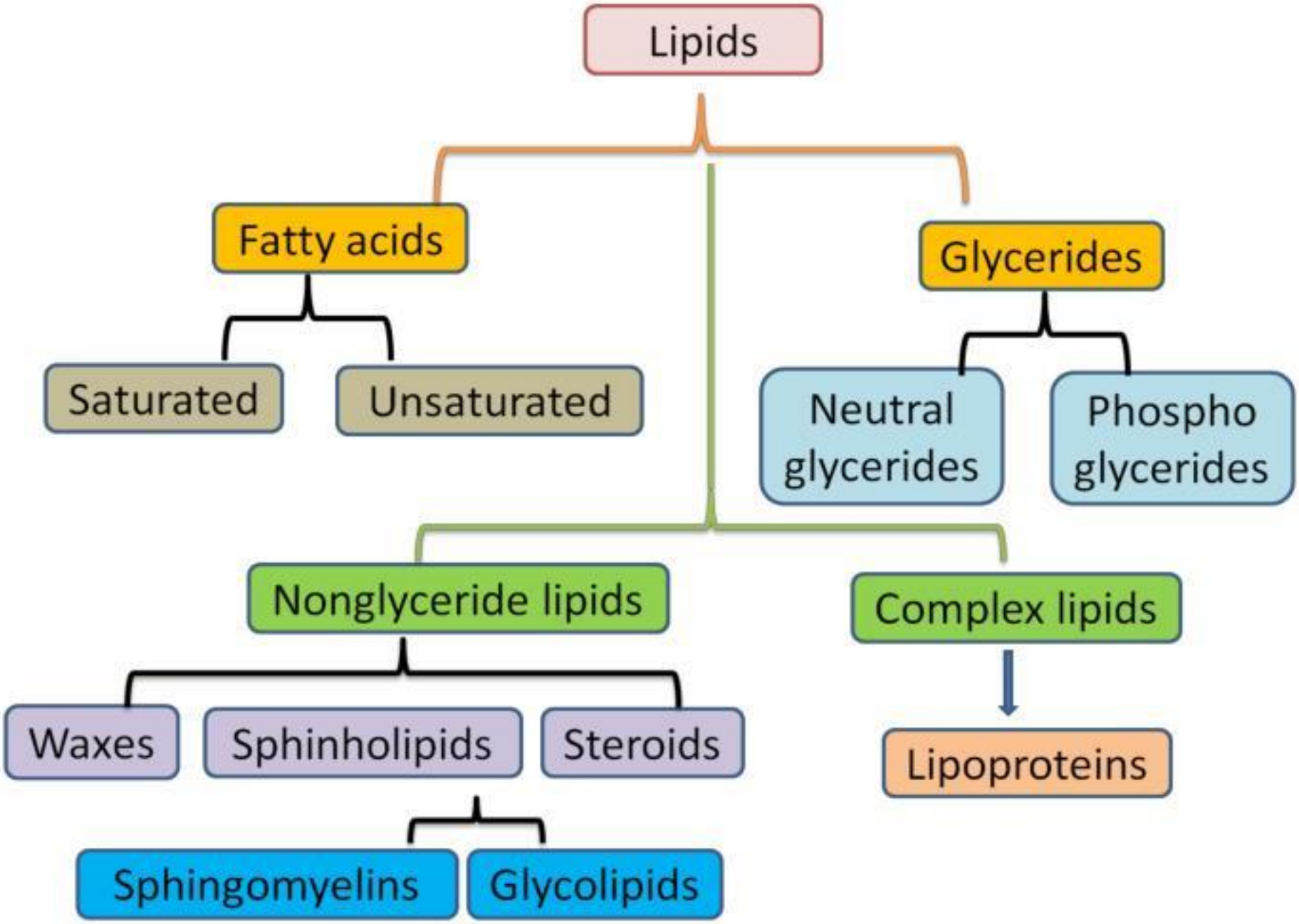
Reaction due to carboxyl group of fatty acid

- Esterification: Esterified form of lipid

Animal fats and vegetable oils are the most widely occurring lipids. Fats and oils are both esters, ester consist of an alcohol portion and an acid portion.

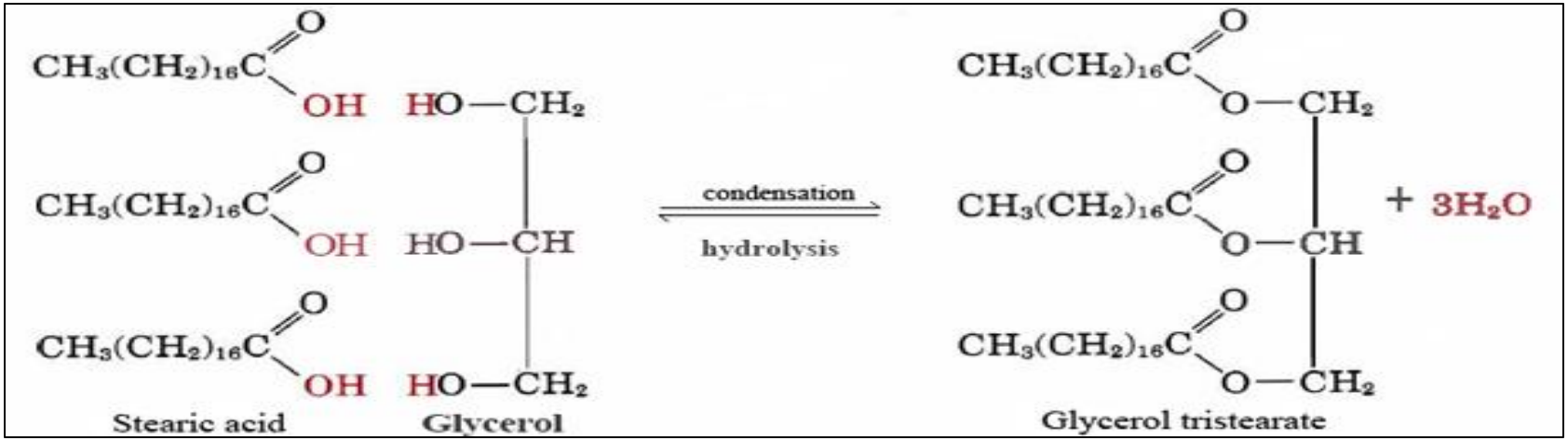
Formation of an ester:



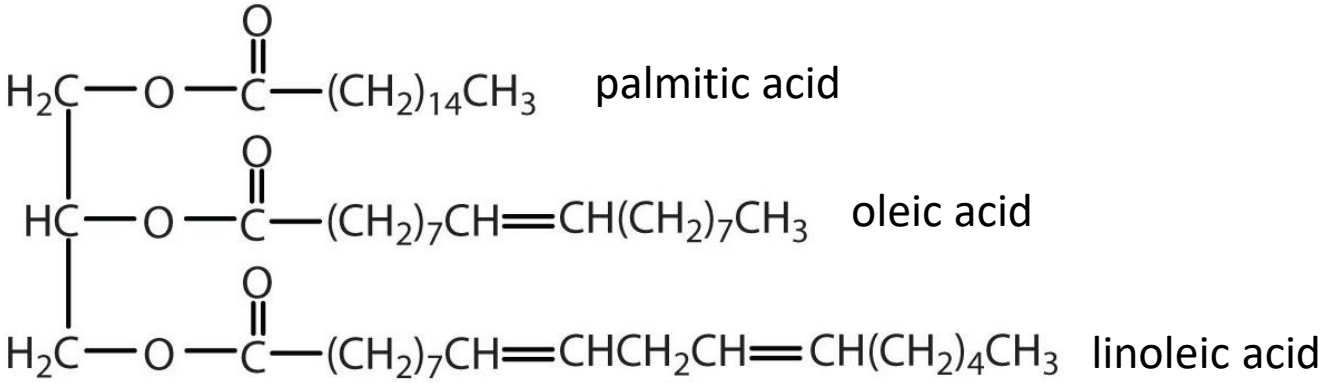

Lipids
Fatty acids
Glycerides
Saturated
Unsaturated
Neutral glycerides
Phospho glycerides
Nonglyceride lipids
Complex lipids
Waxes
Sphinholipids
Steroids
Lipoproteins
Sphingomyelins
Glycolipids

Triglycerides

Animal fats and vegetable oils are esters composed of three molecules of a fatty acid connected to a glycerol molecule, producing a structure called a triglyceride or a triacylglycerol:

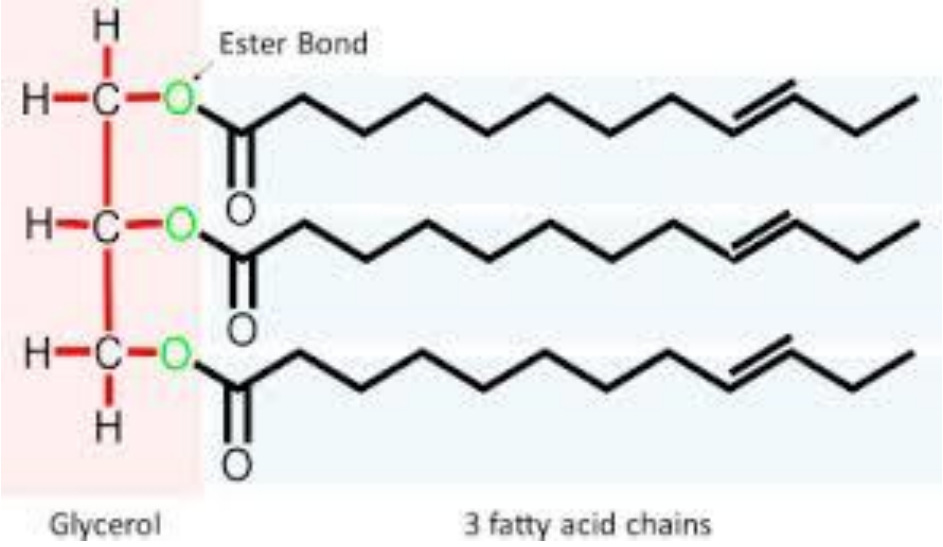


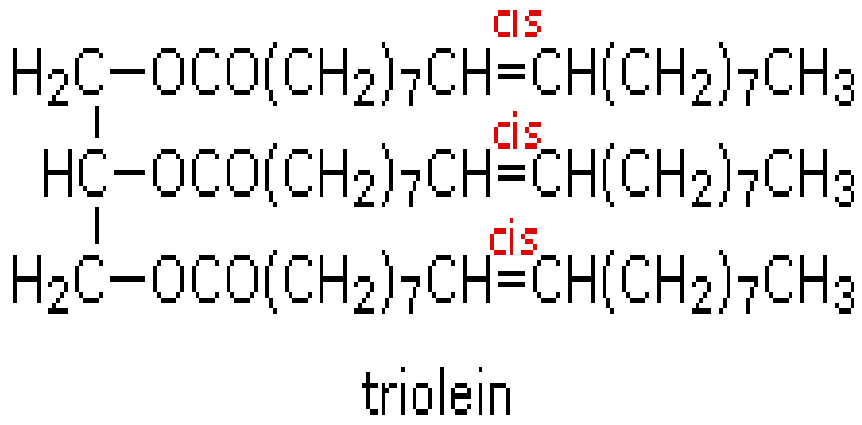
Natural triglycerides are often mixtures of many different triglyceride molecules for example butter fat contains 14 different F.As components



Fats and Oils

- **Fats** are triglycerides that are solids at room temp. They are generally obtained from animals, mostly long chain saturated fatty acids (higher melting points).
- **Oils** are triglycerides that are liquids at room temp. They are derived from plants or fish mostly unsaturated fatty acids (lower melting point).
- Vegetable oil such as corn, sunflower oils
- Olive oil Contains a high percentage of oleic acid, which is a monounsaturated fatty acid with one Cis double bond.
- Oleic Acid is not only reduces bad cholesterol in blood but it serving as a powerful anti-cancer agent.

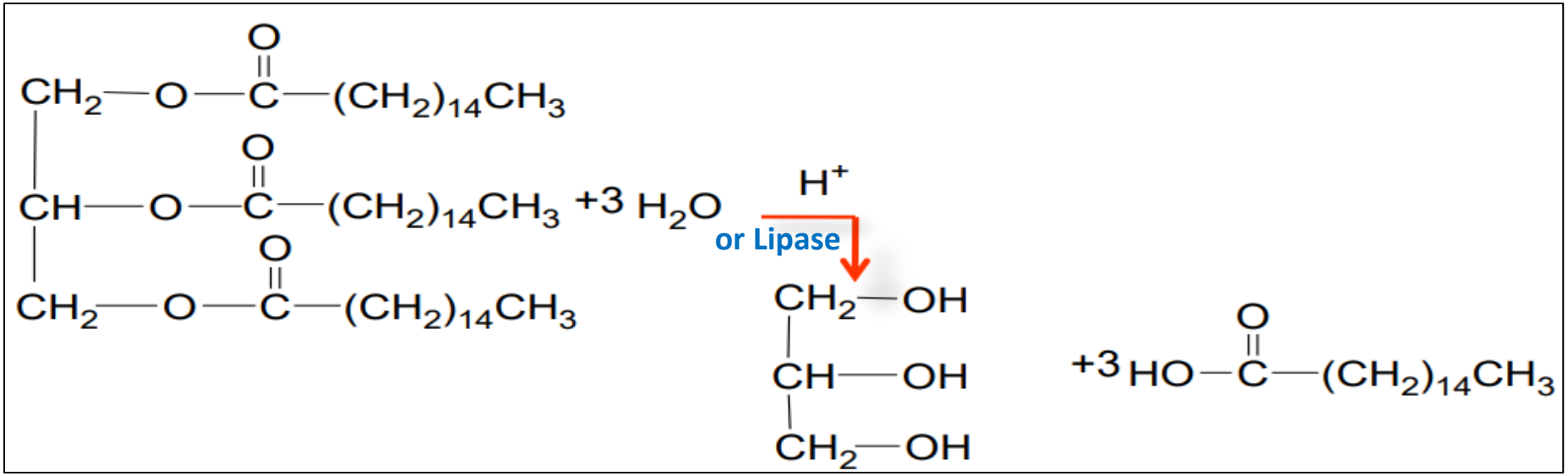




triolein

Triglyceride Reactions

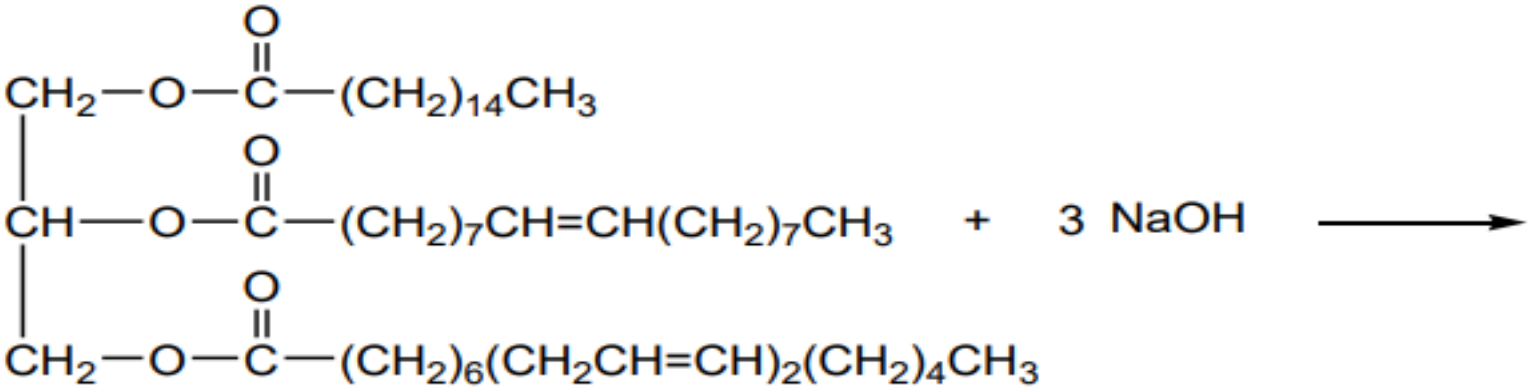
- **Hydrolysis:** most important reaction in fats and oils it's the reveres to ester formation. Triglycerides can be broken apart with water and an acid catalyst (hydrolysis), or by digestive enzymes called lipases to supply energy.

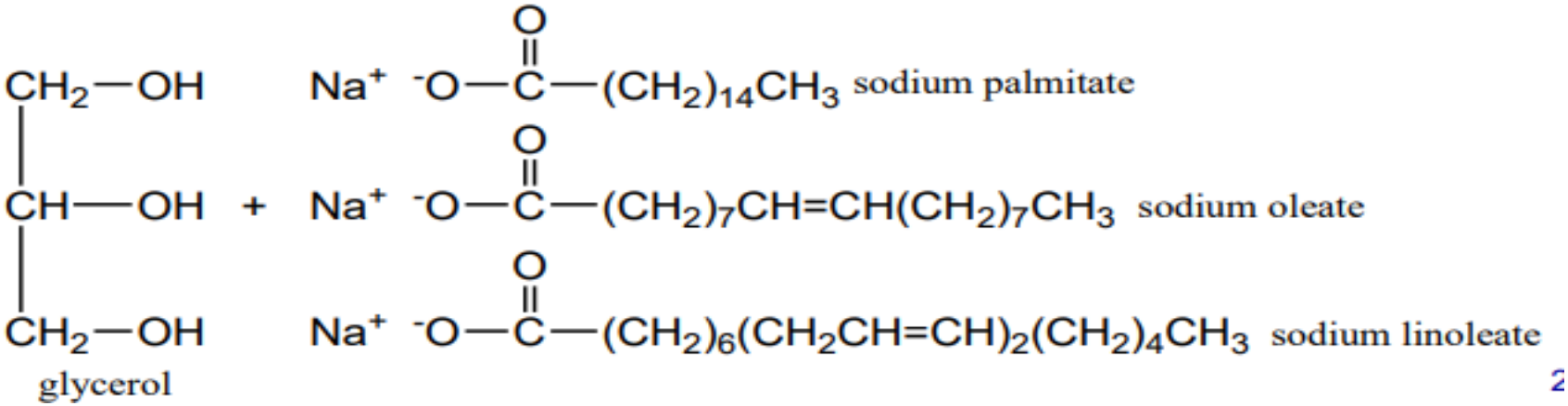


Triglyceride Reactions

❖ **Saponification:** In saponification reactions, triglycerides react with strong bases (NaOH or KOH) to form the carboxylate salts of the fatty acids, called soaps and used as a cleaning agent.

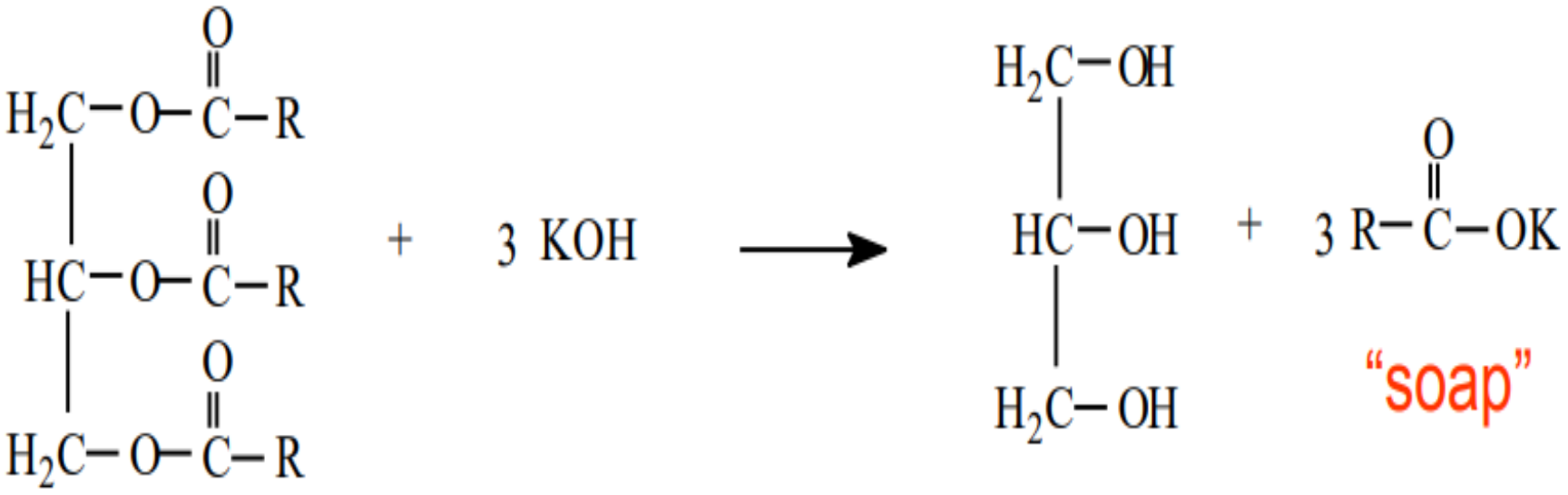
NaOH produces a "hard" soap, commonly found in bar soaps.





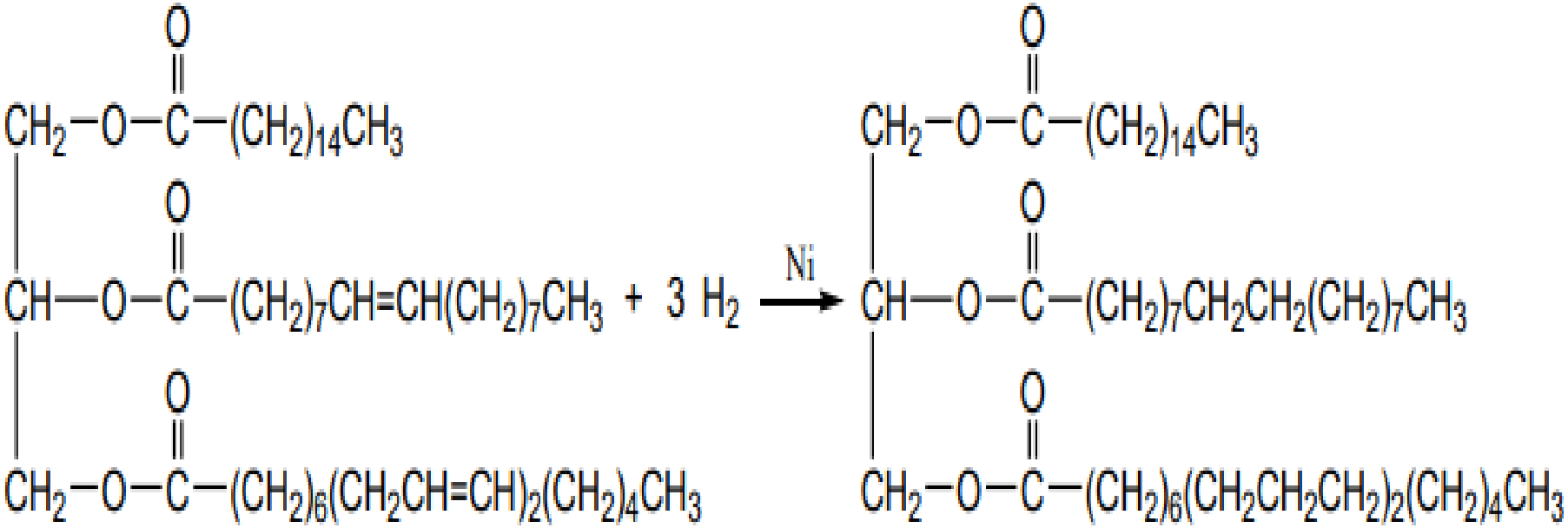
Triglyceride Reactions

KOH produces a “soft” soap, such as those in shaving creams and liquid soaps.



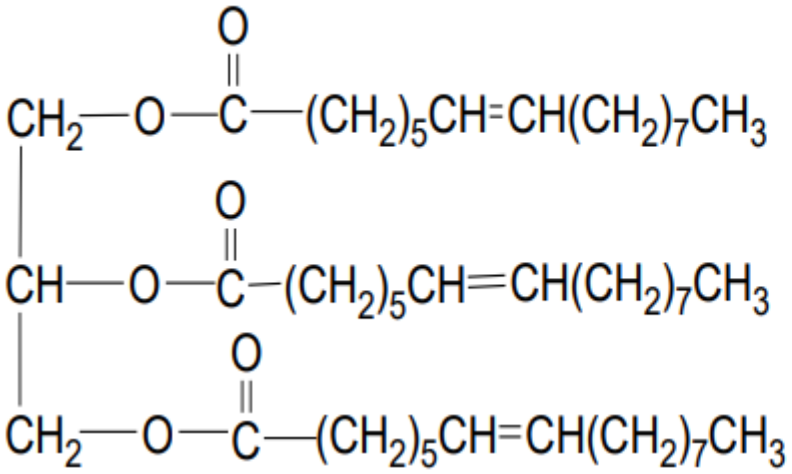
Triglyceride Reactions

- **Hydrogenation:** In hydrogenation reactions, alkenes are converted into alkanes (double bond reduced to single bond) by treating with hydrogen gas (H2) in the presence of catalyst (Pt, Ni, or some other metal). This process is used to convert unsaturated vegetable oils, which are liquids at room temp., to saturated fats, which are solids at room temp. (shortening, etc.).

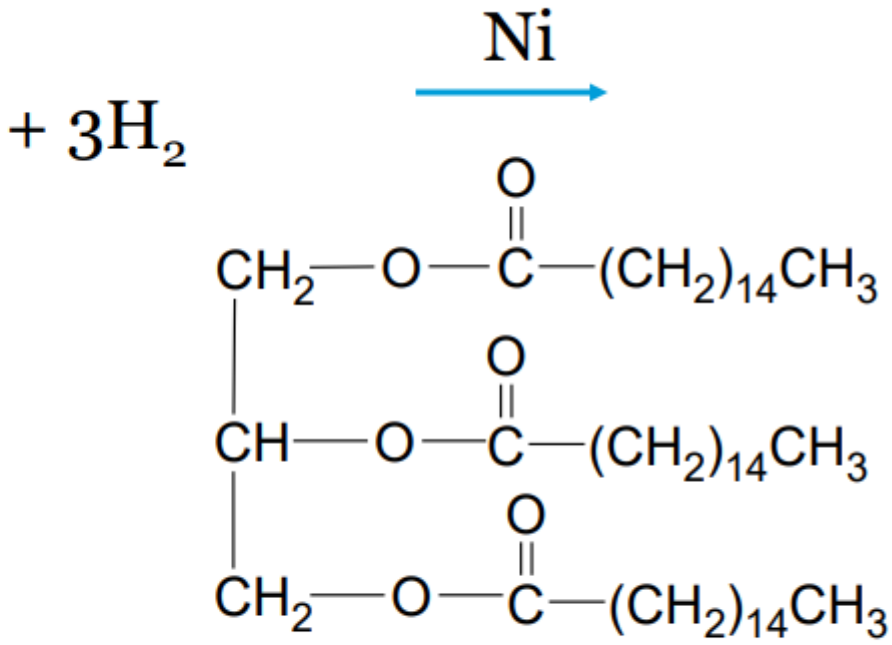


Hydrogenation:

It is commercial reaction of fats and oils and therefore increase the melting point ,it is most often used in the production of semisolid cooking shortening (margarines) from liquid vegetable oils.



glyceryl tripalmitoleate
(tripalmitolean)



glyceryl tripalmitate
(tripalmitin)

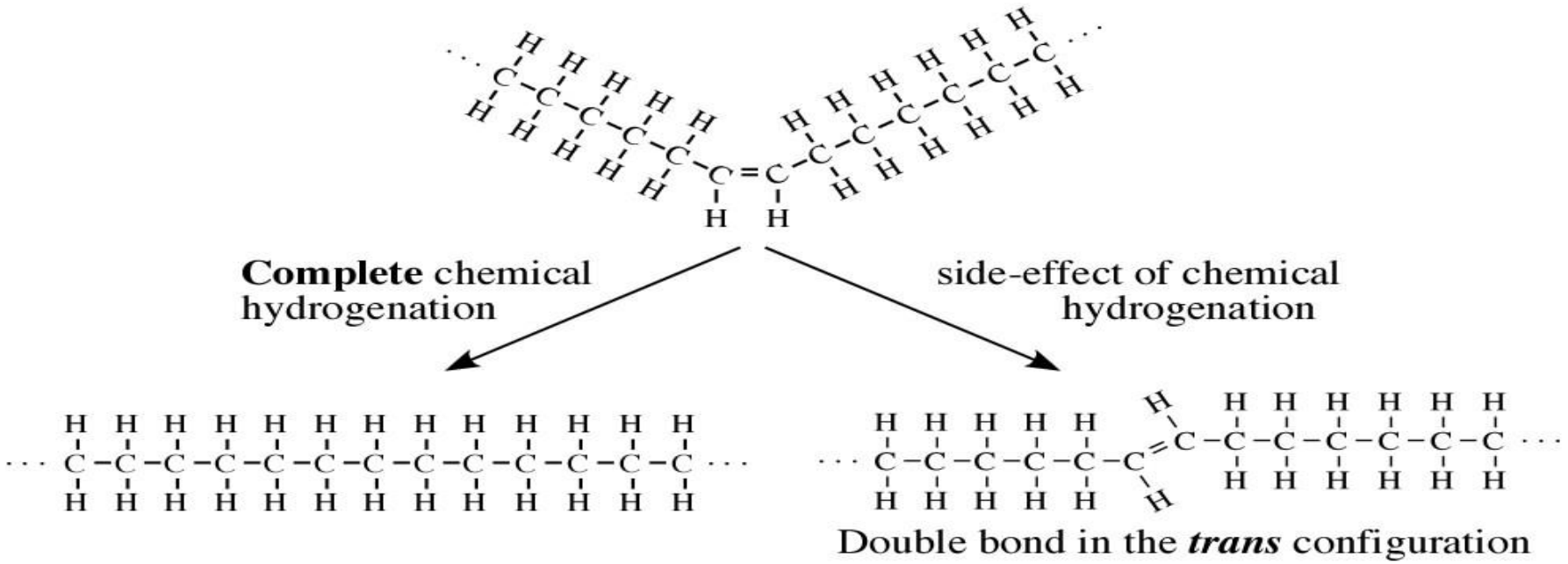
Hydrogenation:

Some **Cis** F.A in hydrogenation isomerizes to **Trans** F.A (Bad F.A).

Cis vs. Trans

Unsaturated fats are healthy because the double bond causes the shape of the molecules to bend. This bent shape is called a "**Cis**" configuration. Fat molecules can not easily stack.

- **Trans** fat is a by product of hydrogenation. There is still a slight bend but they are much more stackable than **Cis** fats.
- When unsaturated fat is hydrogenated, it is converted to a saturated fat.



GOOD FATS

COCONUT OIL

RED PALM OIL

AVOCADO OIL

BUTTER
GHEE

DUCK FAT
GOOSE FAT

LARD
TALLOW

EXTRA VIRGIN OLIVE OIL

BAD FATS

RICE BRAN OIL

CANOLA OIL

SUNFLOWER OIL

CORN OIL

SAFFLOWER OIL

MARGARINE

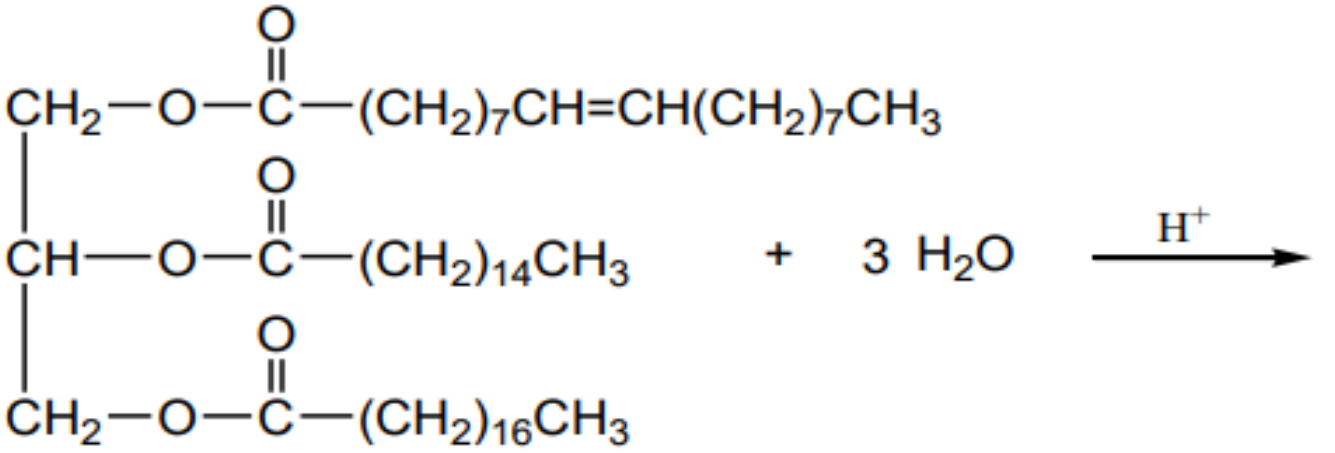
TRANS FATS

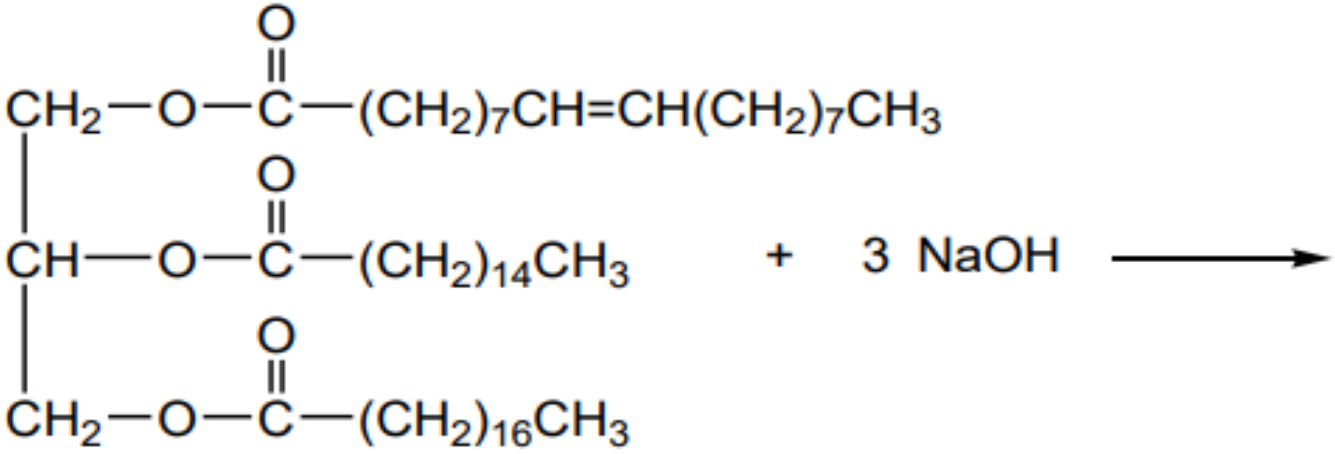
SOYBEAN OIL

Nutrition ADVANCE

Examples: Reactions of Triglycerides

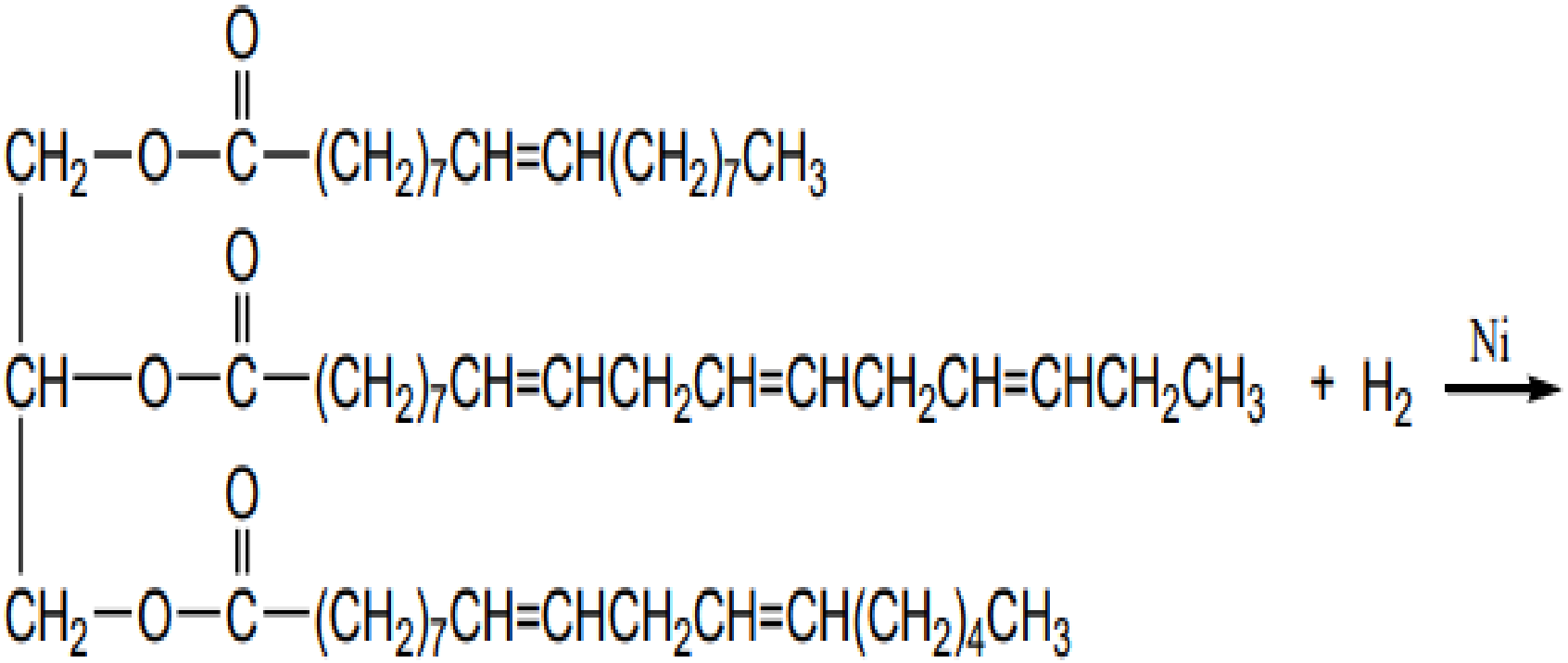
- Write the products of the following reactions:





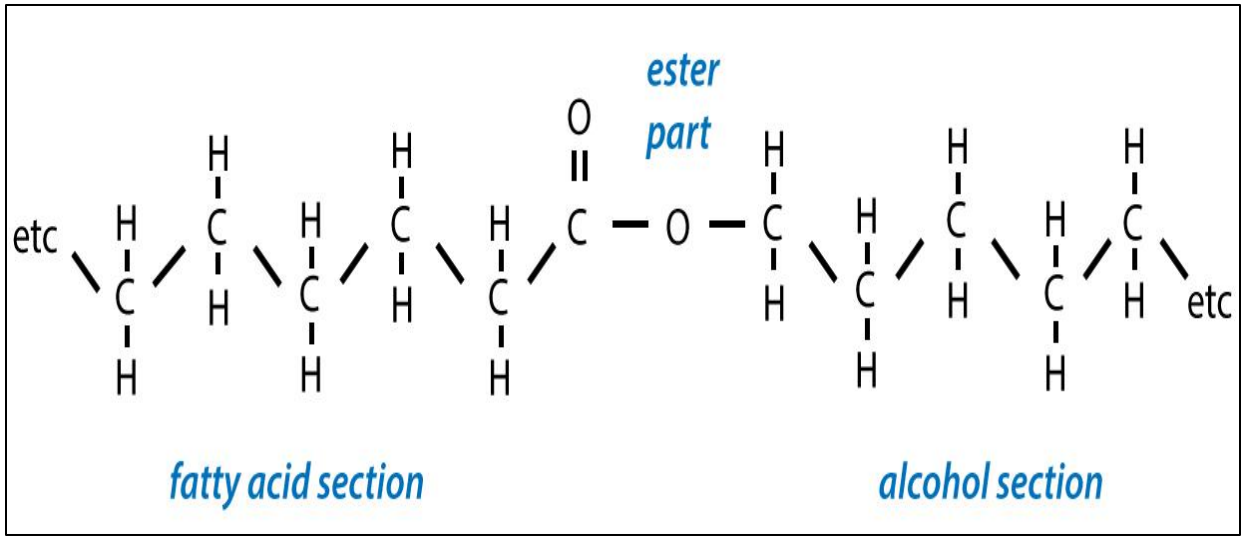
Examples: Reactions of Triglycerides

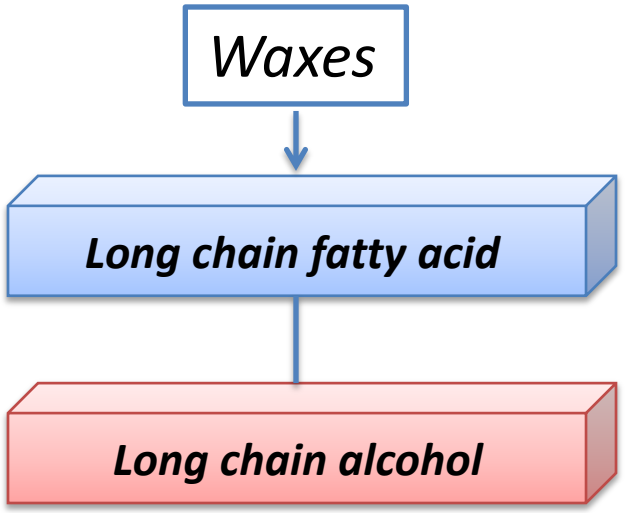
- Write the products of the following reactions:



Waxes

Waxes: An ester of a long chain F.A, which form by joined a long chain F.A to long chain alcohol (13-32 carbon).

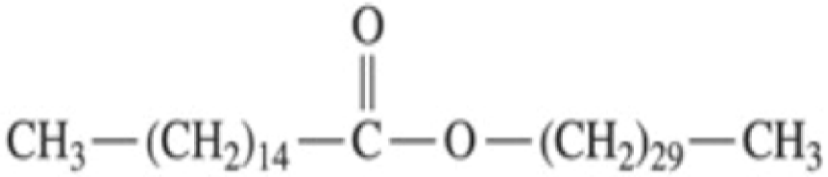
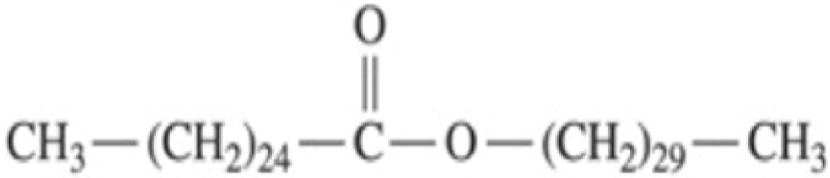
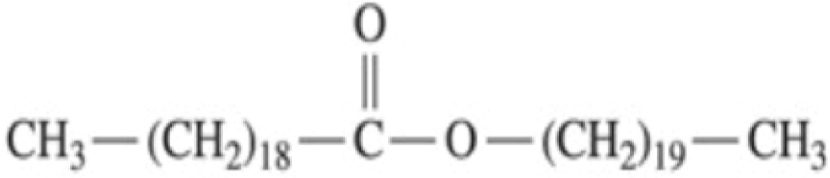




- Waxes insoluble in water and not hydrolyzed as easily as fat and oil

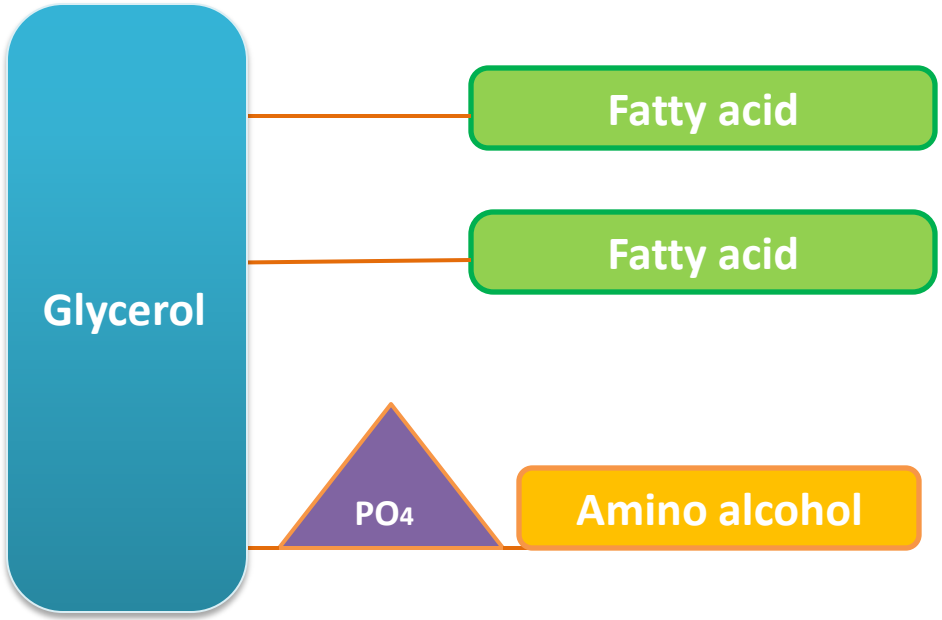
They often occur in nature as protective coatings on feathers, fur, skin, leaves, and fruits.

Some Typical Waxes

Type	condensed structural formula	Source	Uses
Beeswax		Honeycomb	Candles, shoe polish, wax paper
Carnauba wax		Brazilian palm tree	Waxes for furniture, cars, floors, shoes
Jojoba wax		Jojoba bush	Candles, soaps, cosmetics

Phosphoglycerides

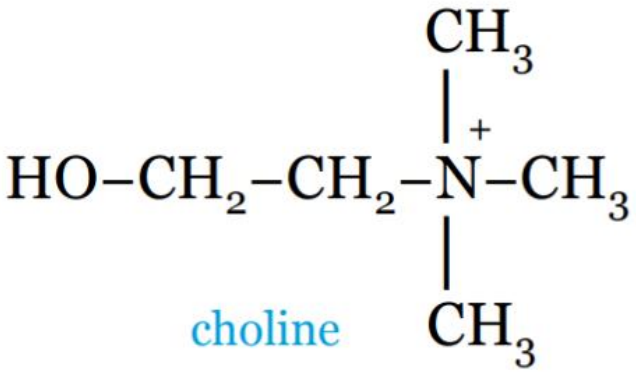
Phosphoglycerides (Phospholipids): A complex lipid contains glycerol, F.As, phosphoric acid , and an amino alcohol component.



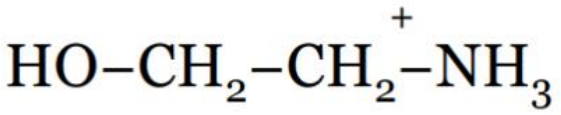
Phosphoglycerides are the major component of cell membranes.

Aminoalcohols in Phosphoglycerides

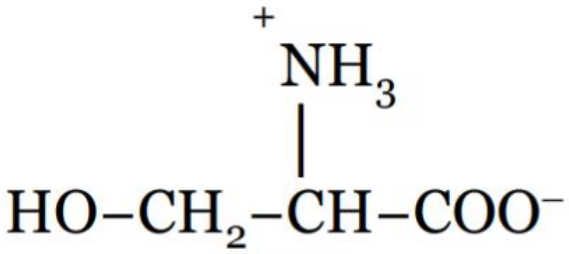
The most abundant phosphoglycerides have alcohols choline, ethanolamine, or serine that attached to the phosphate group:



choline



ethanolamine

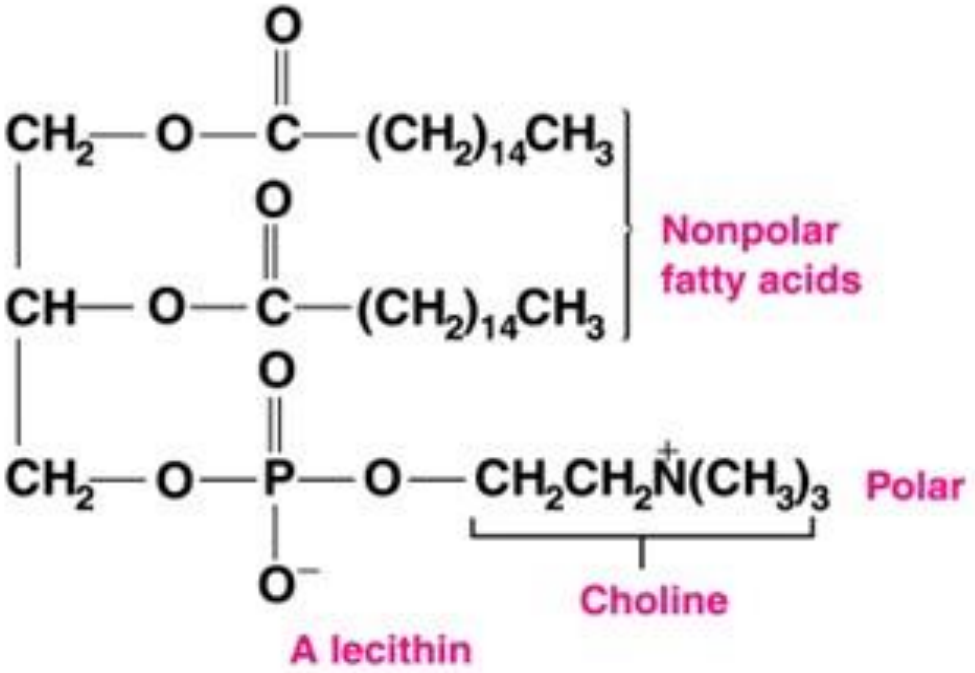


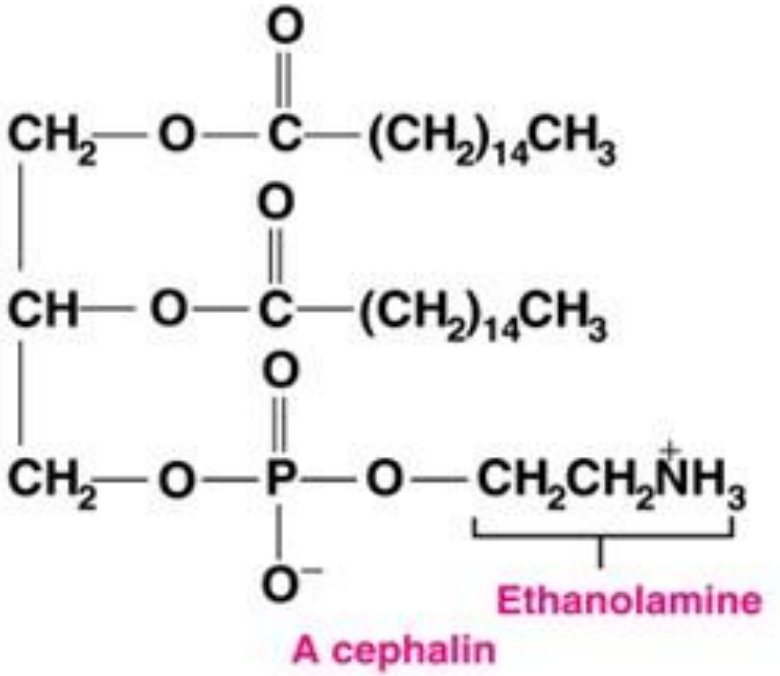
serine

Amino alcohols

Lecithin & Cephalin

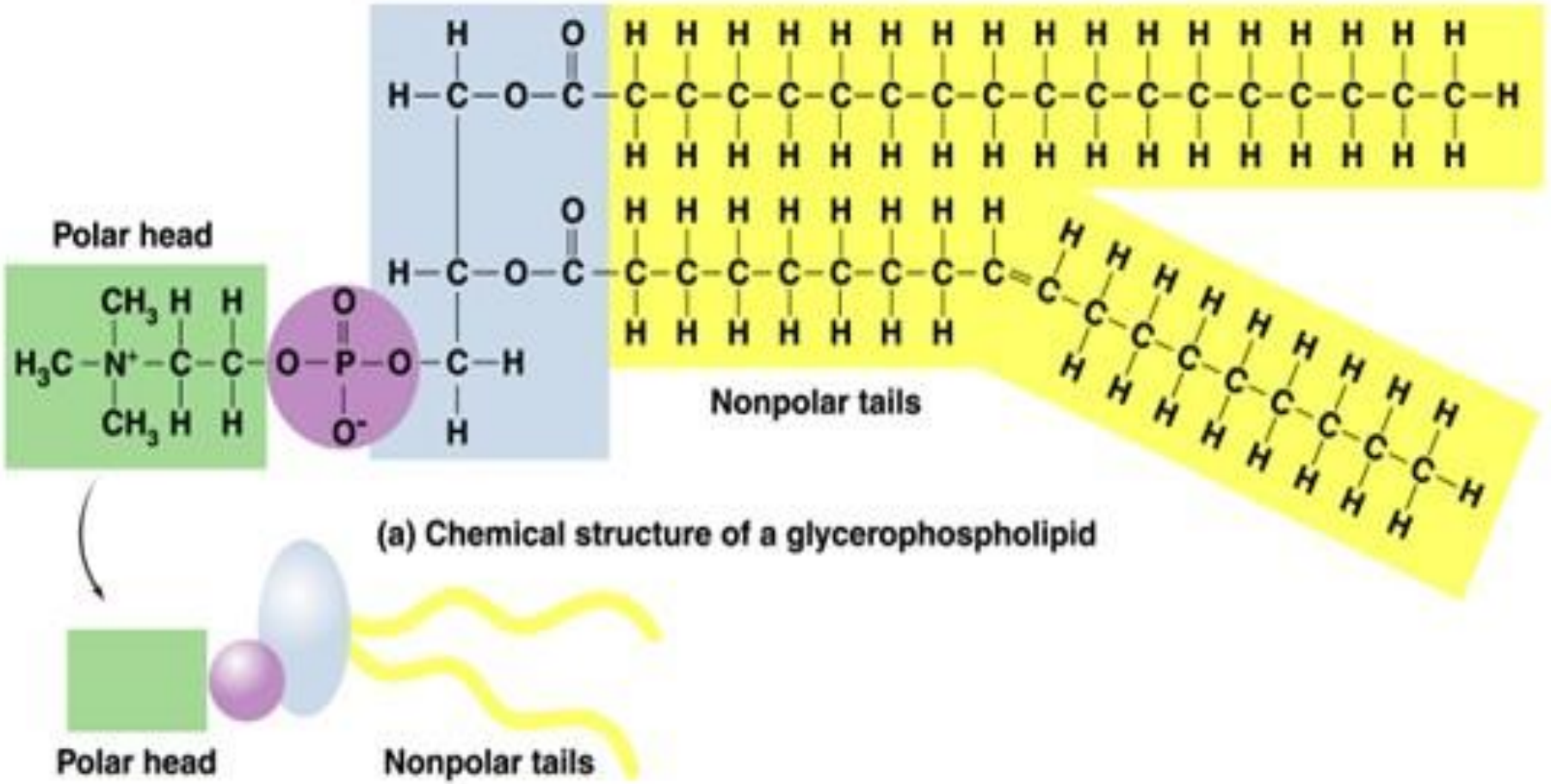
- **Lecithins:** Phosphoglycerides that contains the aminoalcohol choline
- **Cephalins:** Phosphoglycerides that contains the aminoalcohols ethanolamine or serine





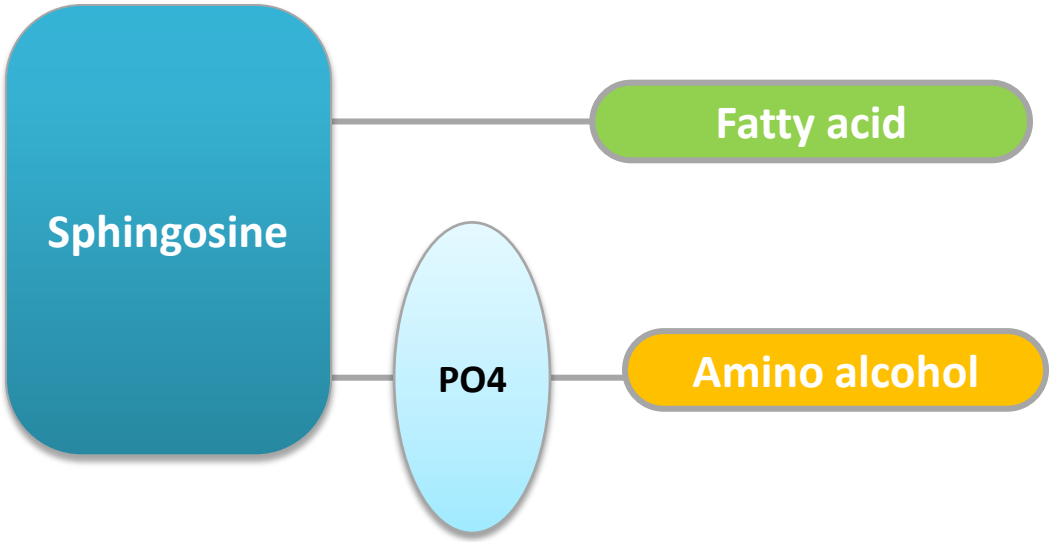
Cephalins are found in most cell membranes, and are particularly abundant in brain and nerve tissue and found in egg yolk, wheat germ, and yeast.

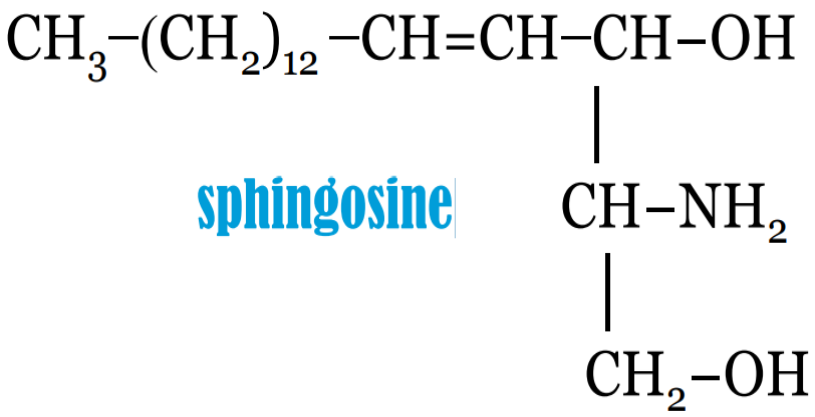
Structure and Polarity of a Glycerophospholipid



Sphingolipids

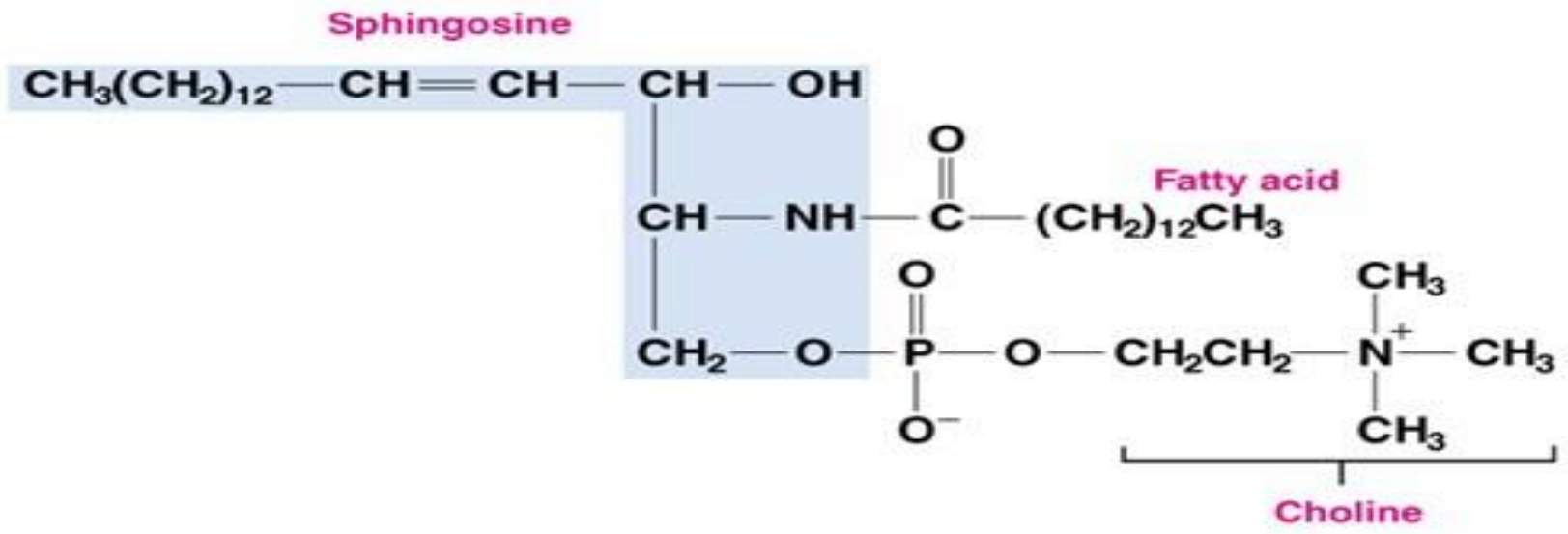
- **Sphingolipids** are complex lipids that contain sphingosine instead of glycerol, as well as F.As, phosphoric acid , and an amino alcohol component.
- The important type of sphingolipids are the sphingomyelins:





Sphingomyelin

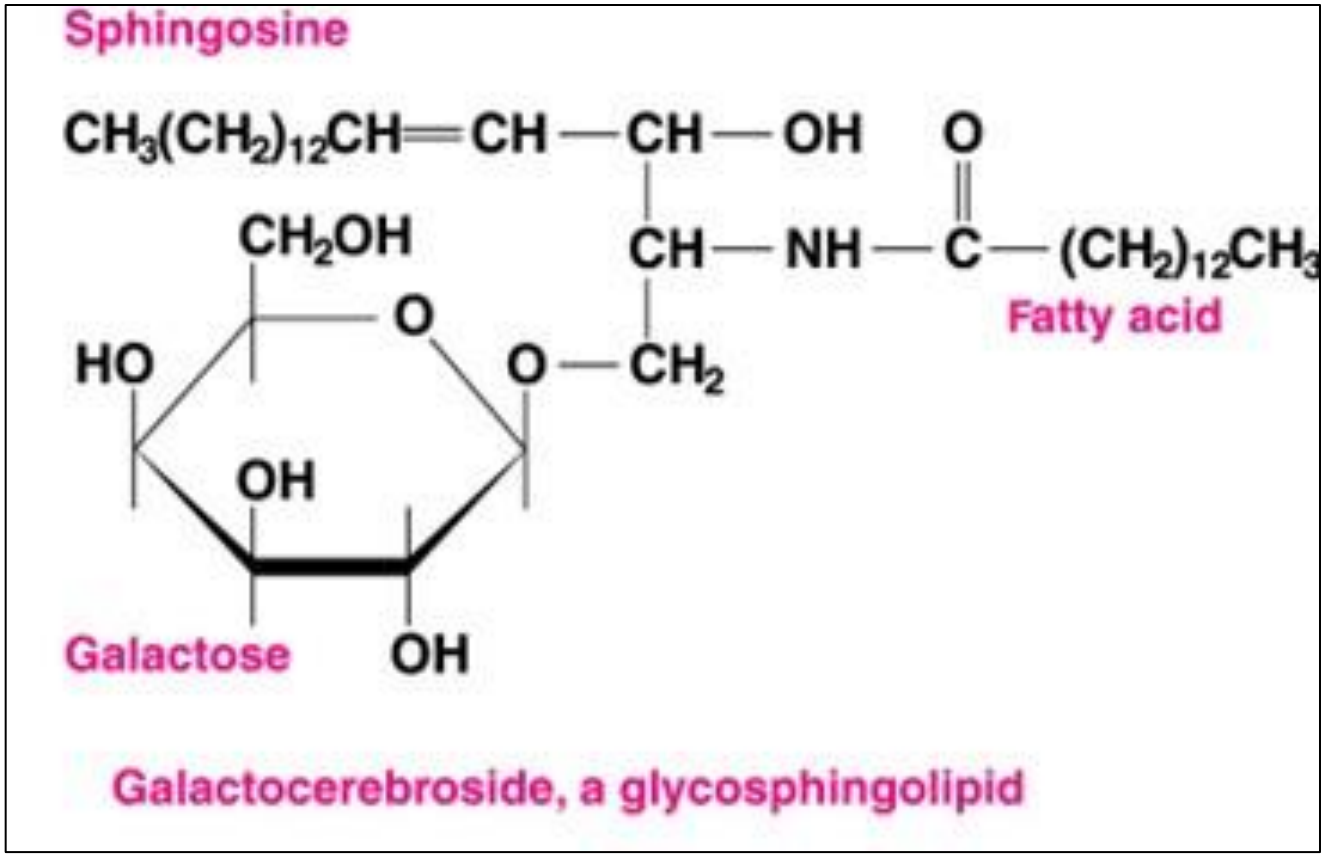
- It is a complex lipid contain a siphingosin, F.A, cholin.
- In the sphingomyelins a choline is attached to sphingosine by a phosphate group, while a single fatty acid attached to the sphingosine N via an amide linkage.
- Sphingomyelins are found brain and nerve tissue, and in the myelin sheath that protects nerves.

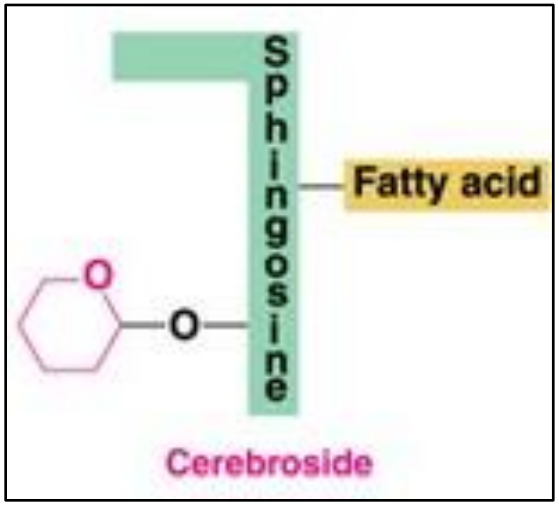


Sphingomyelin, a sphingolipid

Glycolipids

- A complex lipid contain a siphingosin, F.A ,a carbohydrate (glucose or galactose). They are often called cerebrosides due to their abundance in brain tissues.





Biological Membrane

Most cell membranes contain about 60% lipids and 40% proteins. Theses Membranes performed two vital functions in living organisms.

- The external cell membrane acts as a selective barrier between the cell and its environment, enclosing the cellular fluid (cytoplasm) and organelles.
- Internal membranes enclose the organelles, creating cellular compartments that have separate organization and functions.

Organelle
Endoplasmic reticulum
Lysosome
Microfilaments and microtubules
Mitochondrion
Nucleus
Plastids
Ribosome

Structure of Cell Membrane

Cell membranes contain

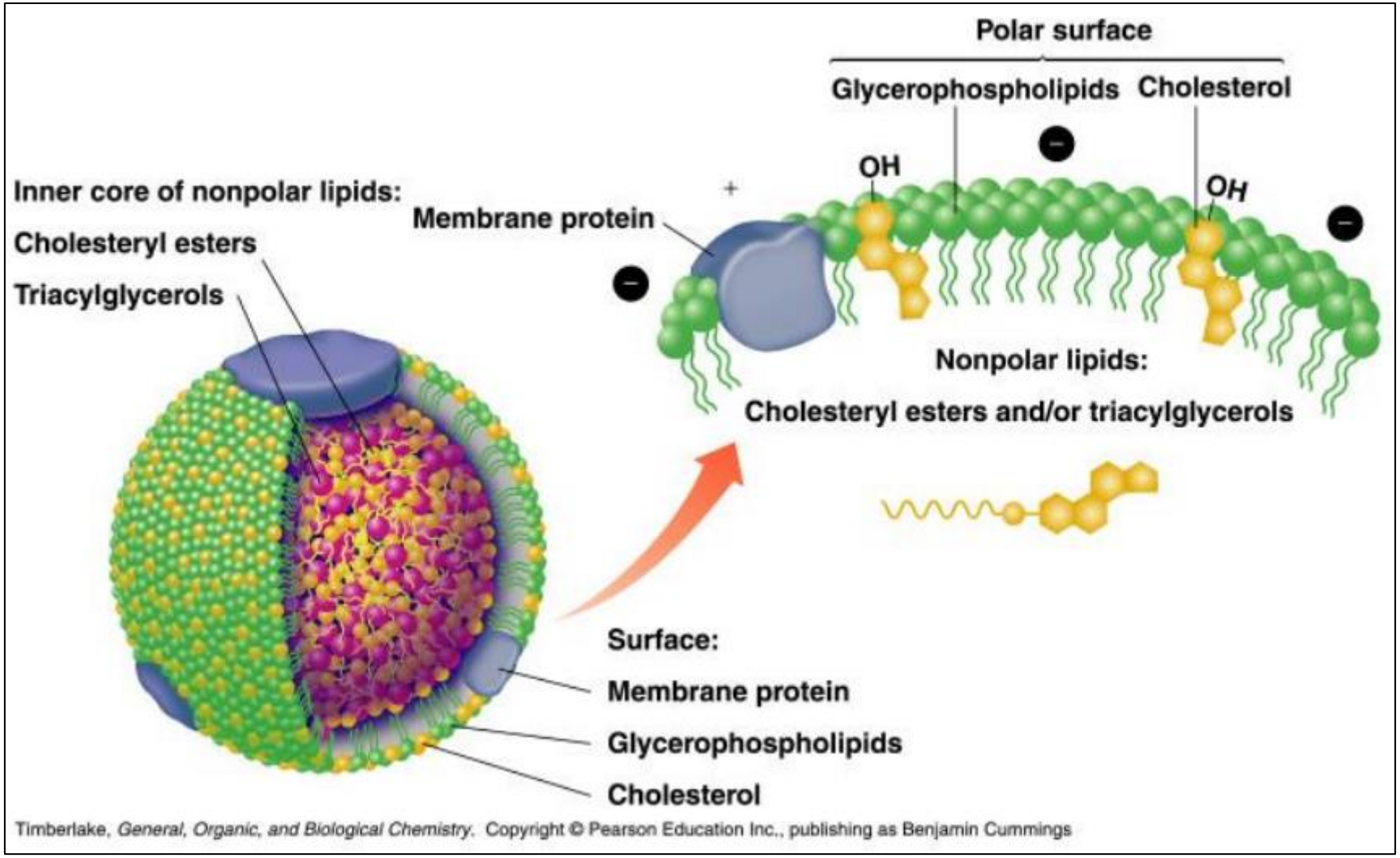
- Lipid, protein and carbohydrates.
- Phosphoglycerides such as (lecithin, cephalin)
- Sphingomyelin
- Cholesterol.

The lipids are organized in **a bilayer** in which the hydrophobic chains (nonpolar tails) extend toward the inside of bilayer and the hydrophilic groups(the phosphate groups and other polar groups) are oriented toward the outside, where they come in contact with water, like the micelle.

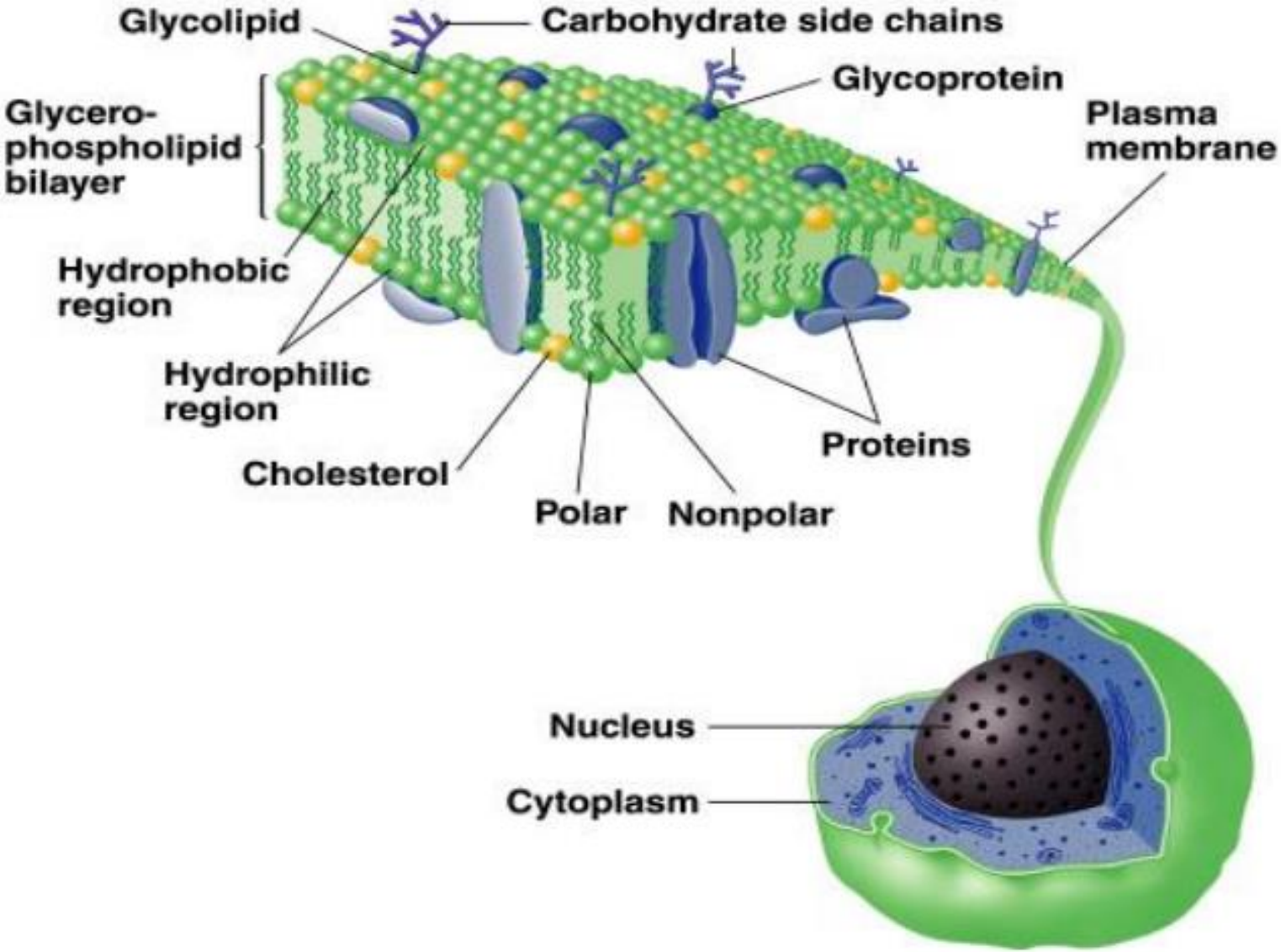
Cell membranes also contain unsaturated fatty acid chains that increase the flexibility or fluidity of the membrane. Unsaturated fatty acid chains fit into bilayer more loosely than do saturated F.As.

Lipid Bilayer

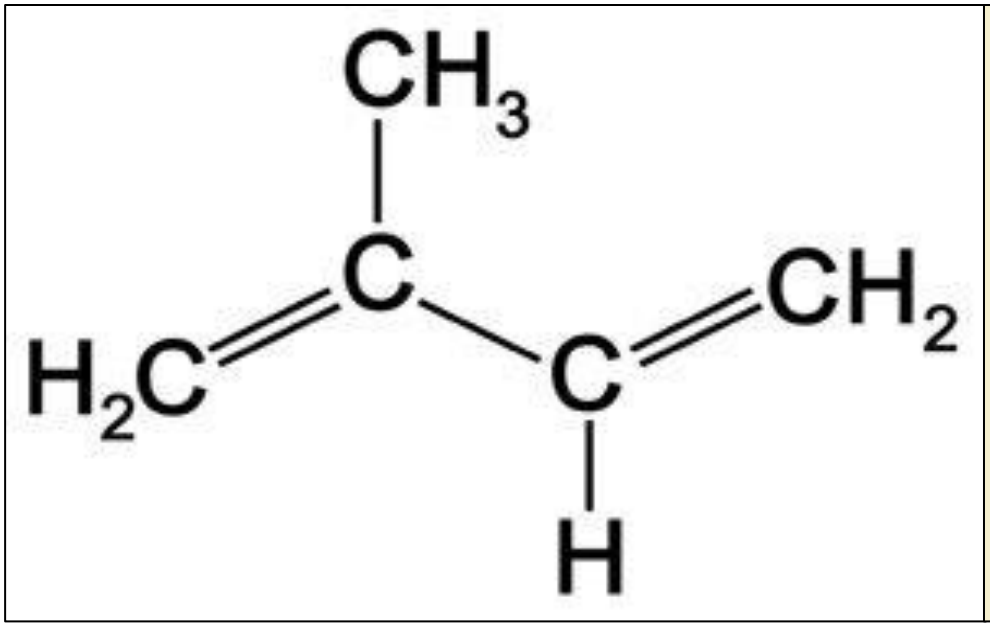
A structure found in membranes, consisting of two sheets of arranged lipid molecules so that the hydrophobic portions are facing each other.

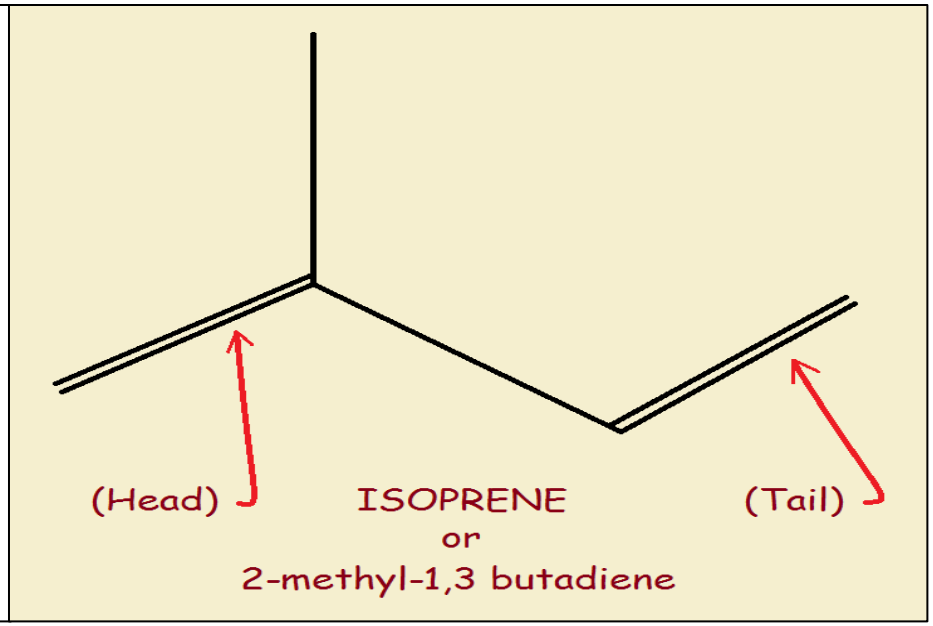


Fluid Mosaic Model of Cell Membranes



Isoprenoids: Are a vast array of biomolecules that are composed of repeating five-carbon structural units known as isoprene (methylbutadiene) units. The Isoprenoids consist of Terpenes and Steroids.



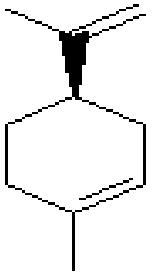


Terpenes

- **Terpenes** are available in nature as a diverse class of lipids. Some of them are used as spices, perfumes and medicines. They are linear or cyclic compounds formed by condensation of two or more units of isoprene, usually in head-to-tail fashion. The terpene having functional groups such as OH and carbonyl group are called terpenoids.
- Terpene can be isolated from in the essential oils of plants such as carotenes, sequaline.
- Terpenes are Classified according to the number of isoprene units they contain.

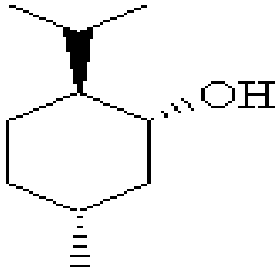
Class	# Isoprene units	# C atoms
Monoterpene	2	10
Sesquiterpene	3	15
Diterpene	4	20
Sesterpene	5	25
Triterpene	6	30
Tetraterpene	8	40

Examples of Monoterpenes



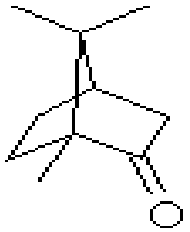
limonene

(found in the skin of citrus fruits)



menthol

(peppermint)

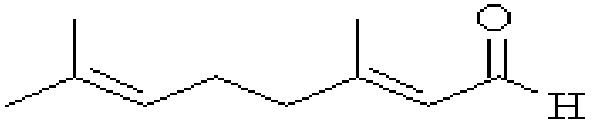


camphor

(camphor tree)

vitamin A

(involved in the chemistry of vision)



citral

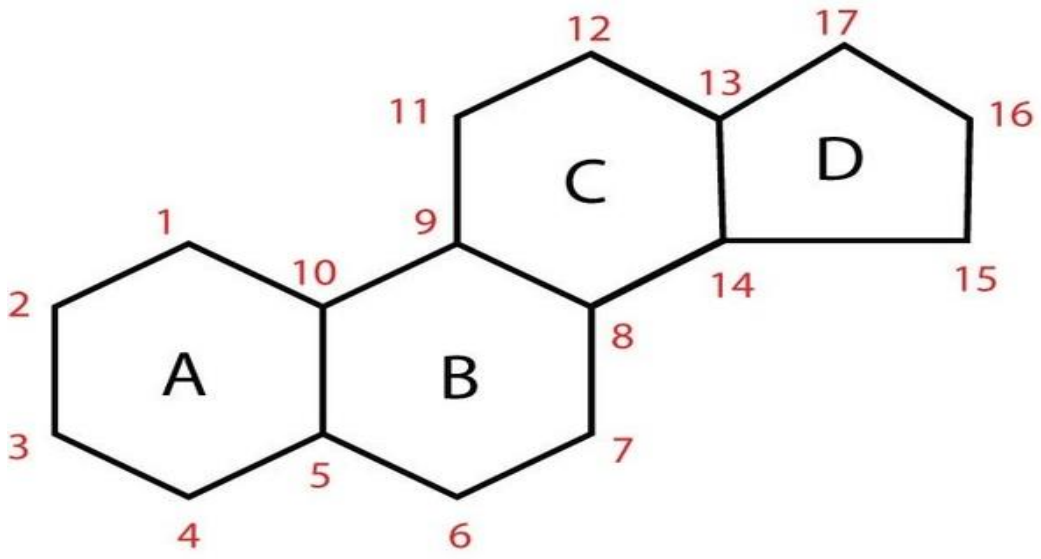
(lemon grass)

β-carotene

(in carrots and other vegetables, enzymes convert it to vitamin A)

Steroid

- They are different from the lipids.
- The basic steroid structure contains four fused rings (three six-membered rings and a single five membered ring fused together)
- They are classified as lipids because they are soluble in nonpolar solvents, but they are non-saponifiable because the components are not held together by ester linkages.

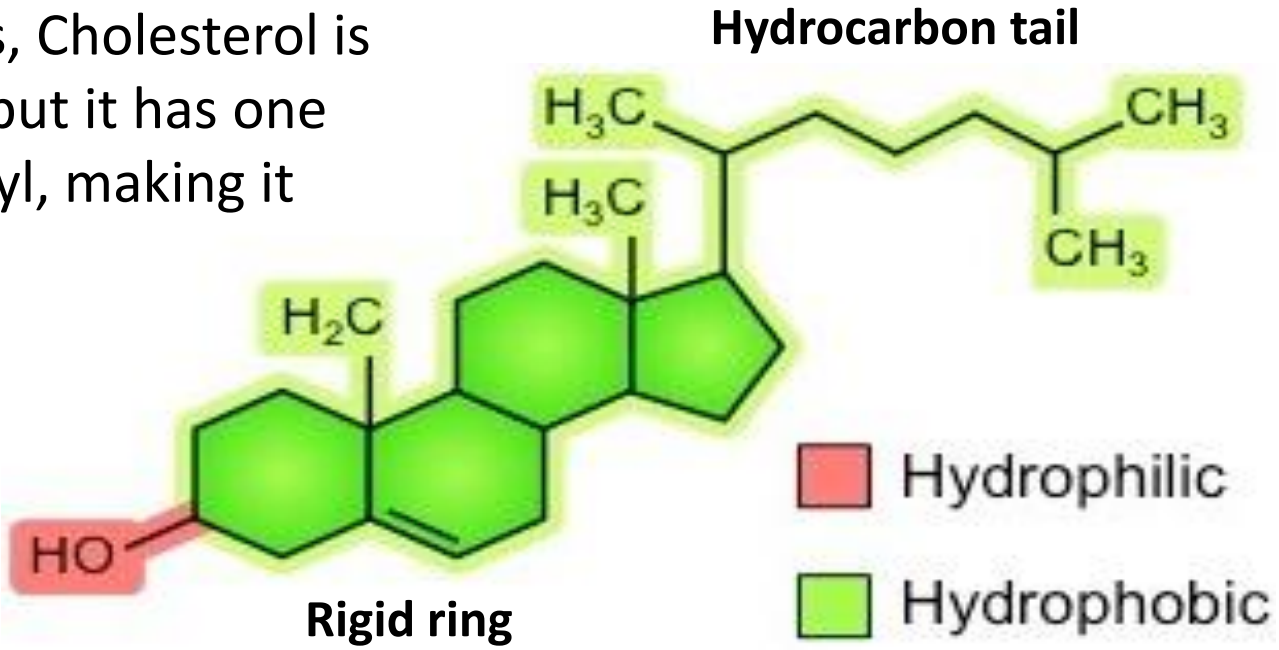


Steroid skeleton

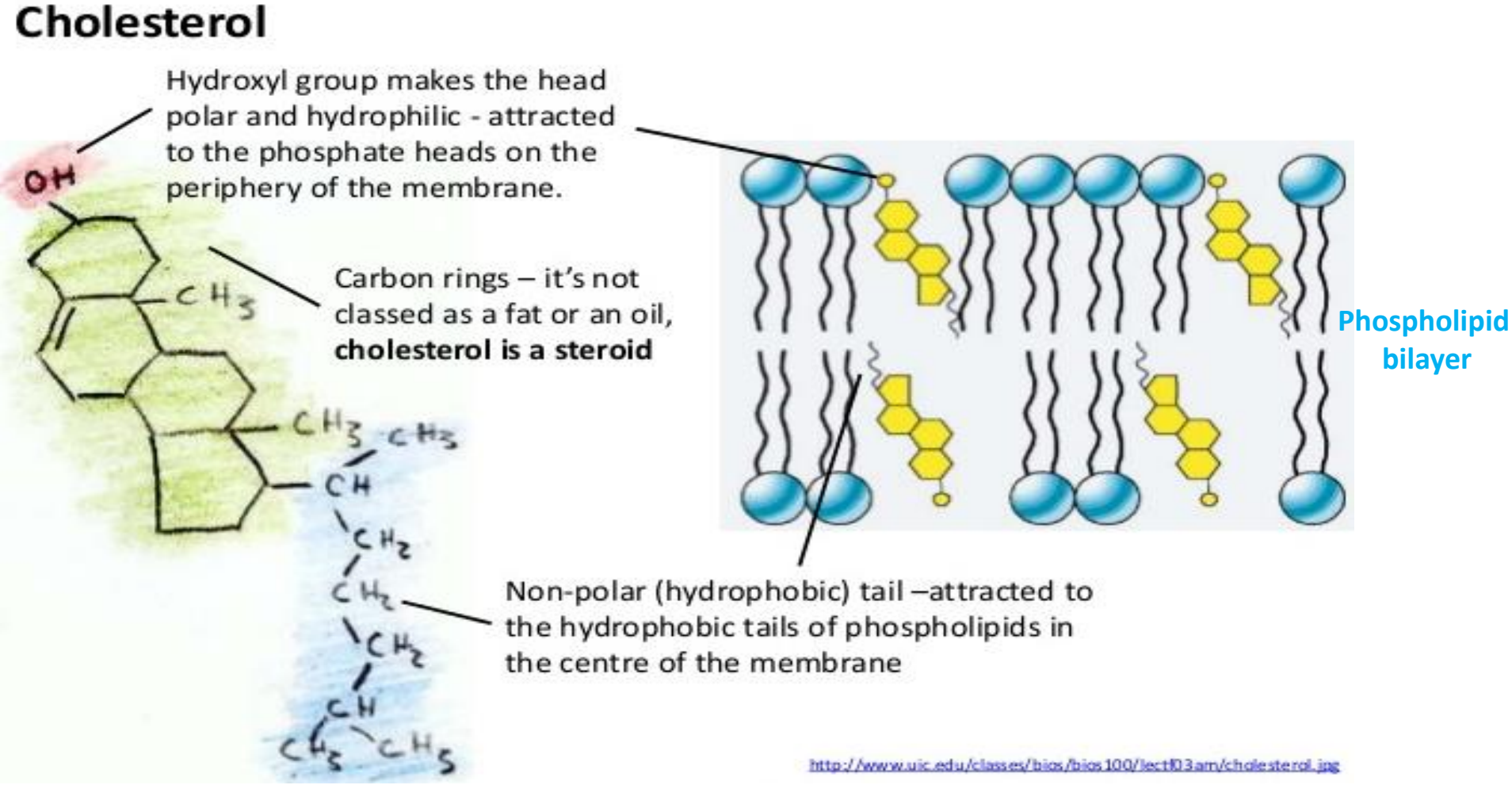
Cholesterol

Cholesterol is the most abundant steroid in the body (myelin sheath, brain, and nerve tissues). It is an essential component of cell membranes, and is a precursor for other steroids, such as the **bile salts**, **sex hormones**, **vitamin D**, and the adrenocorticoid hormones.

- Structurally, Cholesterol has a rigid ring system and a short branched hydrocarbon tail. The OH group of cholesterol forms hydrogen bonds with polar phospholipid head groups.
- In terms of properties, Cholesterol is mainly hydrophobic, but it has one polar group, a hydroxyl, making it amphipathic.

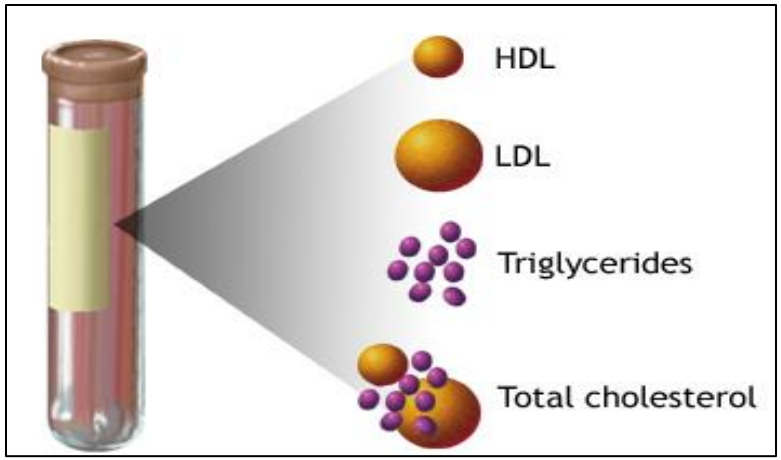


Cholesterol inserts into bilayer membranes with its hydroxyl group oriented toward the aqueous phase & its hydrophobic ring system adjacent to fatty acid chains of phospholipids.

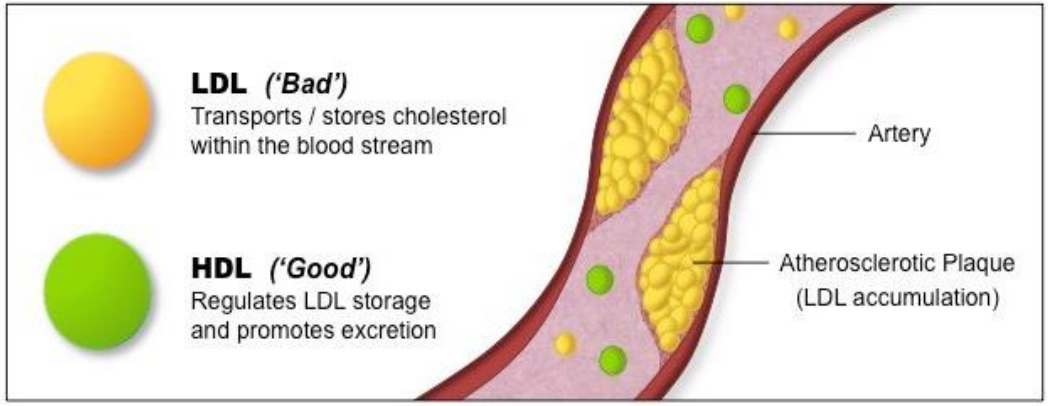


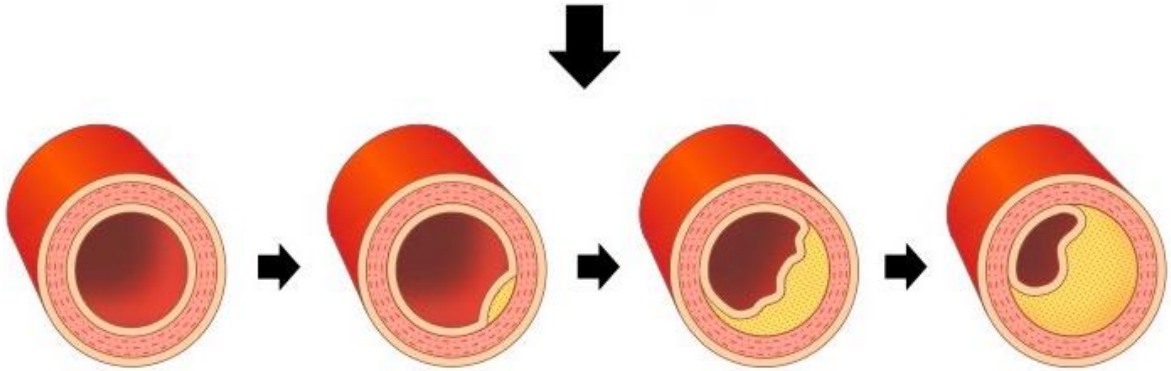
Coronary Heart Diseases

- Usually; saturated fat in diet causes high blood cholesterol level and these consider risk factor of coronary heart diseases.



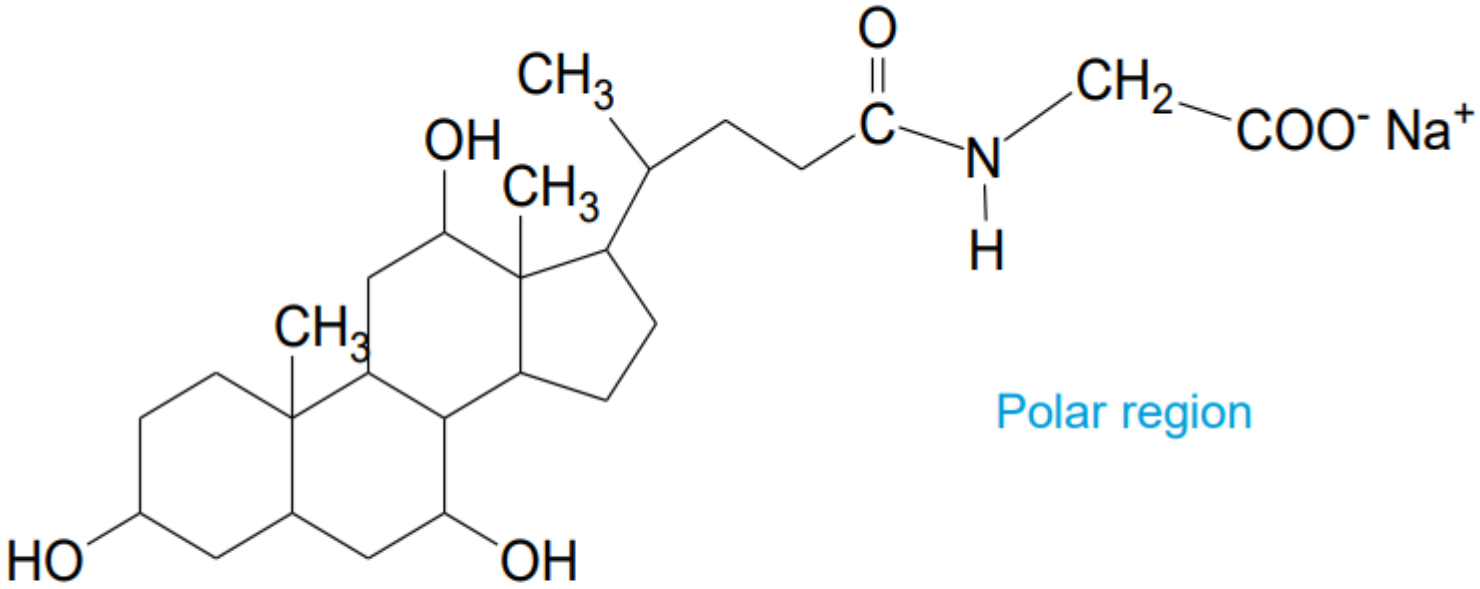
A lipoprotein profile measures the level of cholesterol in the blood





Bile Salt

Bile is a yellowish brown or green fluid produced in the liver and stored in the gall bladder. It is important in lipid digestion.



sodium glycocholate, a bile salt

Steroid Hormone & Prostaglandine

Hormones: A chemical messenger secreted by specific glands and carried by the blood to a target tissue, where it triggers a particular response.

- ***Adrenocorticoid hormones***

The adrenocorticoid hormones are produced in the adrenal glands (located on the top of the kidney).

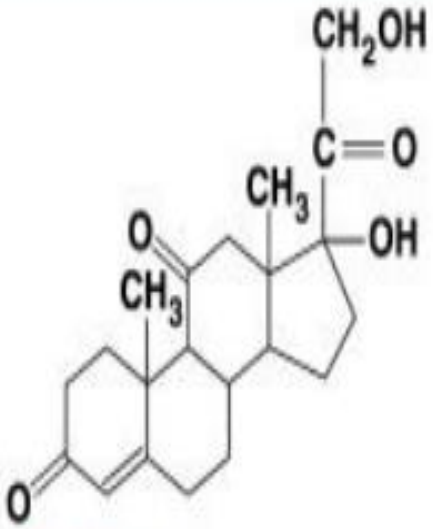
The adrenocorticoid are classified into

- **Glucocorticoids** are involved in metabolism of glucose, proteins and fatty acids. Cortisone is an example for this type of steroid.
- **Mineralocorticoids** are responsible for the increased reabsorption of Na+, Cl- and HCO3- ions by the kidneys. Aldosterone is an example of a mineralocorticoid.

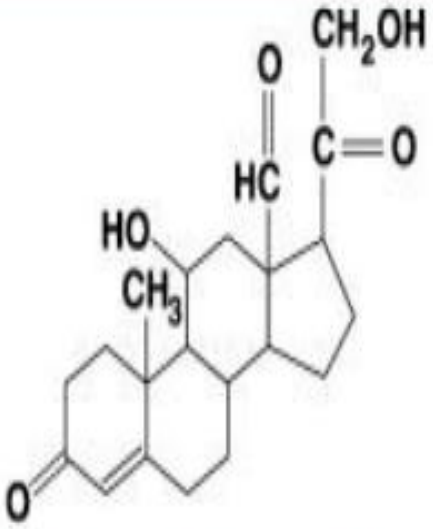
Aldosterone, which regulates electrolytes and water balance by the kidneys.

Cortisone, a glucocorticoid, which increases blood glucose level and stimulates the synthesis of glycogen in the liver.

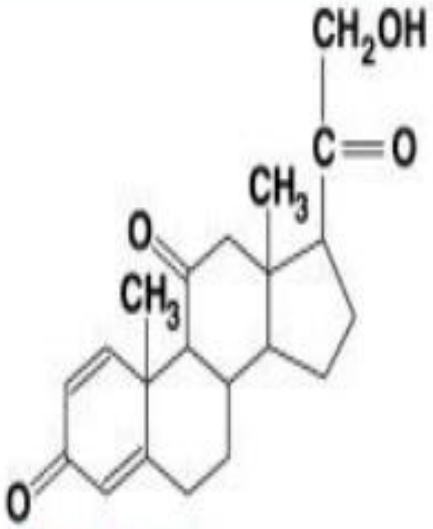
Corticosteroids



Cortisone
(produced in adrenal gland)



Aldosterone (mineralocorticoid)
(produced in adrenal gland)



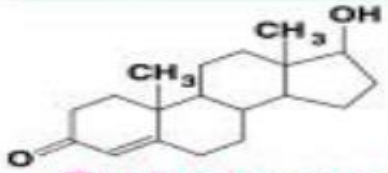
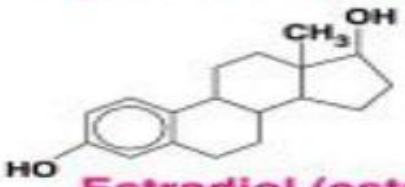
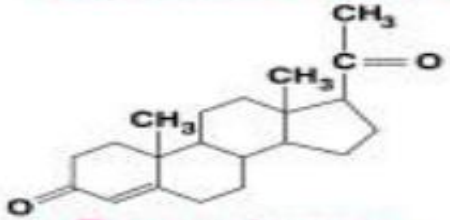
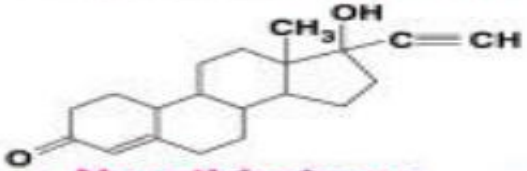
Prednisone
(synthetic corticoid)

Biological Effects

Increases the blood glucose and glycogen levels from fatty acids and amino acids	Increases the reabsorption of Na^+ in kidneys; retention of water	Reduces inflammation; treatment of asthma and rheumatoid arthritis

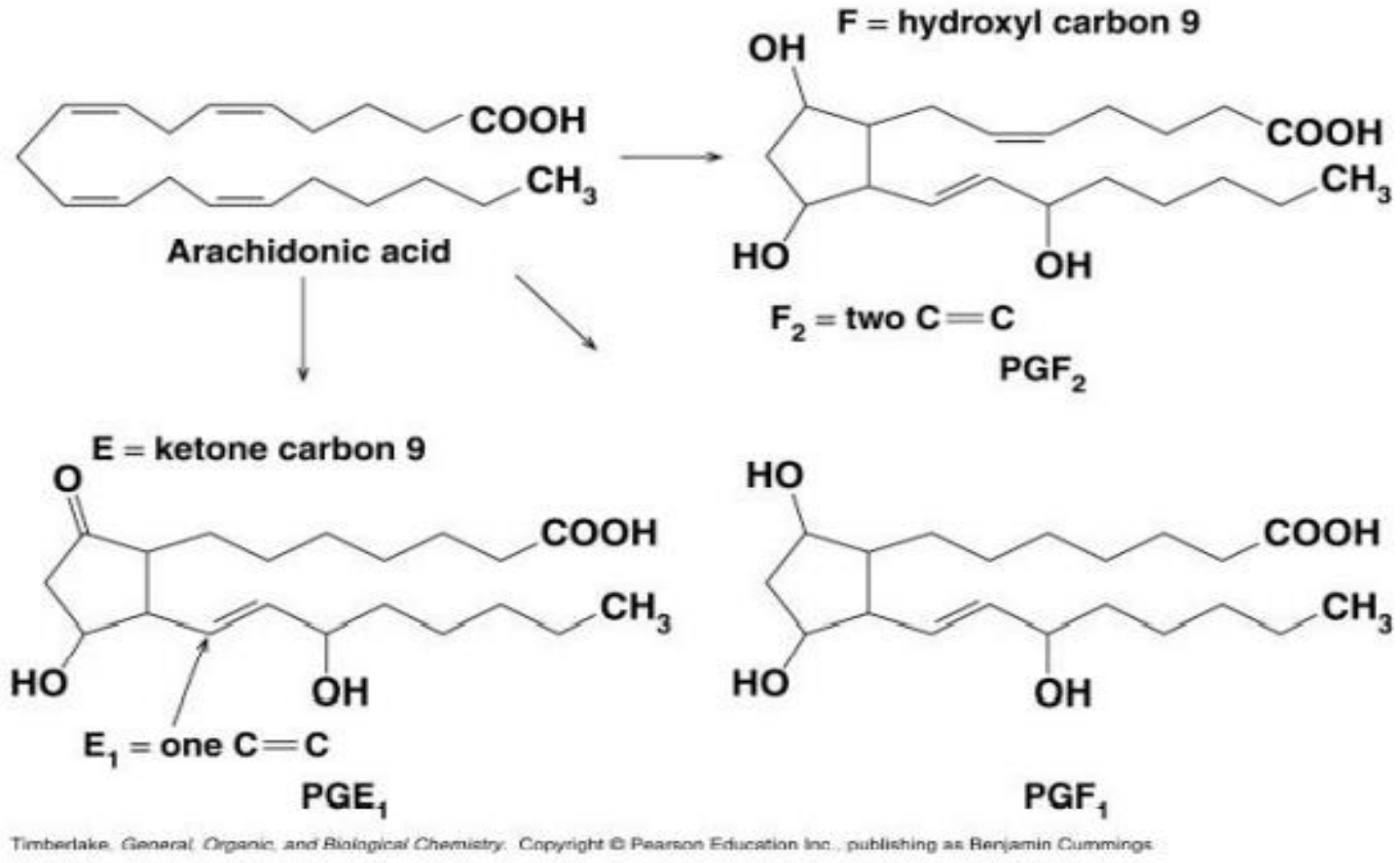
Sex Hormone

Sex hormones produced in the testes and ovaries regulate the production of sperm and eggs and aid in the development of secondary sex characteristics.

Hormone	Biological Effects
 Testosterone (androgen) (produced in testes)	Development of male organs; male sexual characteristics including muscles and facial hair; sperm formation
 Estradiol (estrogen) (produced in ovaries)	Development of female sexual characteristics; ovulation
 Progesterone (produced in ovaries)	Prepares uterus for fertilized egg
 Norethindrone (synthetic progestin)	Contraceptive (birth control) pill

Prostaglandins

- **Prostaglandins** are cyclic compounds synthesized from arachidonic acid (20 carbon unsaturated F.A). Like hormones, they are involved in a host of body processes, including reproduction, blood clotting, inflammation, and fever. like prostaglandin E 2 (PGE 2).
- There are about 20 prostaglandins in a variety of tissues within both male and female



Prostaglandin are

- Produced by injured tissue.
- Involved in pain, fever and inflammation.
- Aspirin (non-steroidal anti-inflammatory drug) works by inhibiting prostaglandin production, alleviating inflammation and fever.