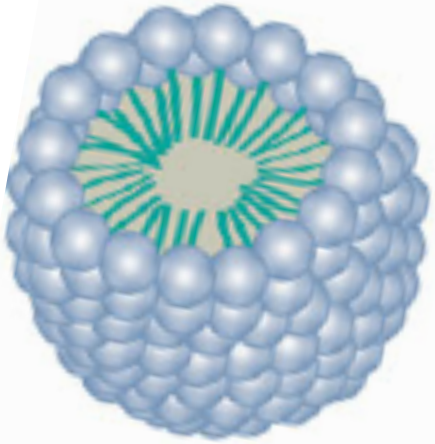
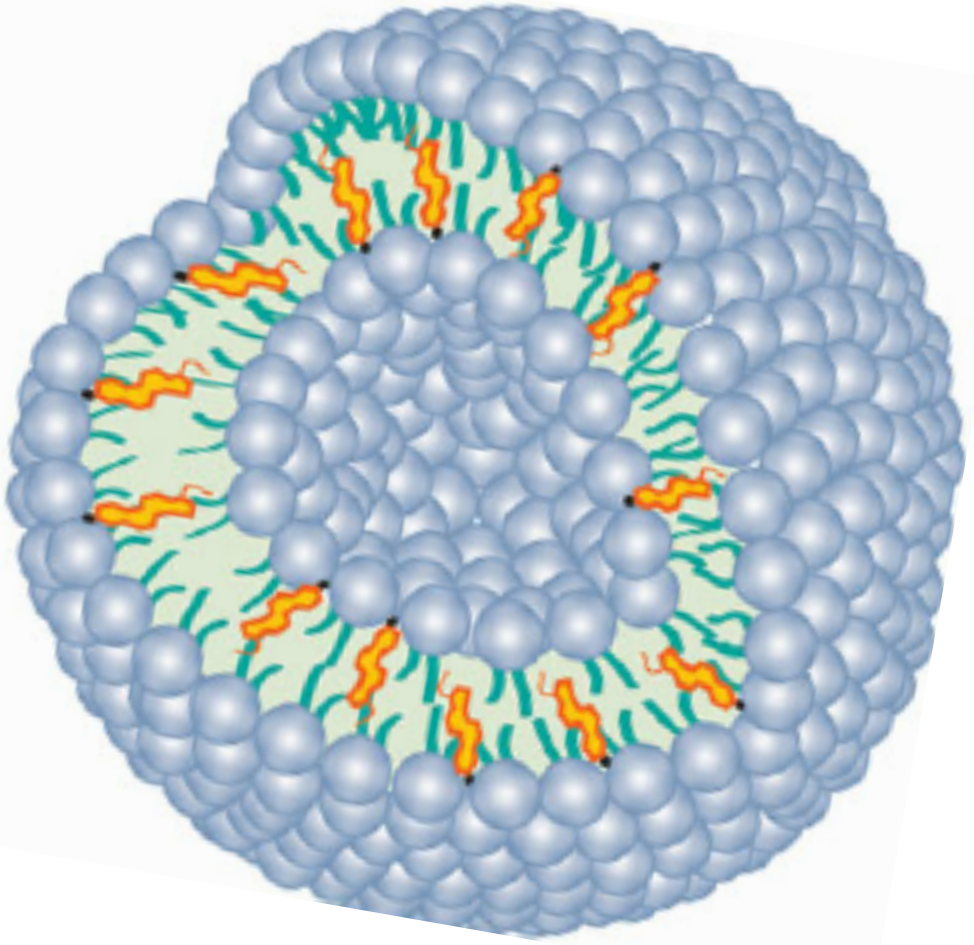
Chemistry of Lipid





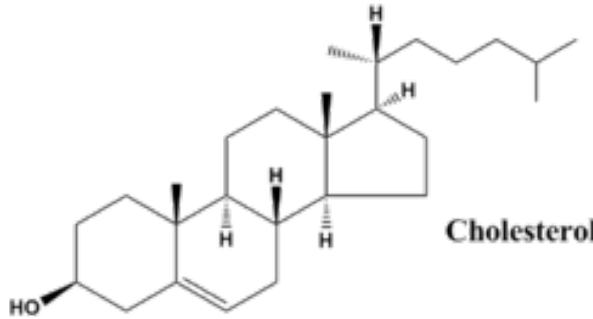
อาทิตย์ ศิลป์ศิริวานิชย์
atitsil@kku.ac.th

วัตถุประสงค์

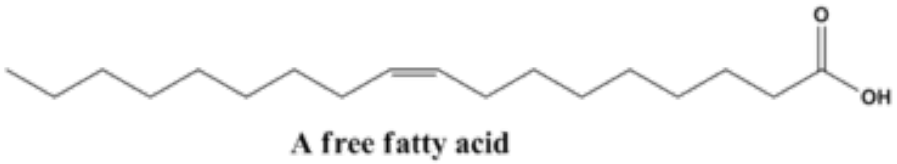
- เข้าใจและสามารถอธิบายลักษณะทางเคมีของ lipid ได้
- เข้าใจหลักการ lipid nomenclature และสามารถเรียกชื่อ lipid ได้อย่างถูกต้อง
- เข้าใจและสามารถอธิบายปฏิกิริยาเคมีของ lipid ได้
- เข้าใจและสามารถอธิบายลักษณะของ lipid ที่พบในร่างกายและในชีวิตประจำวันได้

Lipid

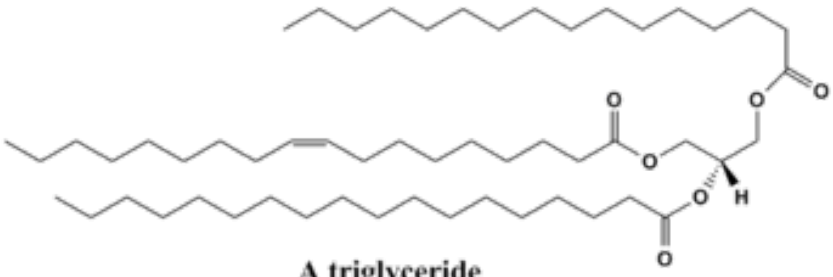
- Biomolecule
- Many forms:
  - Acids: Fatty acids
  - Alcohol: Glycerol
  - Ester: TAG, Wax
  - etc.
- Not biopolymer
- No building bock
- Non/Less water soluble
- Non/Less polar



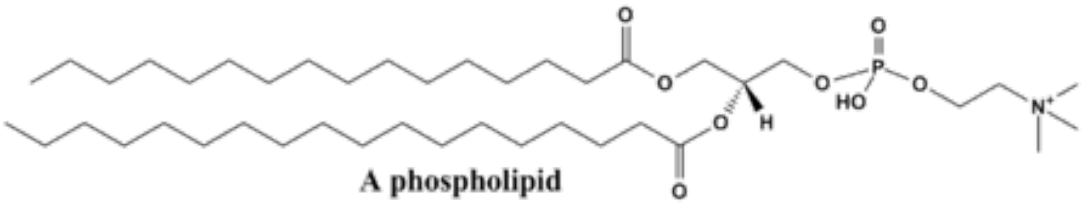
Cholesterol



A free fatty acid



A triglyceride



A phospholipid

Lipid

4 major groups

1. Derivative of lipids

: combine → simple or compound lipid

- Fatty acids + Glycerol

1.Simple lipids

- TAG and Wax

3. Compound lipids

- Phospholipids, Sphingolipids, Glycolipids, Lipoprotein

4.Miscellaneous lipid

- Sterol, Terpene, Prostaglandin, Vit-A, D, E, K

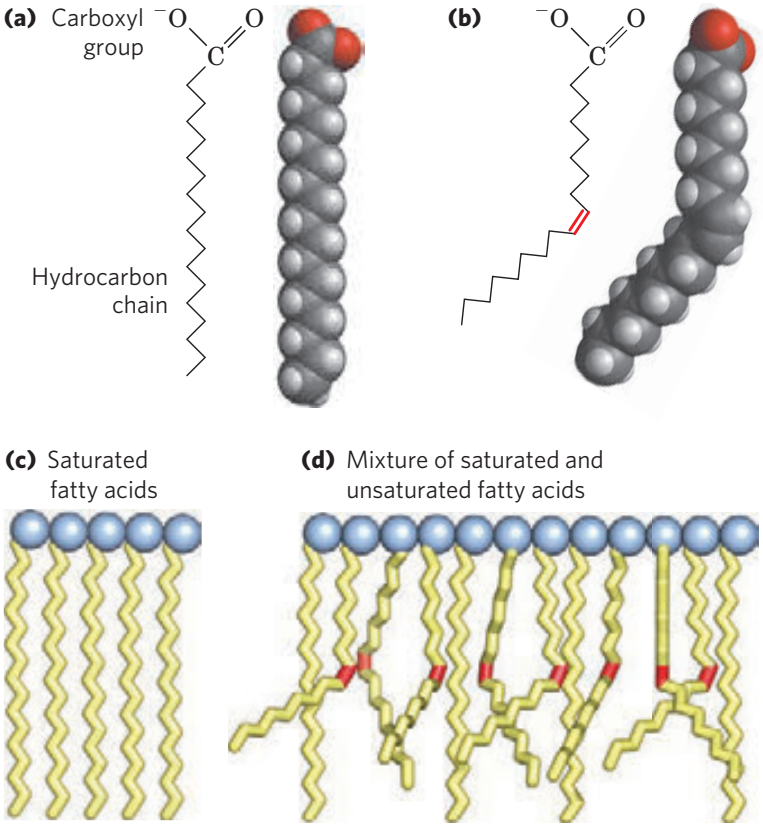
Derivative lipids

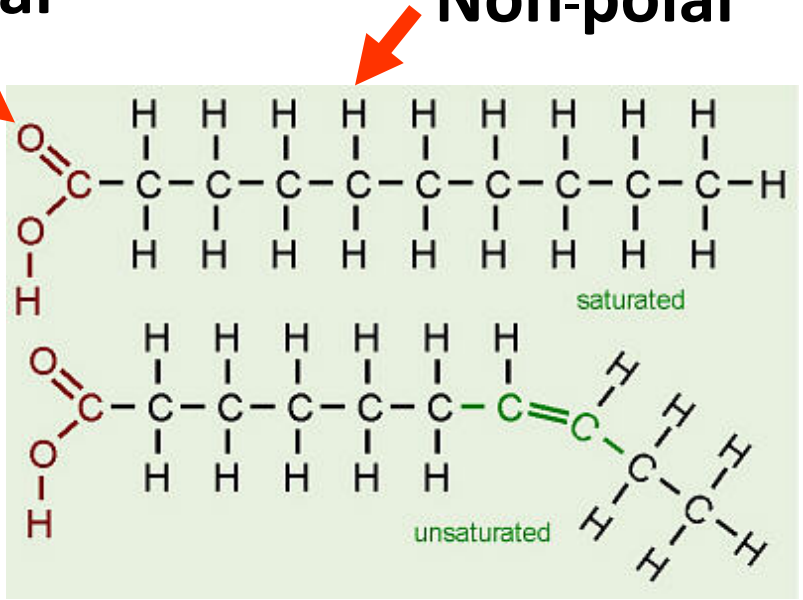
Fatty acids

Carboxylic acids with hydrocarbon chain (4-36 C)

Saturated FA — More stable

Unsaturated FA — Low melting point





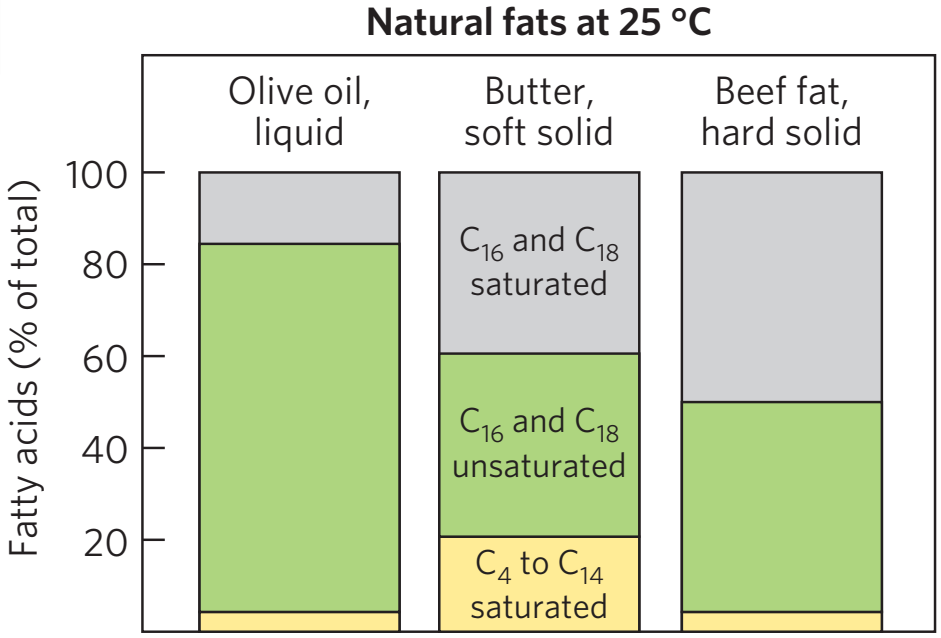


TABLE 10–1 Some Naturally Occurring Fatty Acids: Structure, Properties, and Nomenclature

Carbon skeleton	Structure*	Systematic name†	Common name (derivation)	Melting point (°C)	Solubility at 30 °C (mg/g solvent)	
					Water	Benzene
12:0	$CH_3(CH_2)_{10}COOH$	*n*-Dodecanoic acid	Lauric acid (Latin *laurus*, "laurel plant")	44.2	0.063	2,600
14:0	$CH_3(CH_2)_{12}COOH$	*n*-Tetradecanoic acid	Myristic acid (Latin *Myristica*, nutmeg genus)	53.9	0.024	874
16:0	$CH_3(CH_2)_{14}COOH$	*n*-Hexadecanoic acid	Palmitic acid (Latin *palma*, "palm tree")	63.1	0.0083	348
18:0	$CH_3(CH_2)_{16}COOH$	*n*-Octadecanoic acid	Stearic acid (Greek *stear*, "hard fat")	69.6	0.0034	124
20:0	$CH_3(CH_2)_{18}COOH$	*n*-Eicosanoic acid	Arachidic acid (Latin *Arachis*, legume genus)	76.5		
24:0	$CH_3(CH_2)_{22}COOH$	*n*-Tetracosanoic acid	Lignoceric acid (Latin *lignum*, "wood" + *cera*, "wax")	86.0		
16:1(Δ^9)	$CH_3(CH_2)_5CH{=}CH(CH_2)_7COOH$	*cis*-9-Hexadecenoic acid	Palmitoleic acid	1 to –0.5		
18:1(Δ^9)	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	*cis*-9-Octadecenoic acid	Oleic acid (Latin *oleum*, "oil")	13.4		
18:2($\Delta^{9,12}$)	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$	*cis*-,*cis*-9,12-Octadecadienoic acid	Linoleic acid (Greek *linon*, "flax")	1–5		
18:3($\Delta^{9,12,15}$)	$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$	*cis*-,*cis*-,*cis*-9,12,15-Octadecatrienoic acid	α-Linolenic acid	–11		
20:4($\Delta^{5,8,11,14}$)	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_3COOH$	*cis*-,*cis*-,*cis*-,*cis*-5,8,11,14-Icosatetraenoic acid	Arachidonic acid	–49.5		

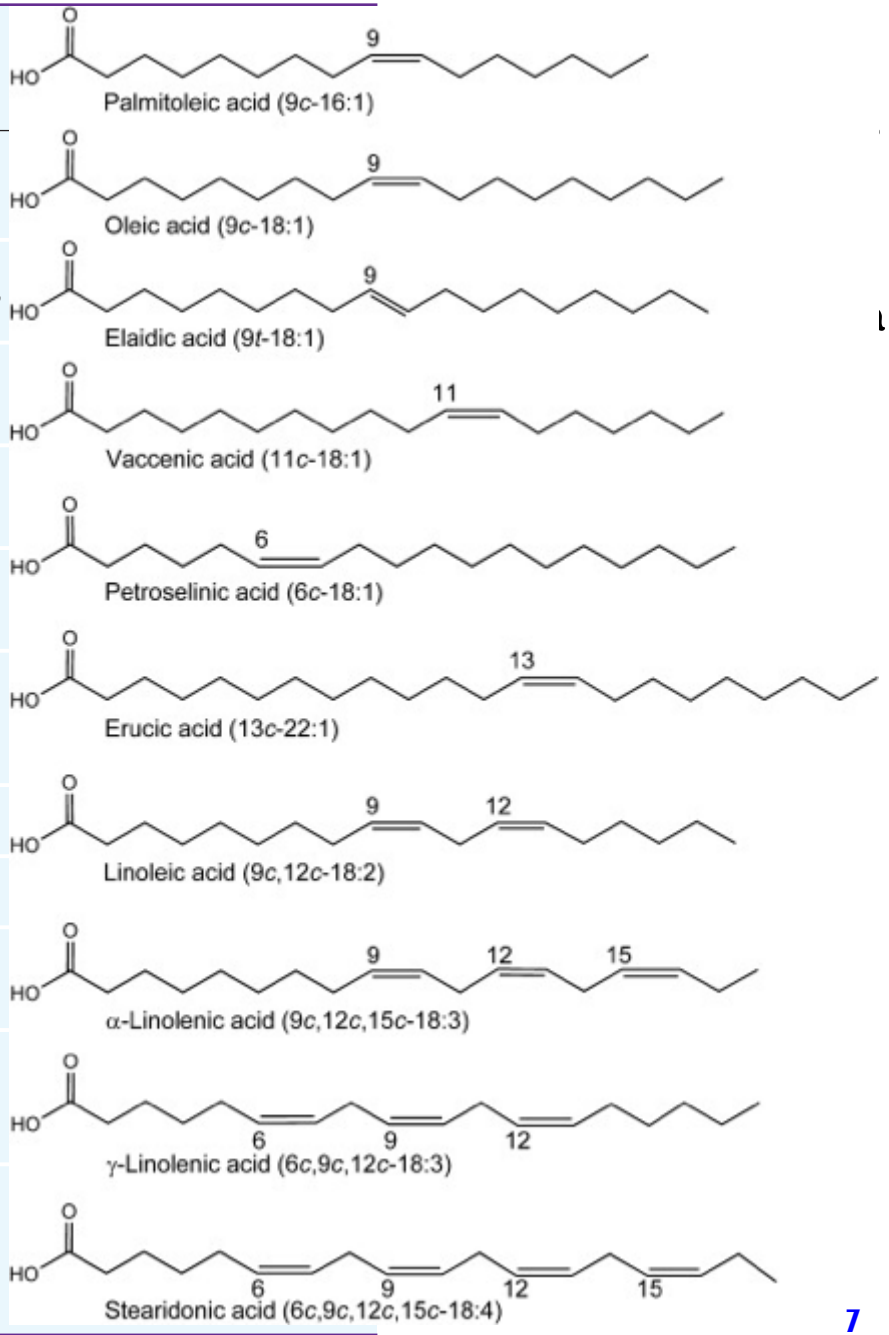
*All acids are shown in their nonionized form. At pH 7, all free fatty acids have an ionized carboxylate. Note that numbering of carbon atoms begins at the carboxyl carbon.

Most commonly occurring fatty acids have even numbers of carbon atoms in an unbranched chain of 12 to 24 carbons.

Naturally occurring unsaturated fatty acids, the double bonds are in the cis configuration. Trans fatty acids are produced by fermentation in the rumen of dairy animals and are obtained from dairy products and meat.

TABLE 10–1 Some Naturally Occurring Fatty Acids: Structure, Properties, and Nomenclature

Carbon skeleton	Structure*	Systematic name†	Common name (derivation)
12:0	$CH_3(CH_2)_{10}COOH$	*n*-Dodecanoic acid	Lauric acid (Latin *laurus*, "laurel plant")
14:0	$CH_3(CH_2)_{12}COOH$	*n*-Tetradecanoic acid	Myristic acid (Latin *Myristica*, nutmeg genus)
16:0	$CH_3(CH_2)_{14}COOH$	*n*-Hexadecanoic acid	Palmitic acid (Latin *palma*, "palm tree")
18:0	$CH_3(CH_2)_{16}COOH$	*n*-Octadecanoic acid	Stearic acid (Greek *stear*, "hard fat")
20:0	$CH_3(CH_2)_{18}COOH$	*n*-Eicosanoic acid	Arachidic acid (Latin *Arachis*, legume genus)
24:0	$CH_3(CH_2)_{22}COOH$	*n*-Tetracosanoic acid	Lignoceric acid (Latin *lignum*, "wood" + *cera*, "wax")
16:1(Δ^9)	$CH_3(CH_2)_5CH{=}CH(CH_2)_7COOH$	*cis*-9-Hexadecenoic acid	Palmitoleic acid
18:1(Δ^9)	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	*cis*-9-Octadecenoic acid	Oleic acid (Latin *oleum*, "oil")
18:2($\Delta^{9,12}$)	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$	*cis*-,*cis*-9,12-Octadecadienoic acid	Linoleic acid (Greek *linon*, "flax")
18:3($\Delta^{9,12,15}$)	$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$	*cis*-,*cis*-,*cis*-9,12,15-Octadecatrienoic acid	α-Linolenic acid
20:4($\Delta^{5,8,11,14}$)	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_3COOH$	*cis*-,*cis*-,*cis*-,*cis*-5,8,11,14-Icosatetraenoic acid	Arachidonic acid

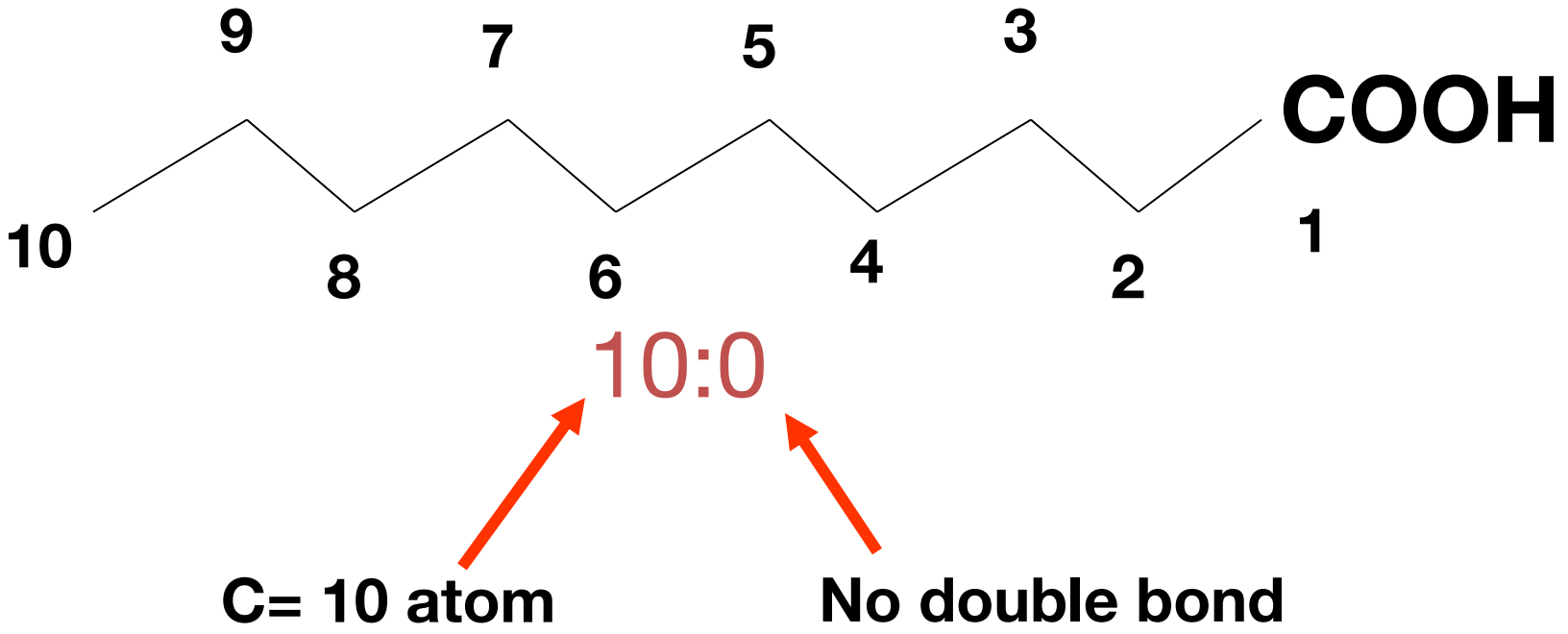


*All acids are shown in their nonionized form. At pH 7, all free fatty acids have an ionized carboxylate. Note that numbering of carbon atoms begins at the carboxyl carbon.

Fatty acid nomenclature

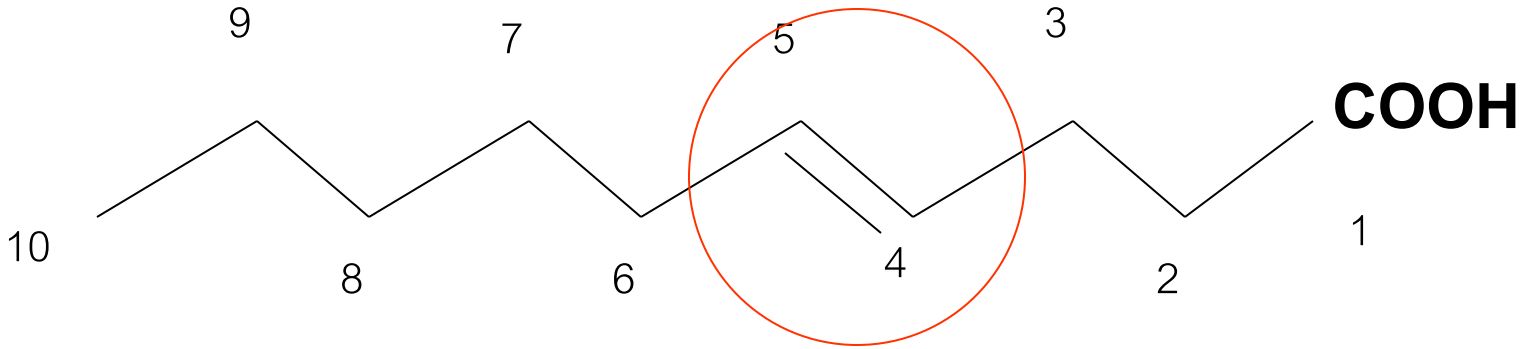
International unit of pure and applied chemistry (IUPAC)
- number of C in hydrocarbon chain
- cut -e and add -oic acid such as butane ➔ butanoic acid

Δ (delta, from COOH-end) and ω (omega, from CH-end) are used for the position of double bond

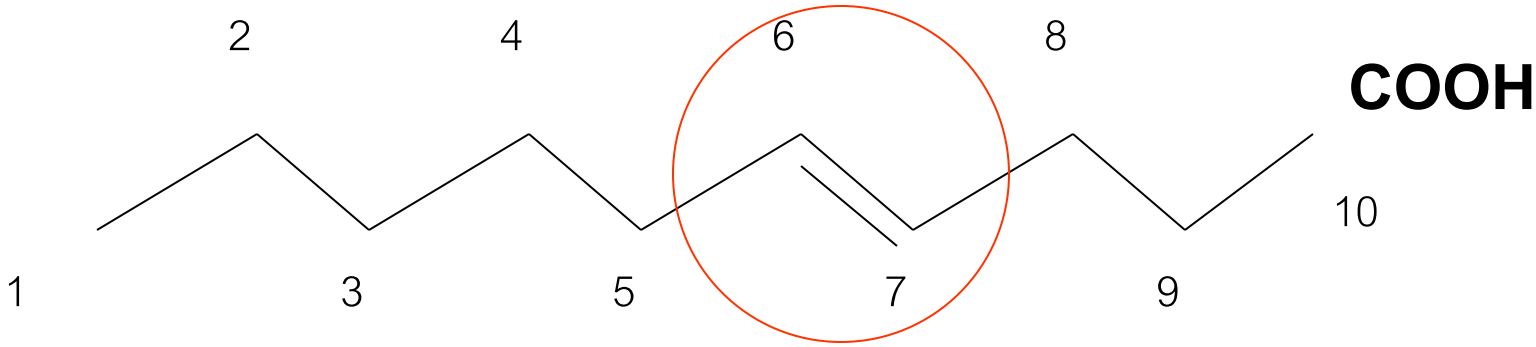


From COOH → **10:1 Δ4**

10 C , 1 double bond, position 4 (from COOH)

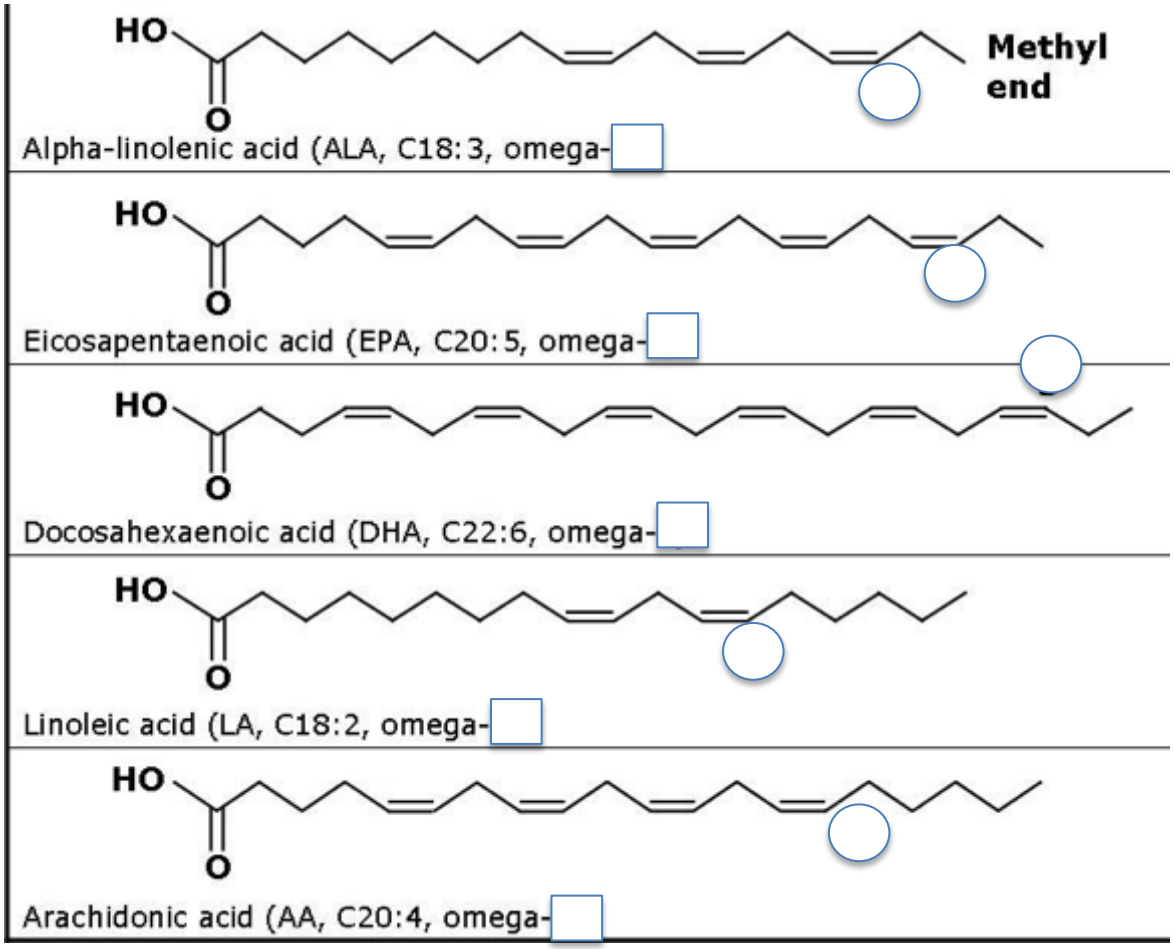


From Hydrocarbon → **10:1 ω6**



10 C, 1 double bond, position 6 (from hydrocarbon)

Essential fatty acids



Poly unsaturated fatty acid (PUFA)

PUFAs

Omega-3 Content of Frequently Consumed Seafood Products

SEAFOOD PRODUCT		OMEGA-3s PER 3 OUNCE COOKED PORTION
Herring, Wild (Atlantic & Pacific)	♥♥♥♥♥	>1,500 milligrams
Salmon, Farmed (Atlantic)	♥♥♥♥♥	
Salmon, Wild (King)	♥♥♥♥♥	
Mackerel, Wild (Pacific & Jack)	♥♥♥♥♥	

SEAFOOD PRODUCT		OMEGA-3s PER 3 OUNCE COOKED PORTION
Salmon, Canned (Pink, Sockeye & Chum)	♥♥♥♥	1,000 to 1,500 milligrams
Mackerel, Canned (Jack)	♥♥♥♥	
Mackerel, Wild (Atlantic & Spanish)	♥♥♥♥	
Tuna, Wild (Bluefin)	♥♥♥♥	

SEAFOOD PRODUCT		OMEGA-3s PER 3 OUNCE COOKED PORTION
Salmon, Wild (Sockeye, Coho, Chum & Pink)	♥♥♥	500 to 1,000 milligrams
Sardines, Canned	♥♥♥	
Tuna, Canned (White Albacore)	♥♥♥	
Swordfish, Wild	♥♥♥	
Trout, Farmed (Rainbow)	♥♥♥	
Oysters, Wild & Farmed	♥♥♥	
Mussels, Wild & Farmed	♥♥♥	

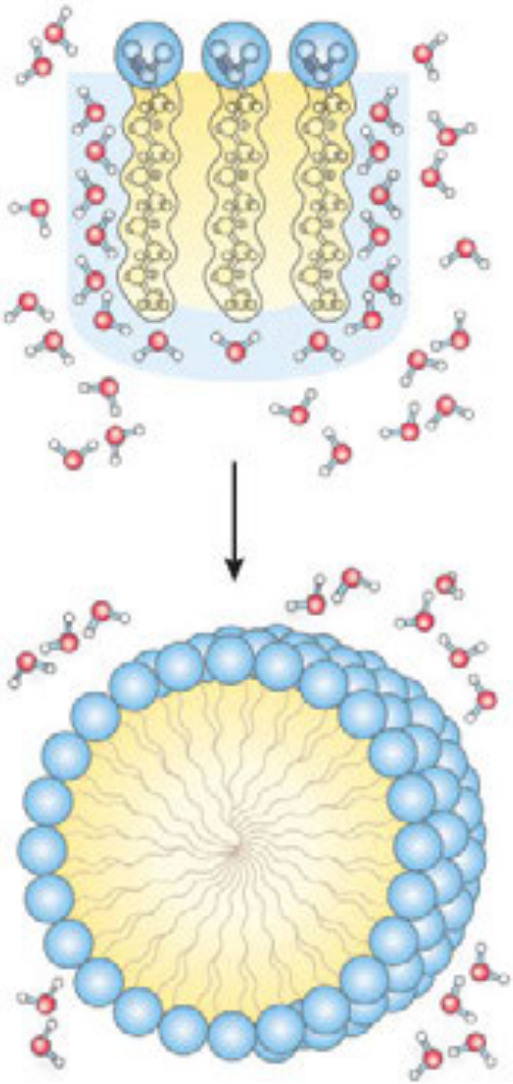
PUFAs

SEAFOOD PRODUCT		OMEGA-3s PER 3 OUNCE COOKED PORTION
Scallops, Wild	♥	<200 milligrams
Shrimp, Wild & Farmed	♥	
Lobster, Wild (Northern)	♥	
Crab, Wild (Blue)	♥	
Cod, Wild	♥	
Haddock, Wild	♥	
Tilapia, Farmed	♥	
Catfish, Farmed	♥	
Mahimahi, Wild *	♥	
Tuna, Wild (Yellowfin) *	♥	
Orange Roughy, Wild	♥	
Surimi Product (Imitation Crab)	♥	

DHA: structure of brain and nerve tissue
EPA: Prostaglandin, Thromboxane

Physical Properties of FA

1.water insoluble (nonpolar)

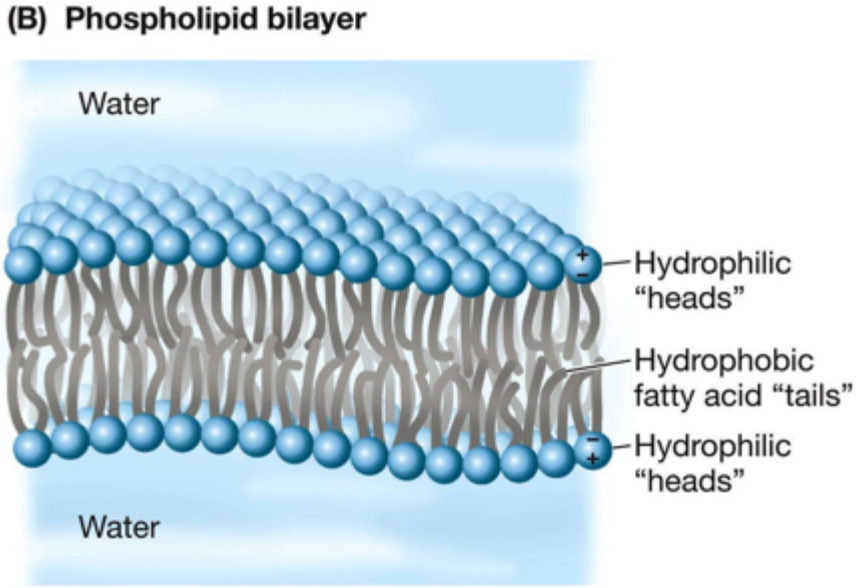


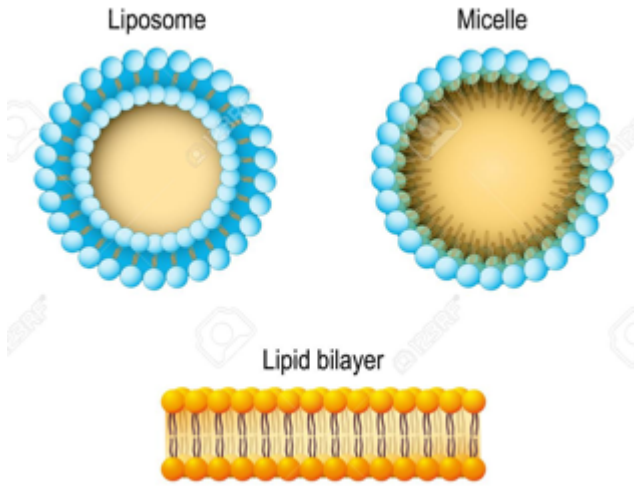
Clusters of lipid molecules

Only lipid portions at the edge of the cluster force the ordering of water. Fewer H_2O molecules are ordered, and entropy is increased.

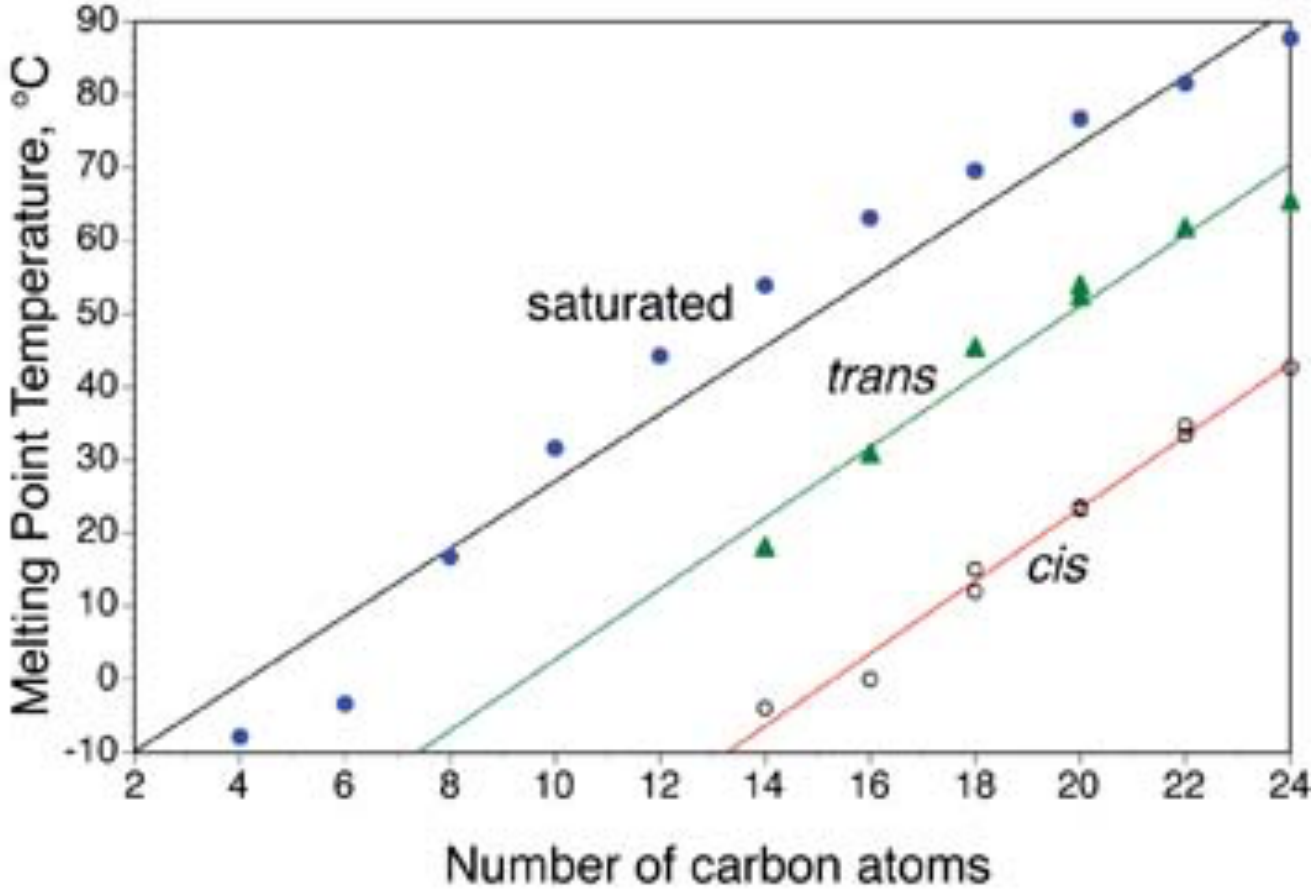
Micelles

All hydrophobic groups are sequestered from water; ordered shell of H_2O molecules is minimized, and entropy is further increased.





2. melting point



C ⇧ M.T. ⇧

= bond ⇧ M.T. ⇩

M.T. *cis* < *trans*

Chemical properties of FA

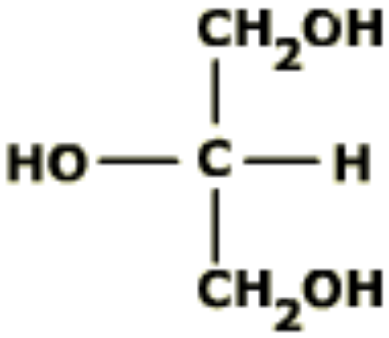
1. Acid + Base → Salt + H_2O

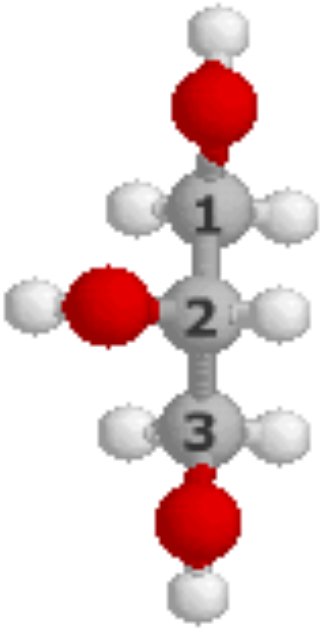
2. Acid + Alcohol → Ester + H_2O

Formation of an ester:

3. Addition rx. (at double bond)

Glycerol





Formation of an ester:

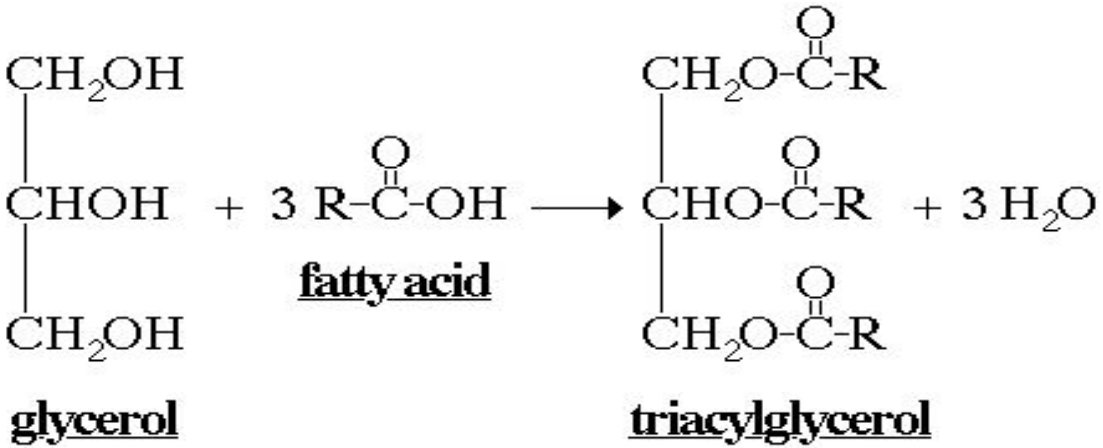
Simple lipids

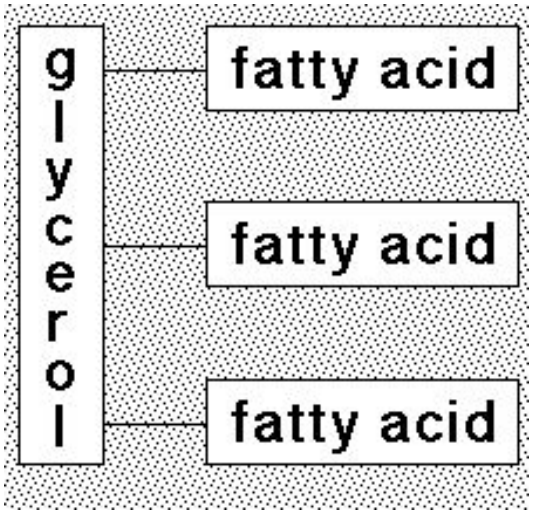
Triacylglycerol

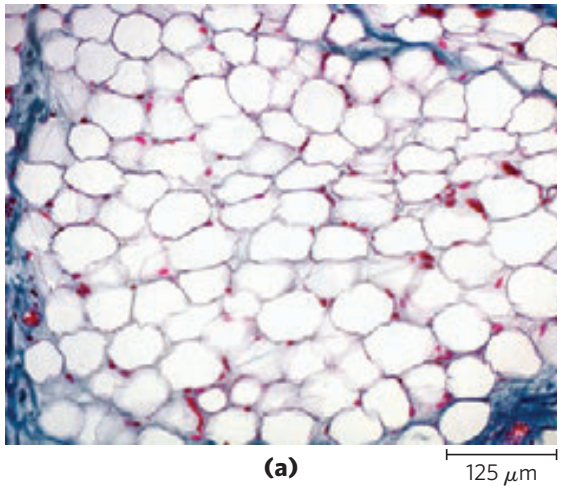
Ester

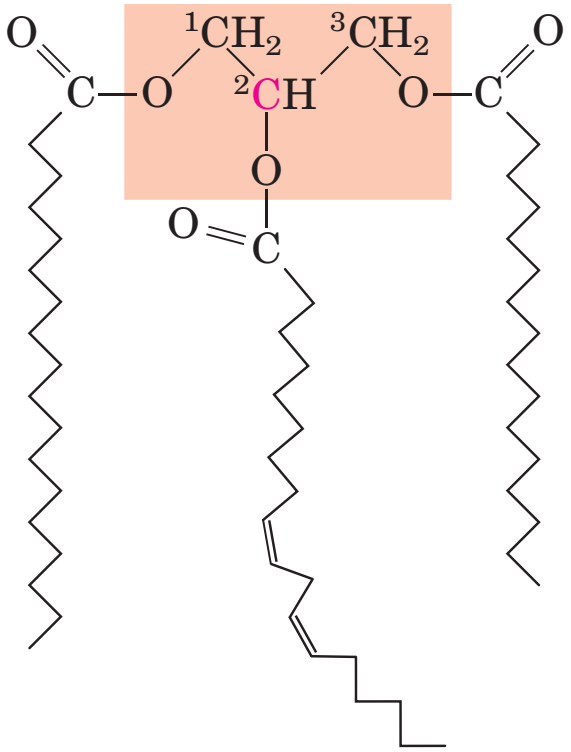
Glycerol + 3 FA

Esterification

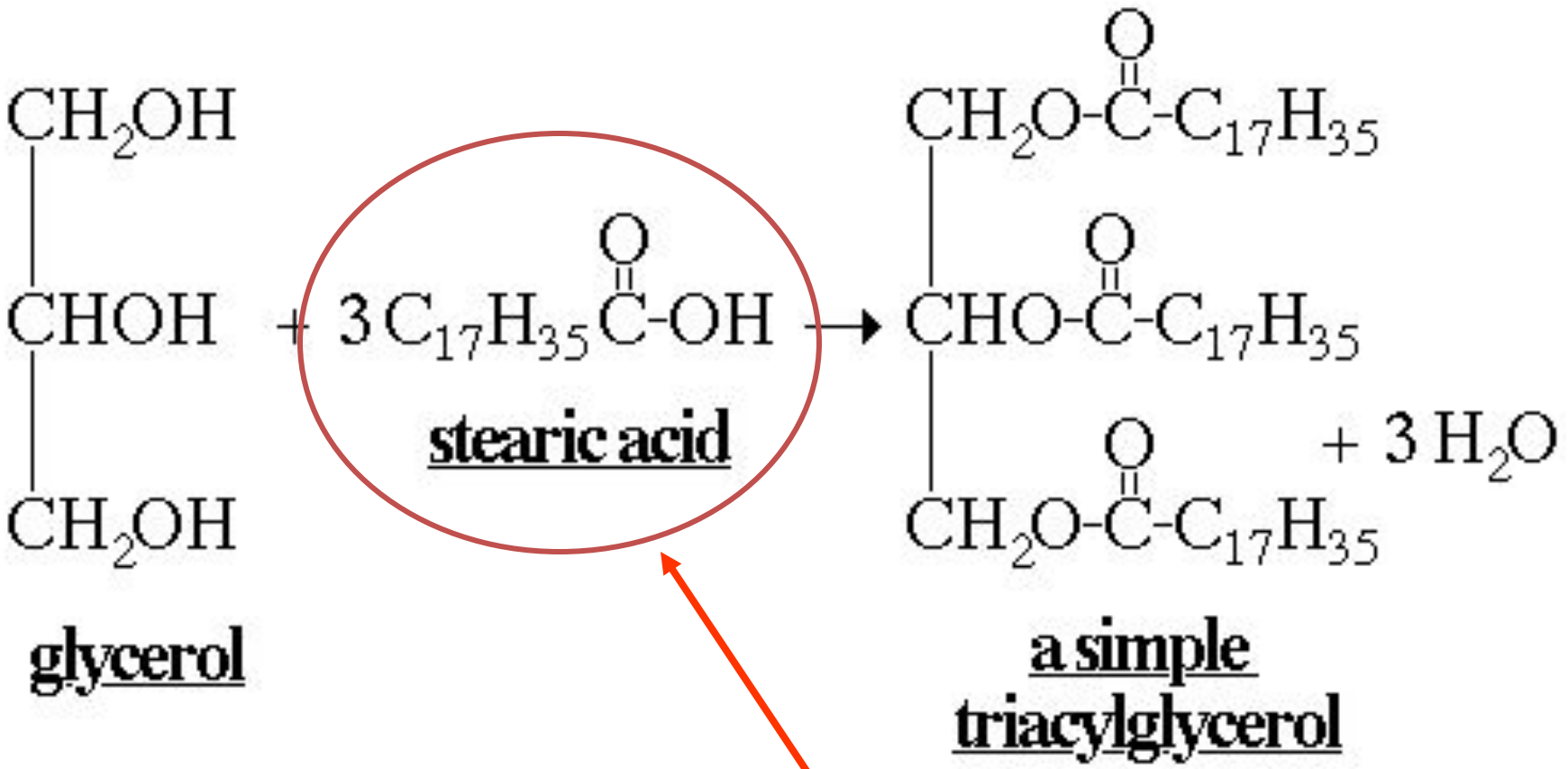






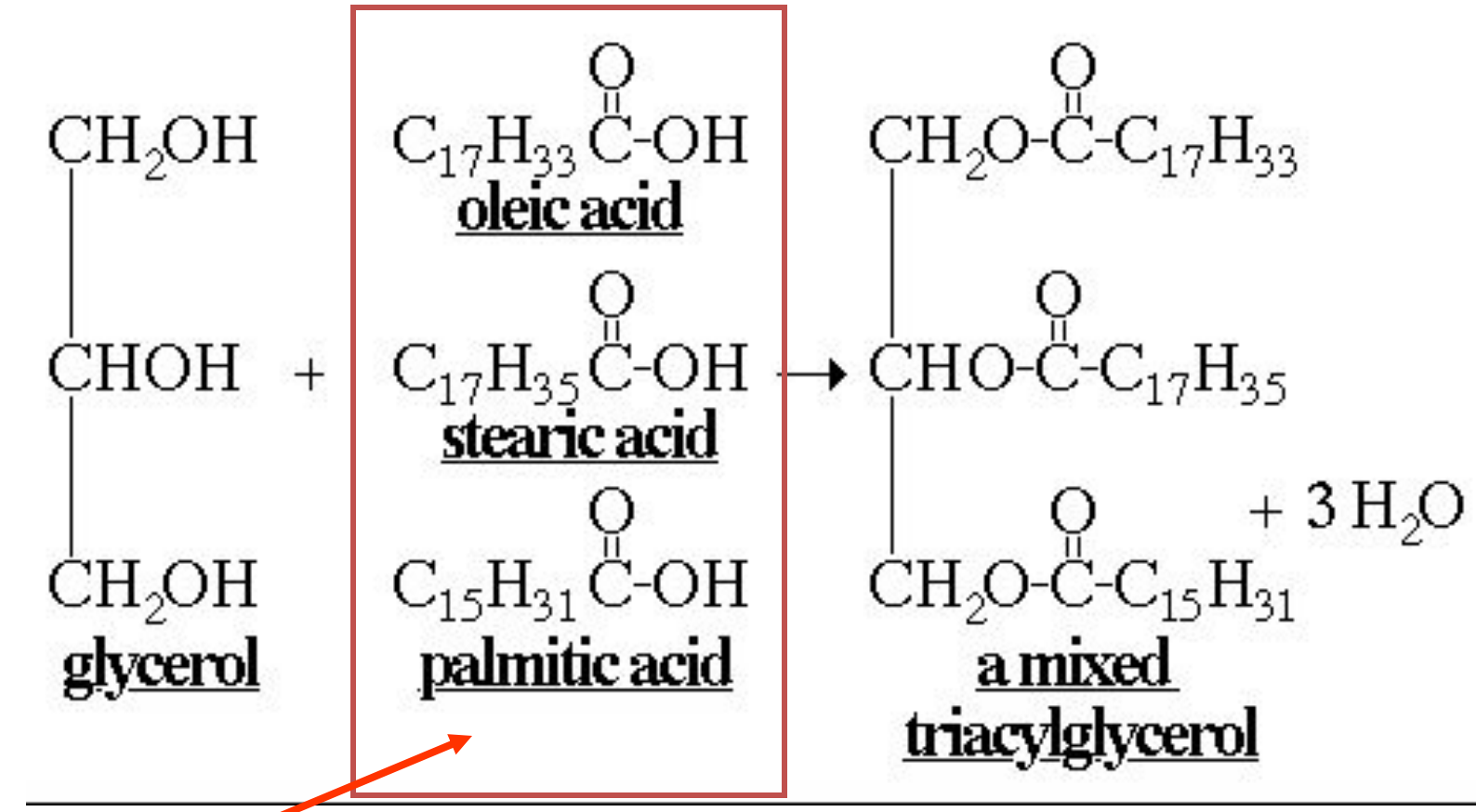


Nomenclature of triacylglycerol



tristerin

Nomenclature of triacylglycerol

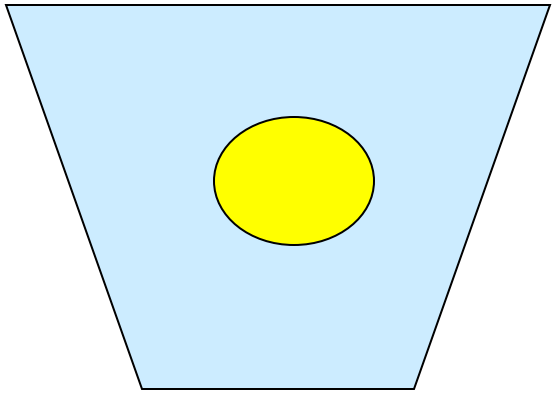


Different FA

oleostearopalmitin

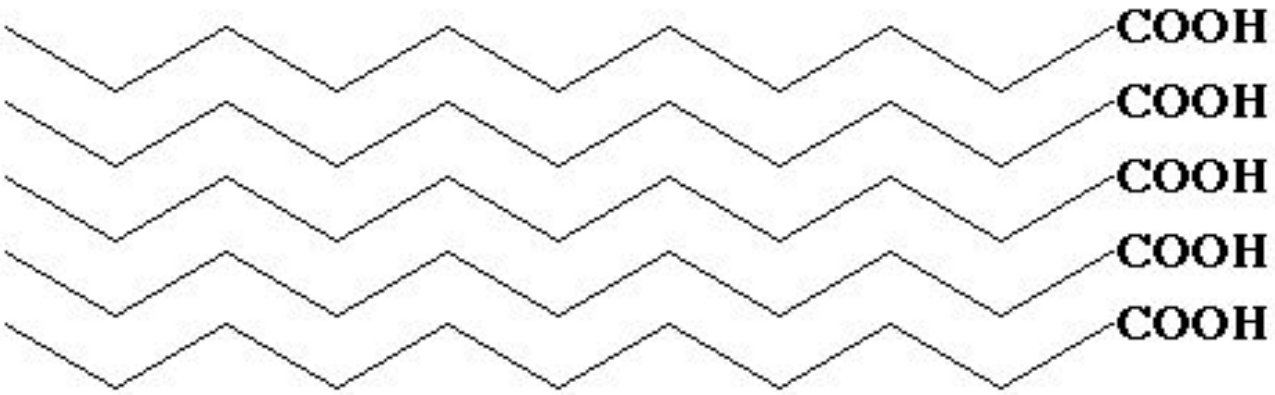
Physical Properties of TAG

1. Water insoluble (nonpolar)

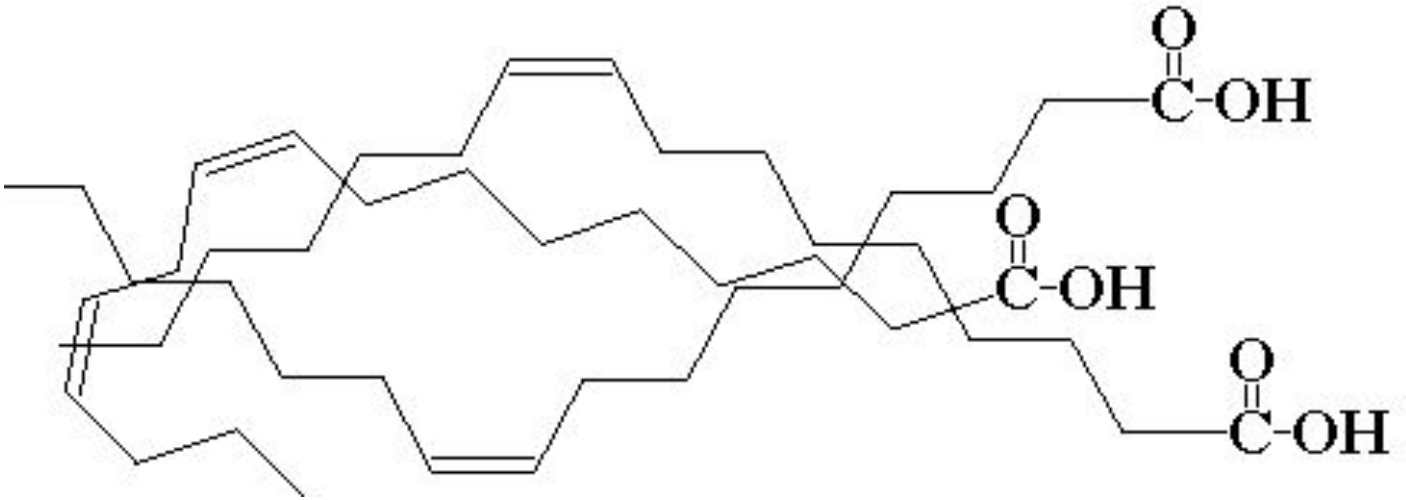


2. Boiling & melting point (depend on FA composition)

sat.FA --> solid at room temp



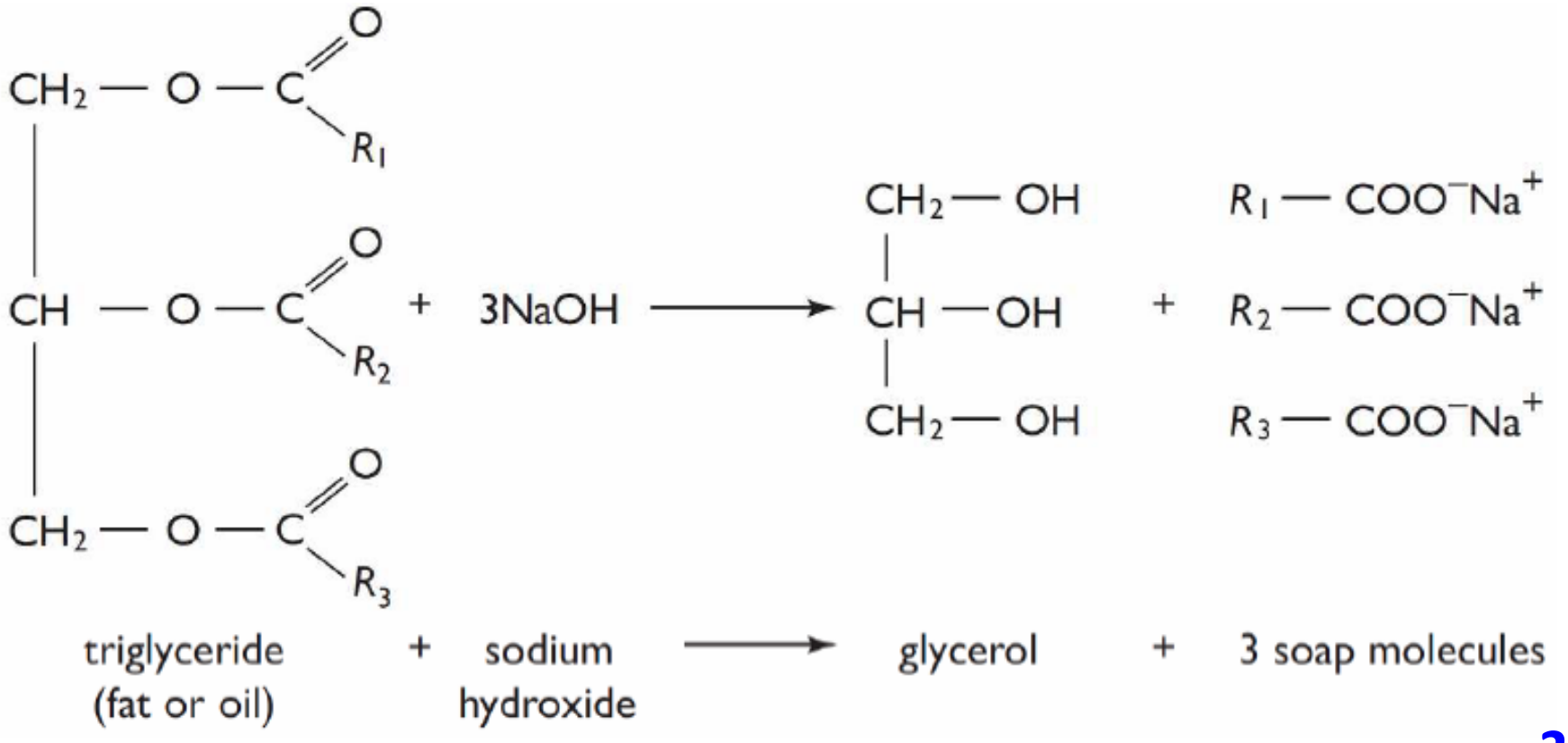
unsat. FA---> liquid at room temp



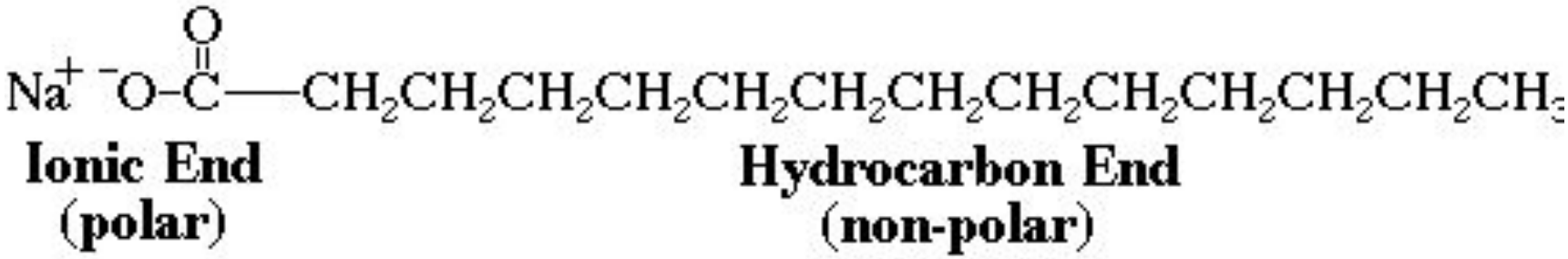
Chemical properties of TAG

1. Saponification rx.

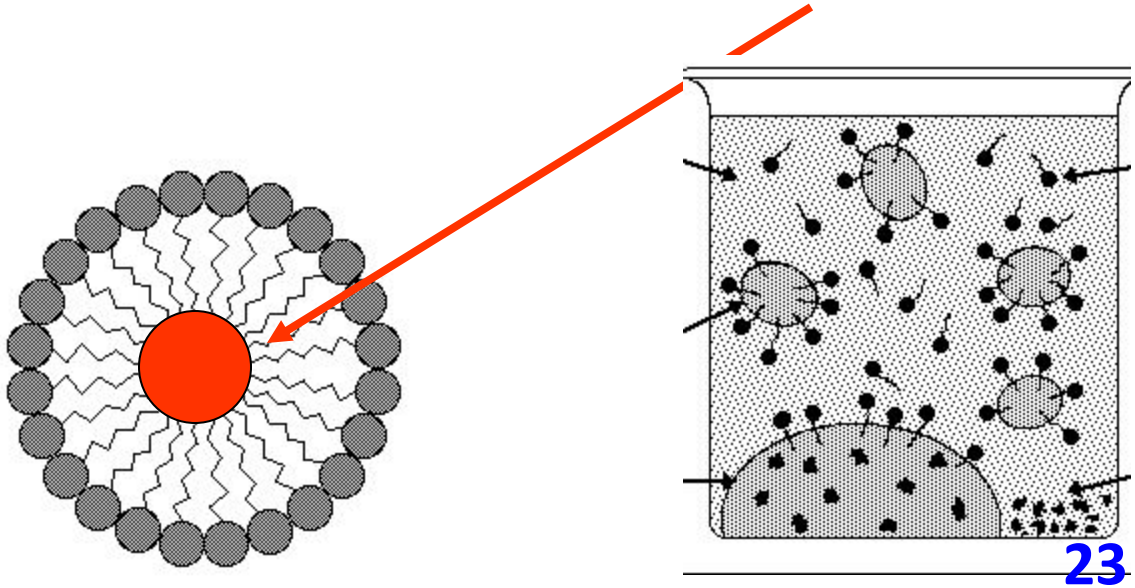
TAG + Base --> Glycerol + Soap



Soap (amphipatic)

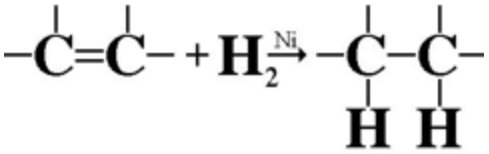


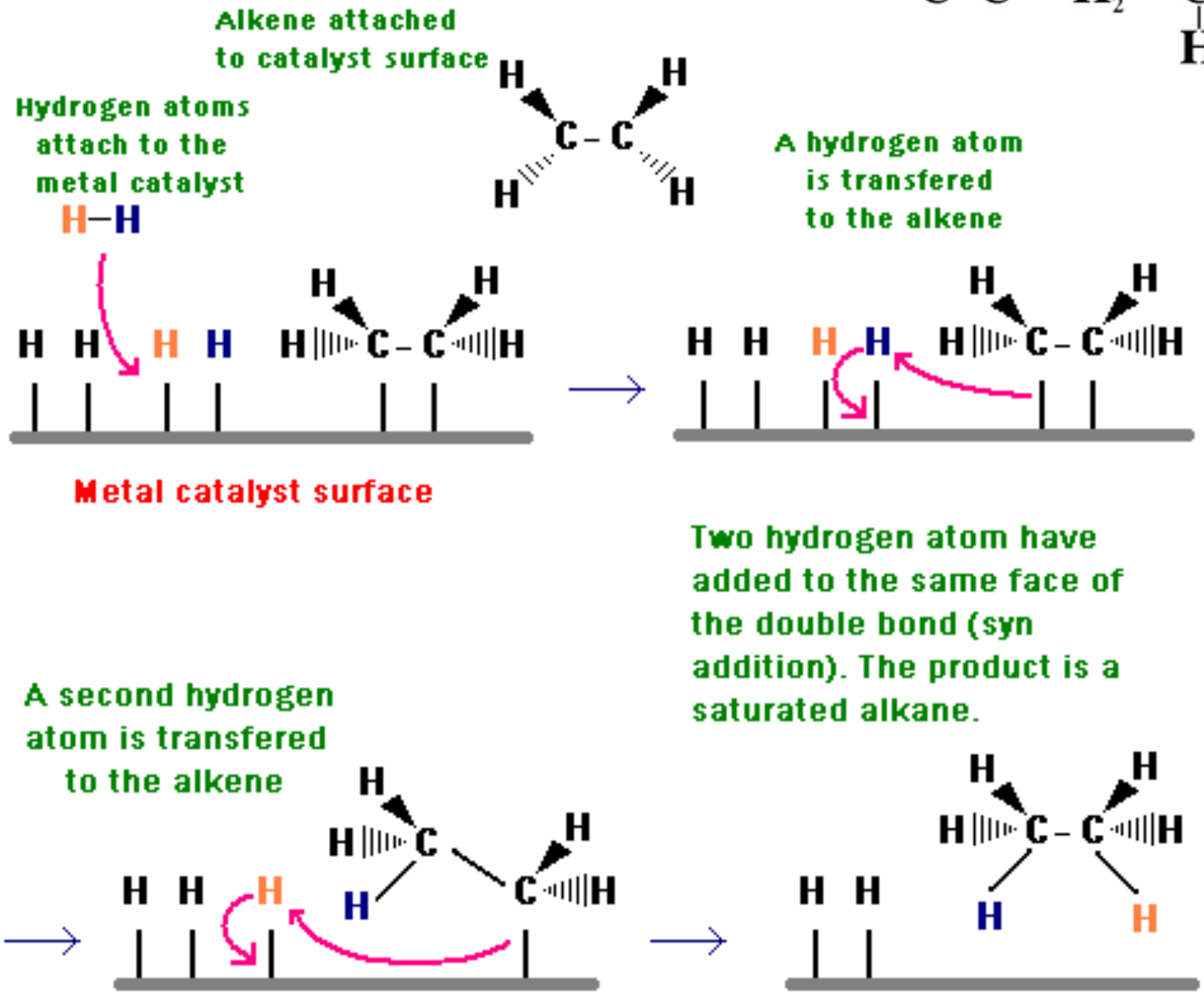
Mechanism of soap



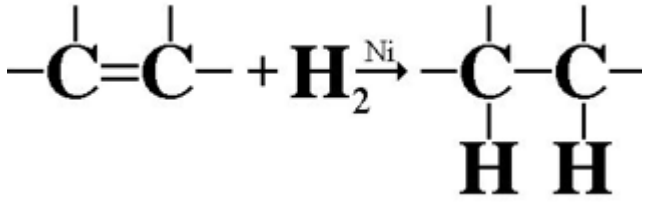
2. Addition rx.

Hydrogenation

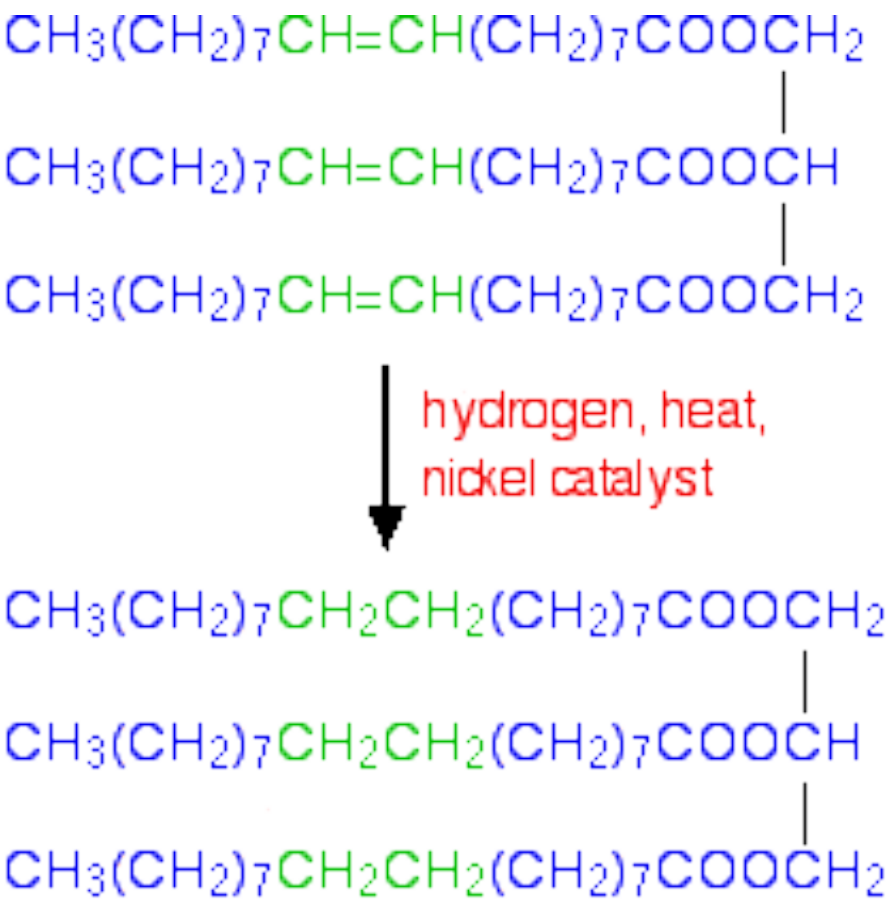




2. Addition rx.



Hydrogenation



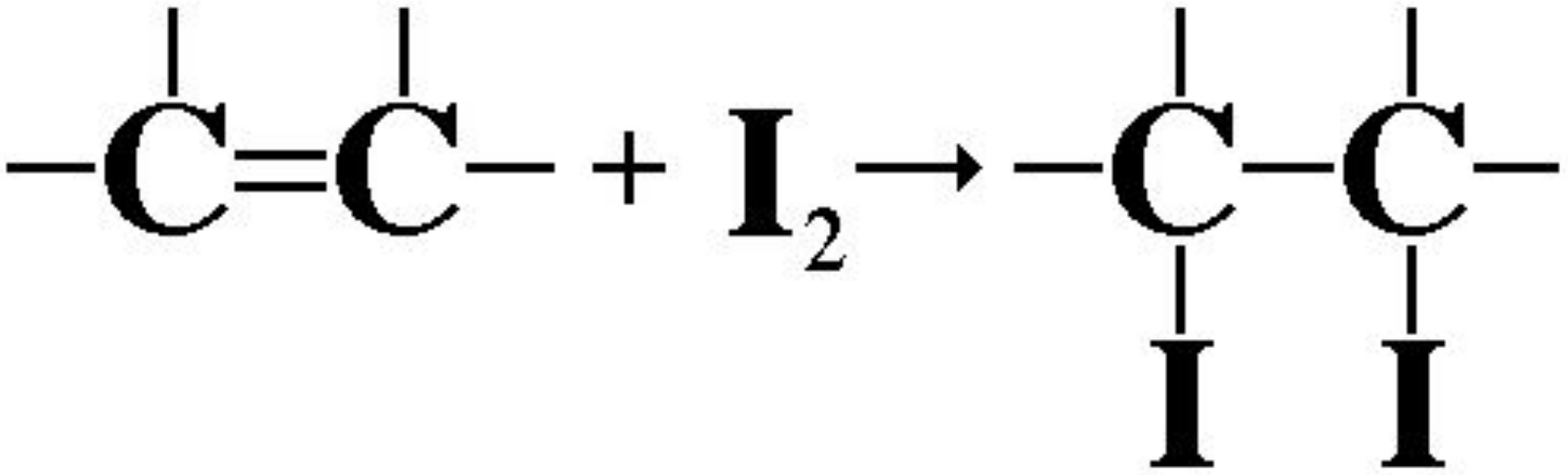
Vegetable or Animal oil

Magarine

Halogenation ex.iodination

Iodine Number

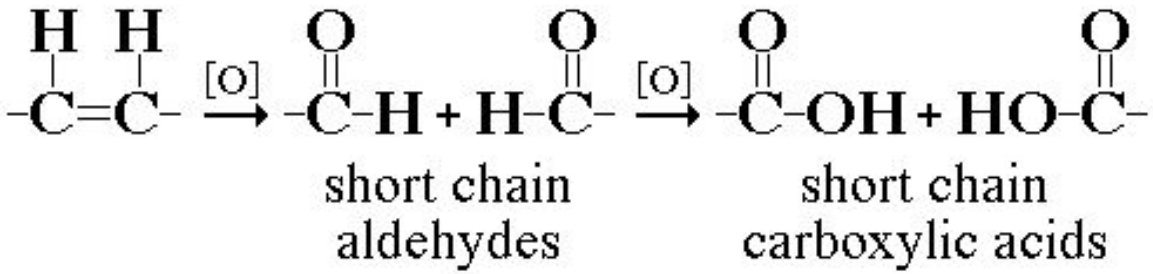
The degree of unsaturation of a fat or oil can be measured in terms of the Iodine Number which is the number of grams of iodine that will be consumed in a reaction with 100 g of fat or oil.



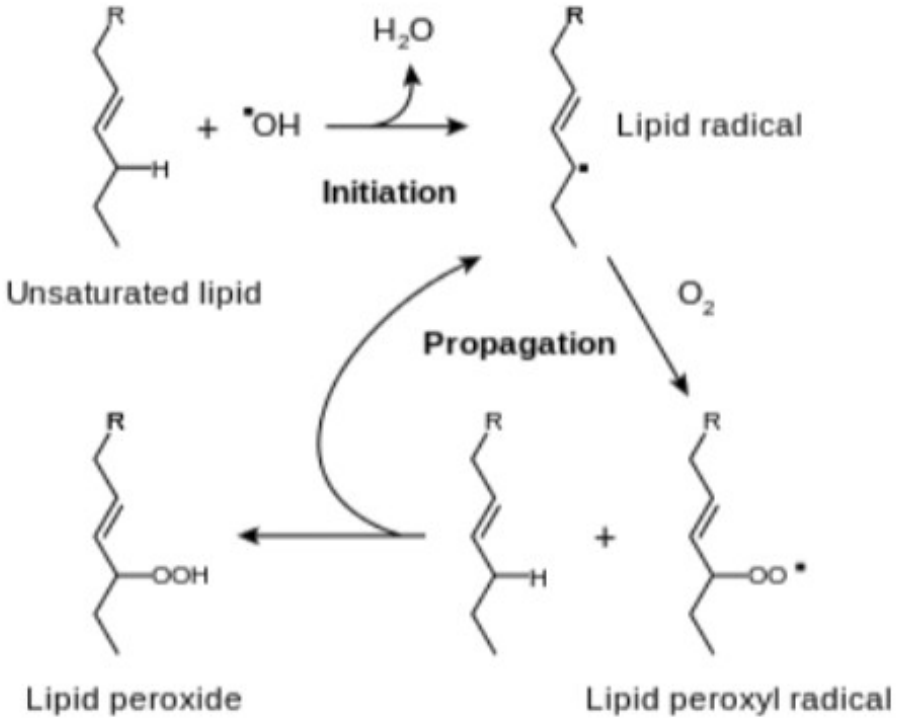
Iodine Number

Coconut Oil	8-10
Butter	25-40
Beef Tallow	30-45
Palm Oil	37-54
Lard	45-70
Olive Oil	75-95
Peanut Oil	85-100
Cottonseed Oil	100-117
Corn Oil	115-130
Fish Oil	120-180
Soybean Oil	125-140
Safflower Oil	130-140
Sunflower Oil	130-145
Linseed Oil	170-205

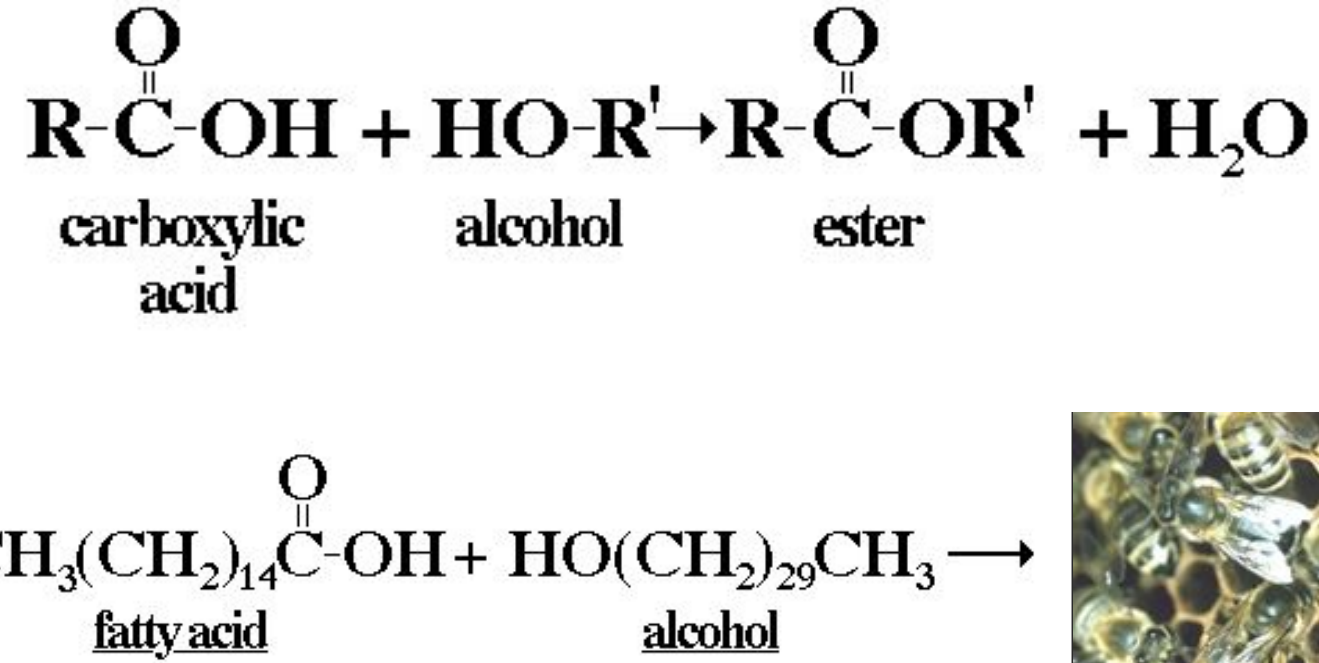
3. oxidation

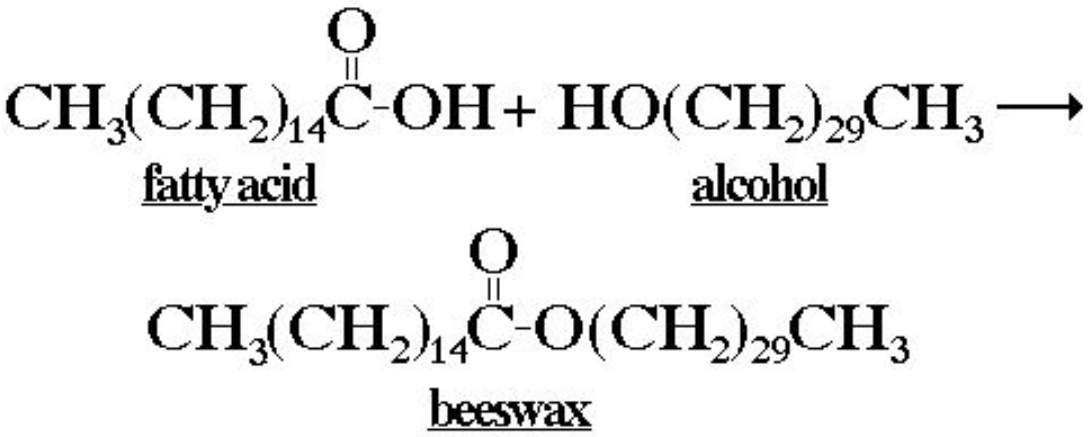


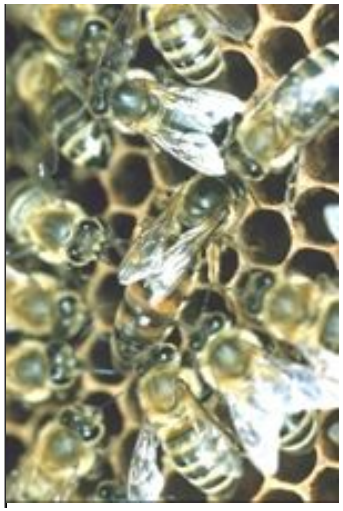
Rancidity Oxidation of fats, generally known as **rancidity**, is **caused** by a biochemical reaction between fats and oxygen. Long-chain fatty acids are degraded and short-chain compounds are formed. One of the reaction products is butyric acid, which **causes** the typical **rancid** taste.



Wax

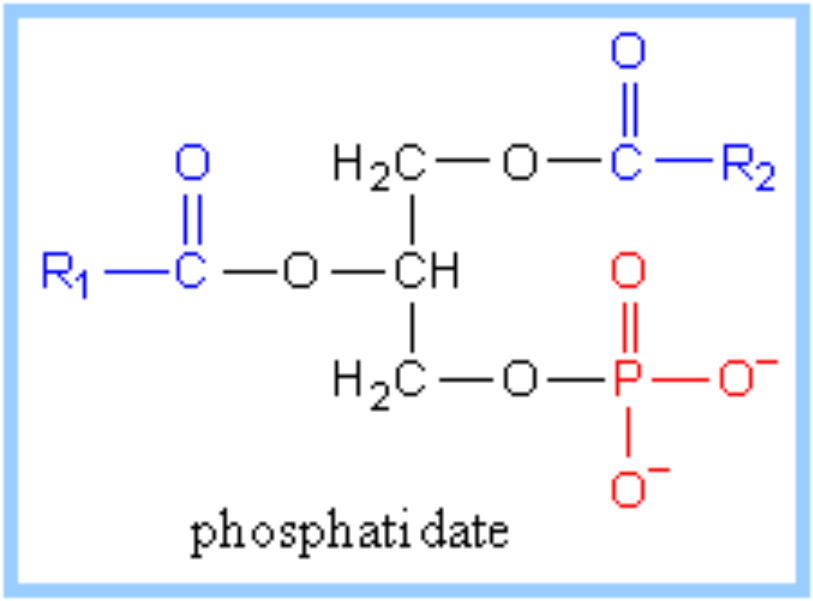

R-C-OH + HO-R' → R-C-OR' + H2O
carboxylic acid
alcohol
ester

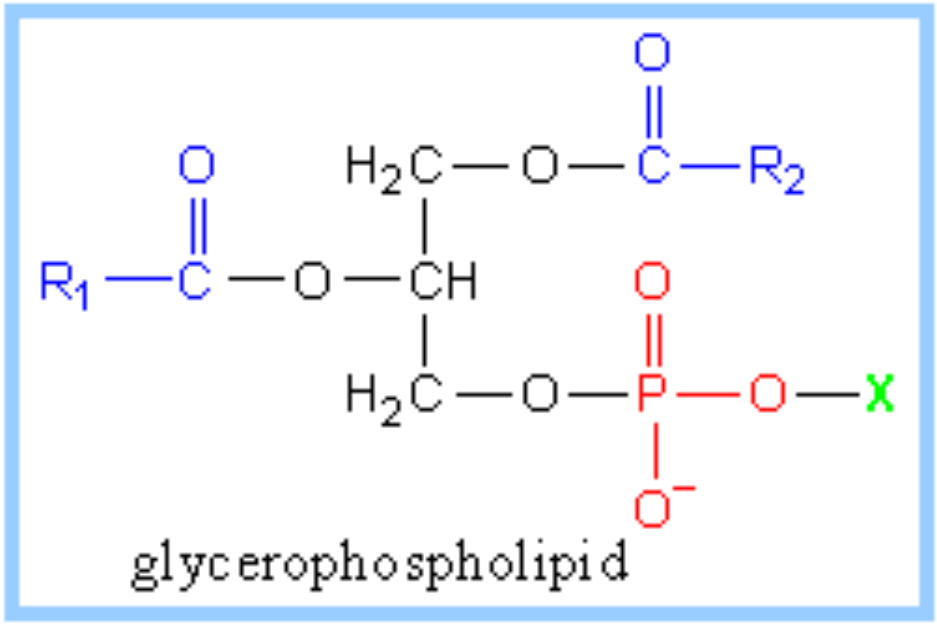

CH3(CH2)14C-OH + HO(CH2)29CH3 ⟶
fatty acid
alcohol
CH3(CH2)14C-O(CH2)29CH3
beeswax

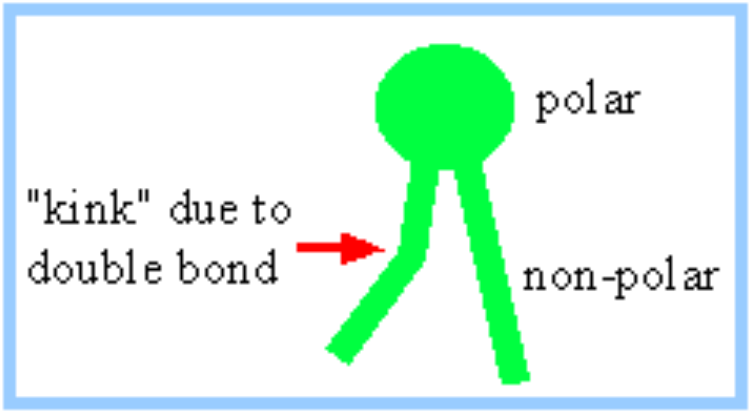


Compound lipid

Phospholipid

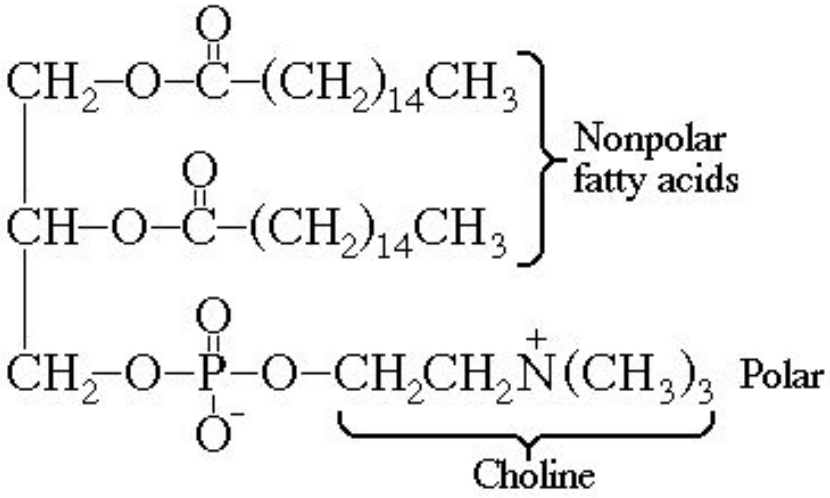






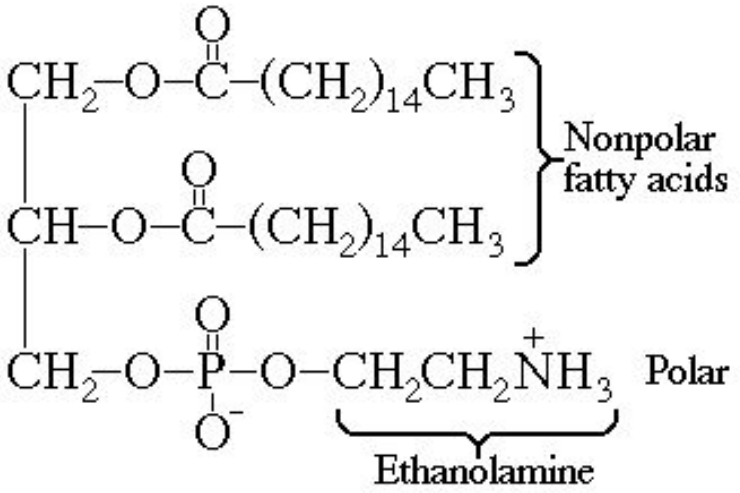
amphipathic

Lecithin



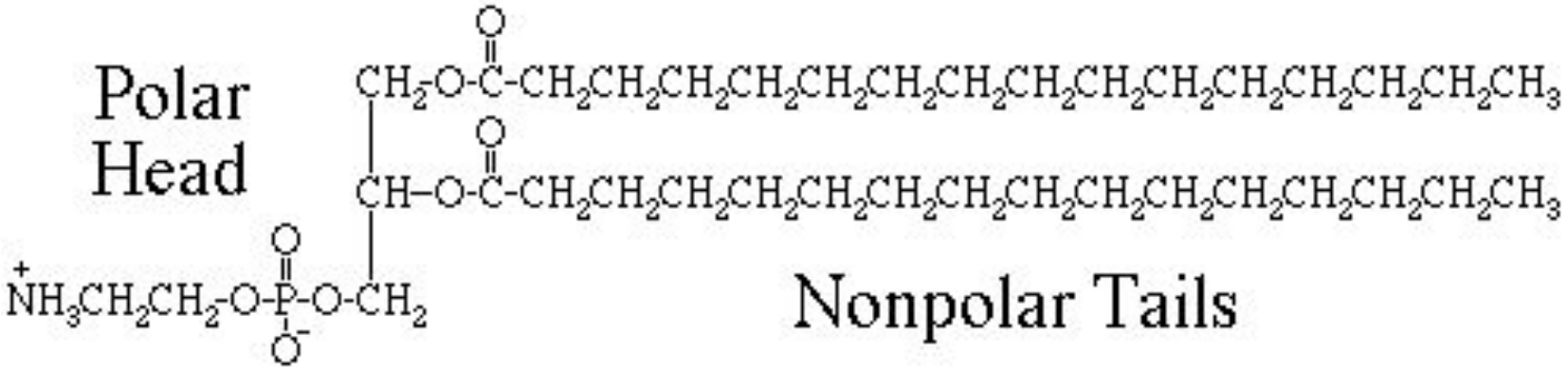
Phosphatidyl choline

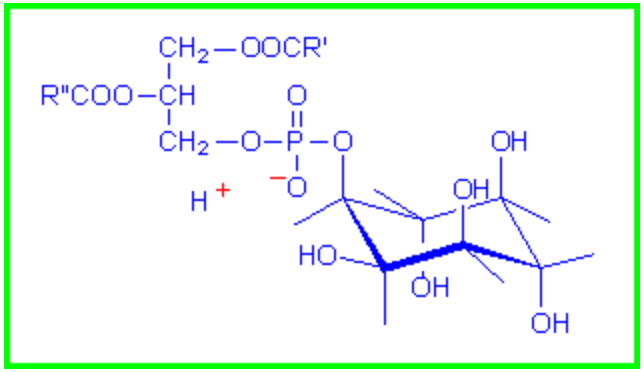
Cephalin



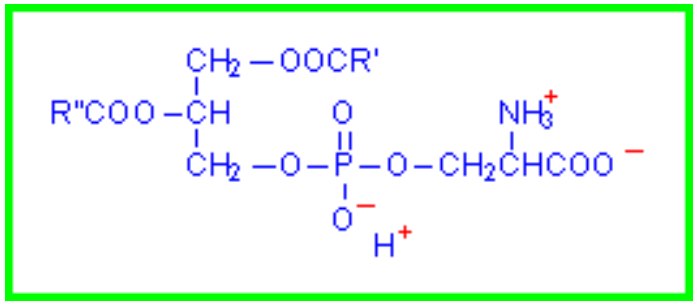
Phosphatidyl ethanolamine

Cephalin



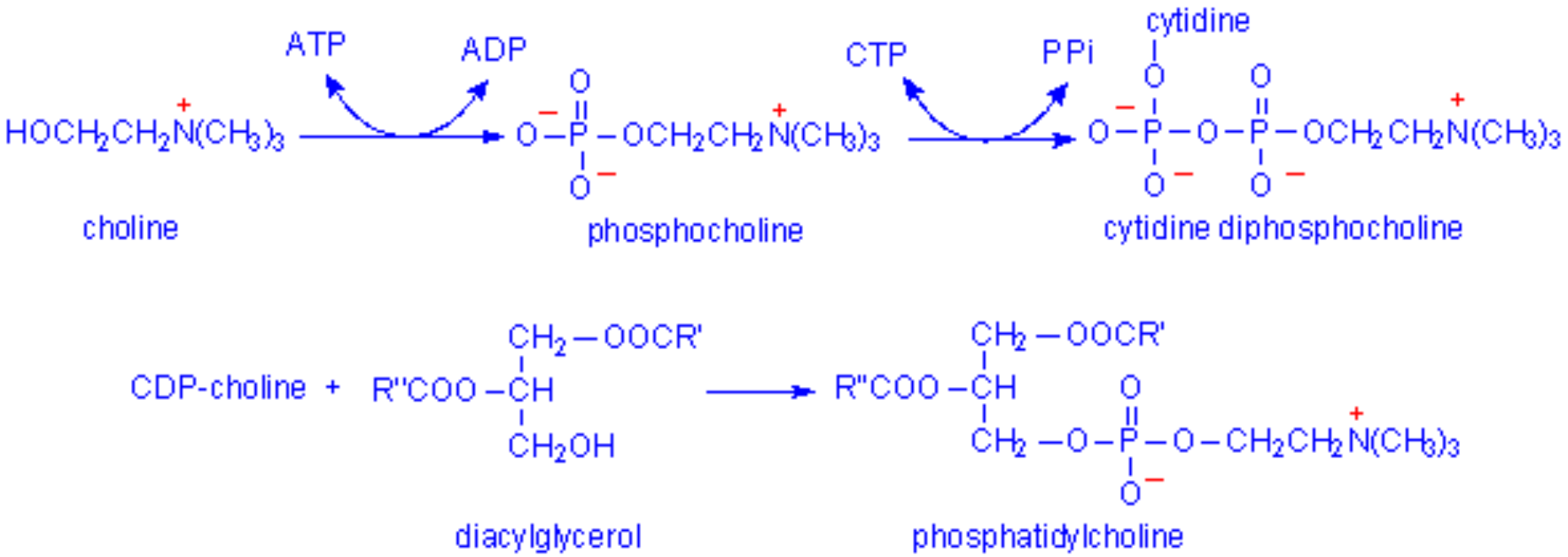


Phosphatidyl inositol

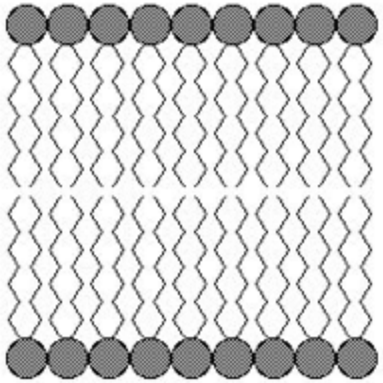


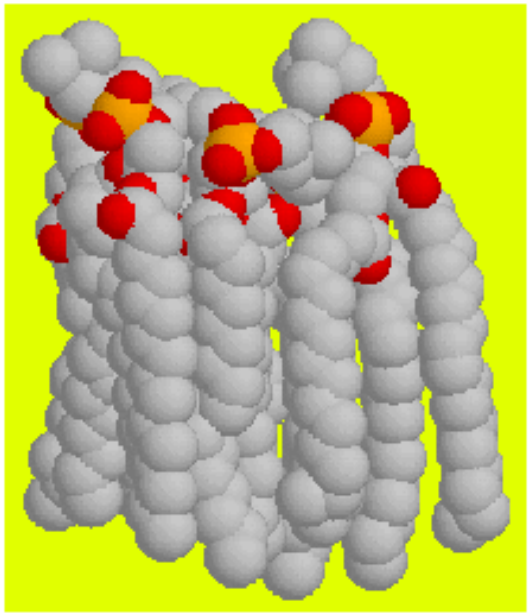
Phosphatidyl serine

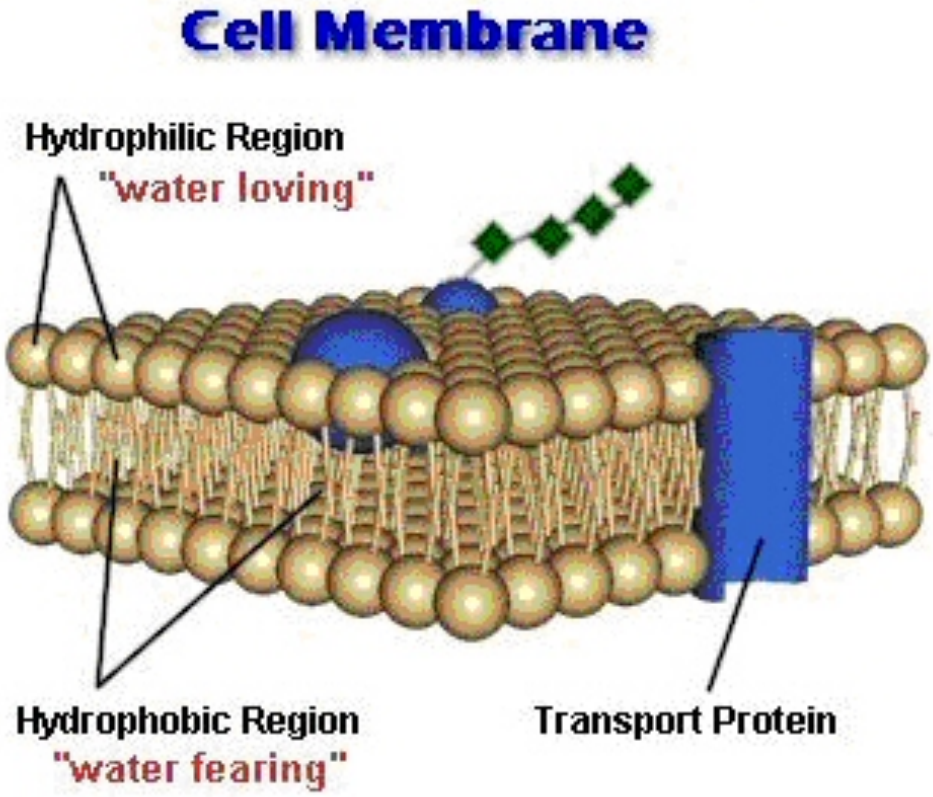
Phosphatidyl choline synthesis



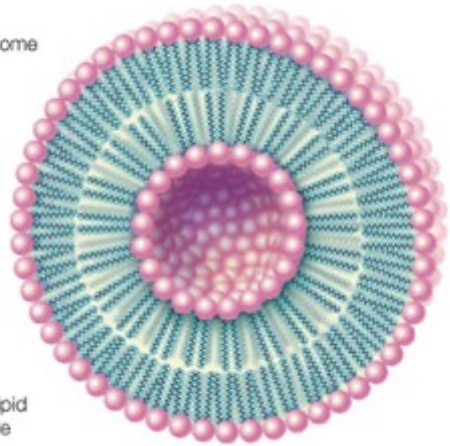
Lipid bilayer

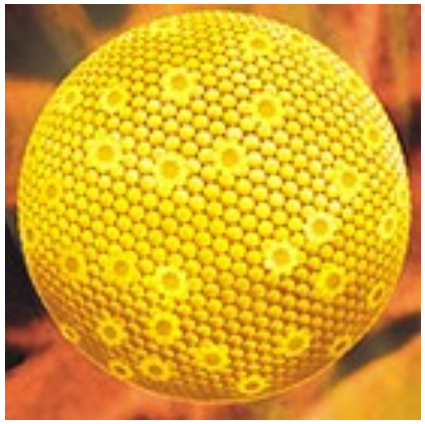


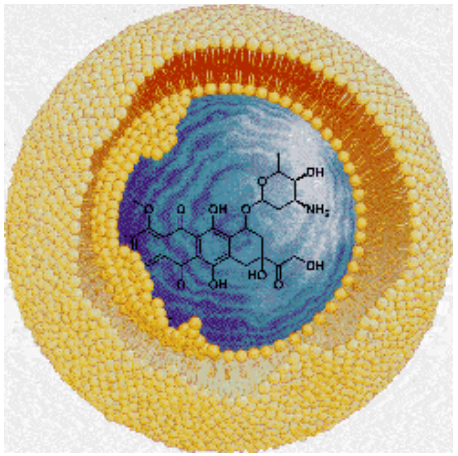


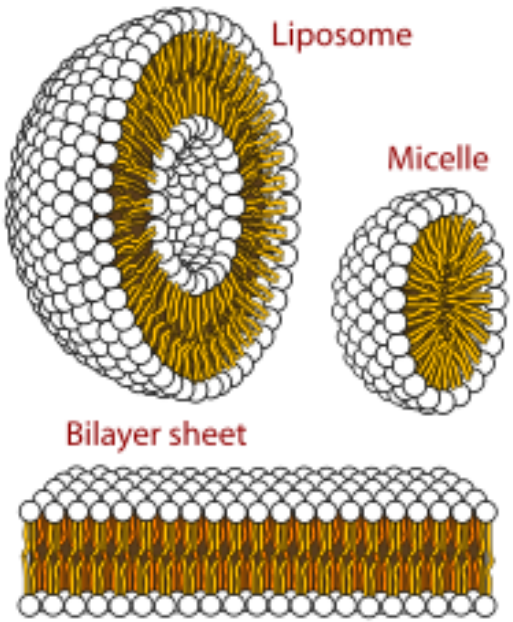


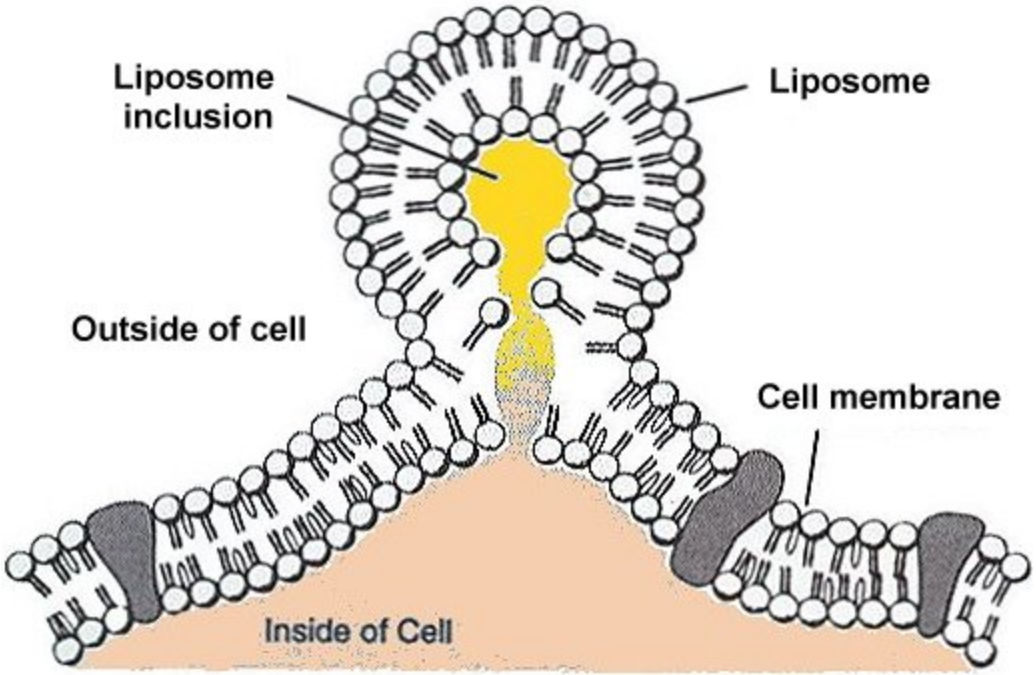
liposome







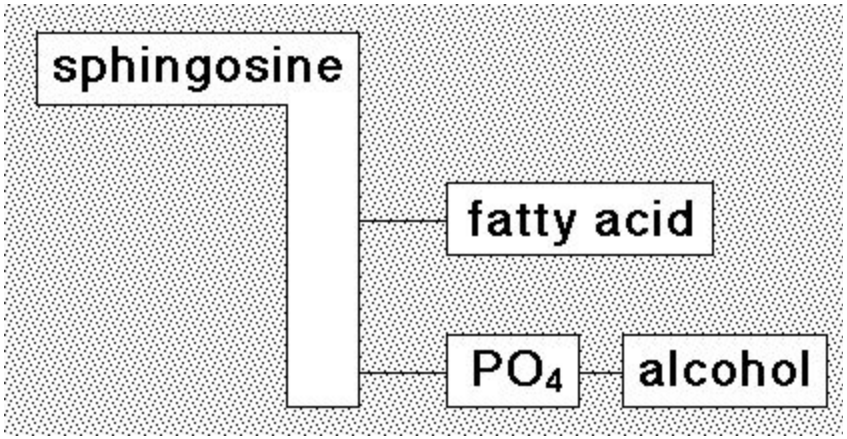




Acceptance of liposome into cell

Sphingolipids

Alcohol (sphingosine, not glycerol) amphipathic molecule

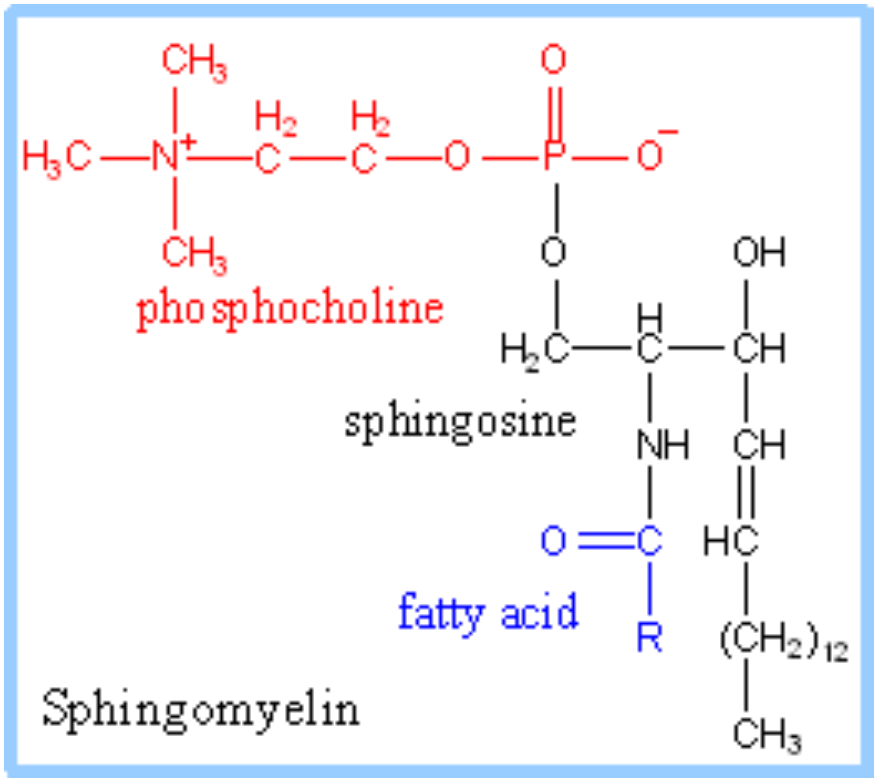


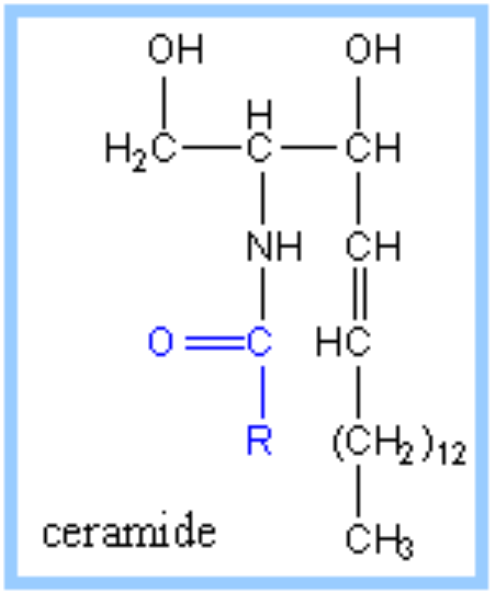
Sphingosine

$$CH_3(CH_2)_{12}CH{=}CH{-}CH{-}OH$$
$$\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\quad CH{-}NH_2$$
$$\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\quad CH_2{-}OH$$

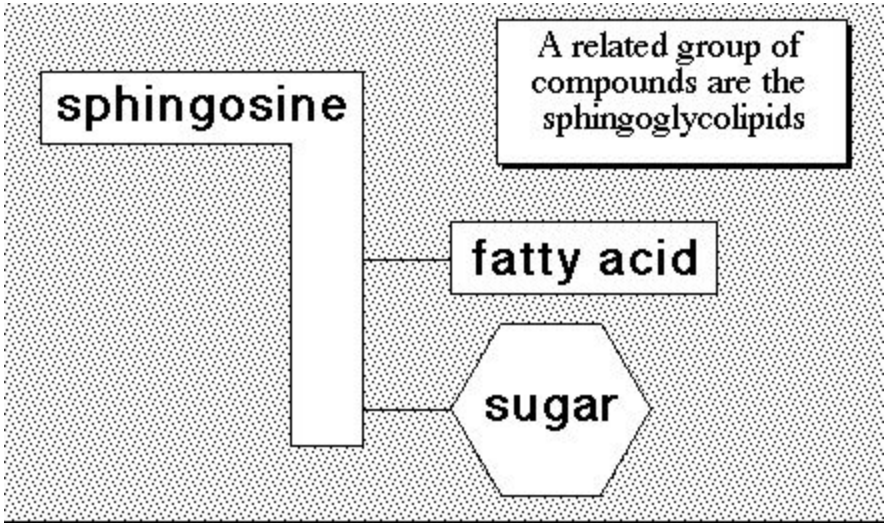
Sphingomyelin

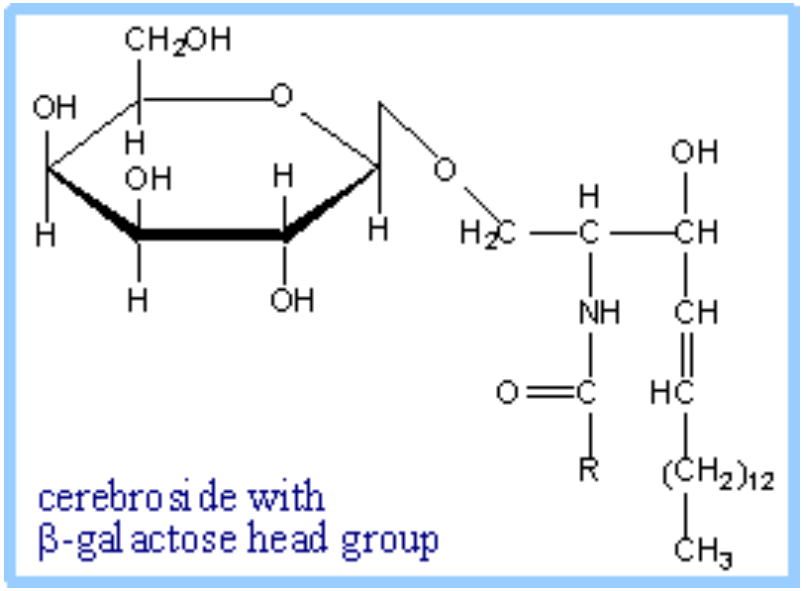
พบที่เยื่อสมอง และประสาท

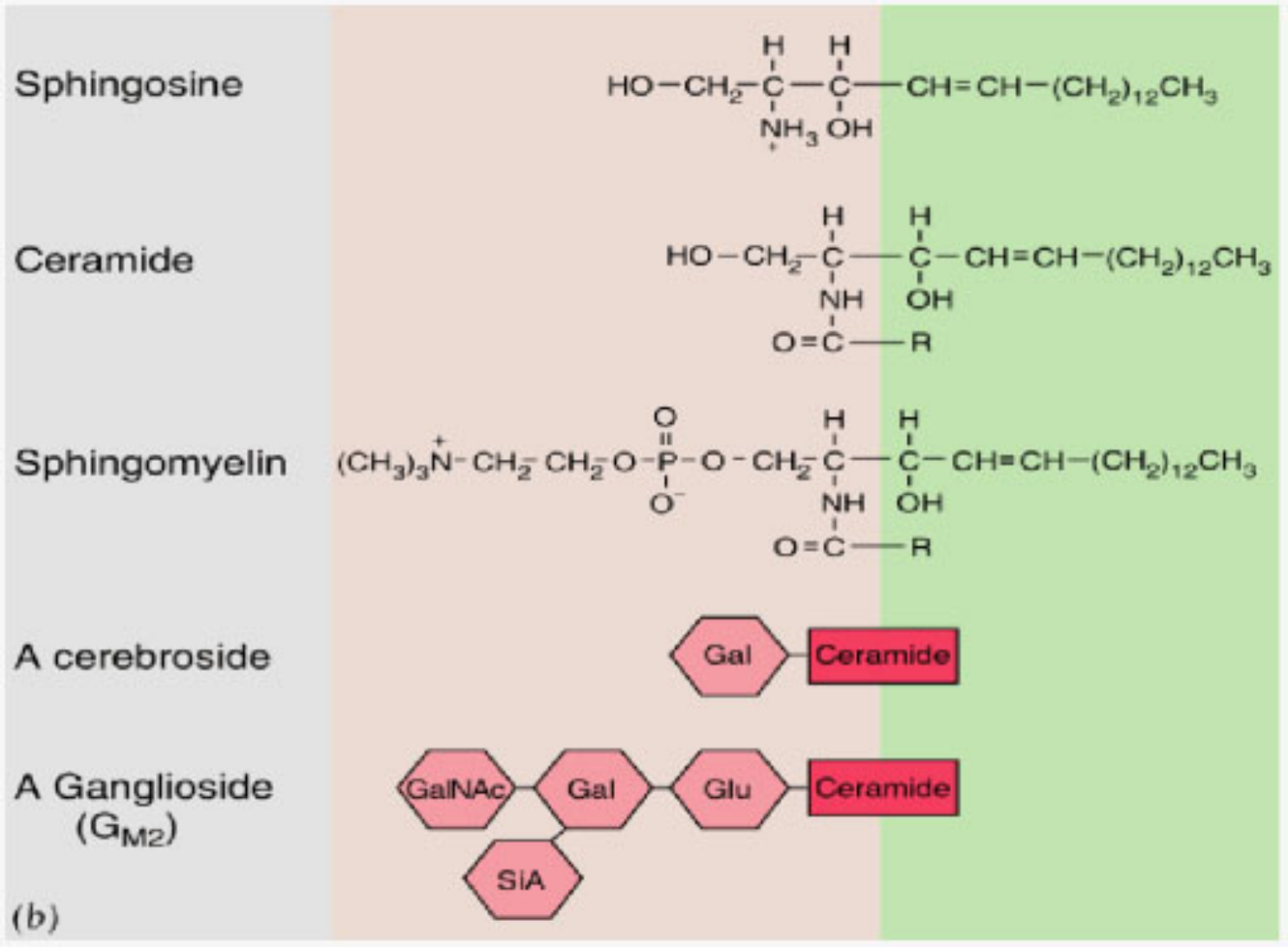




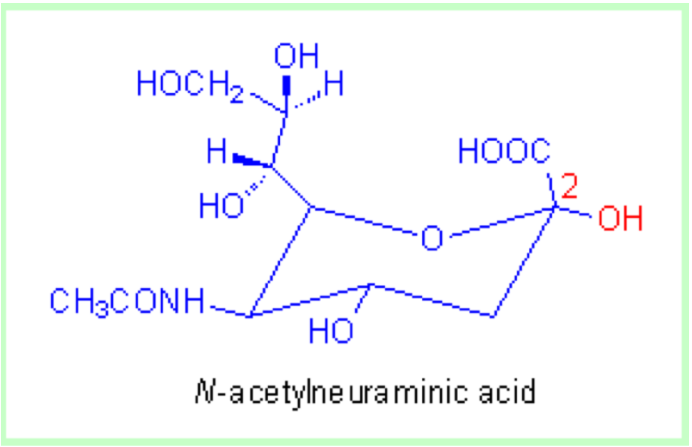
Glycosphingolipids

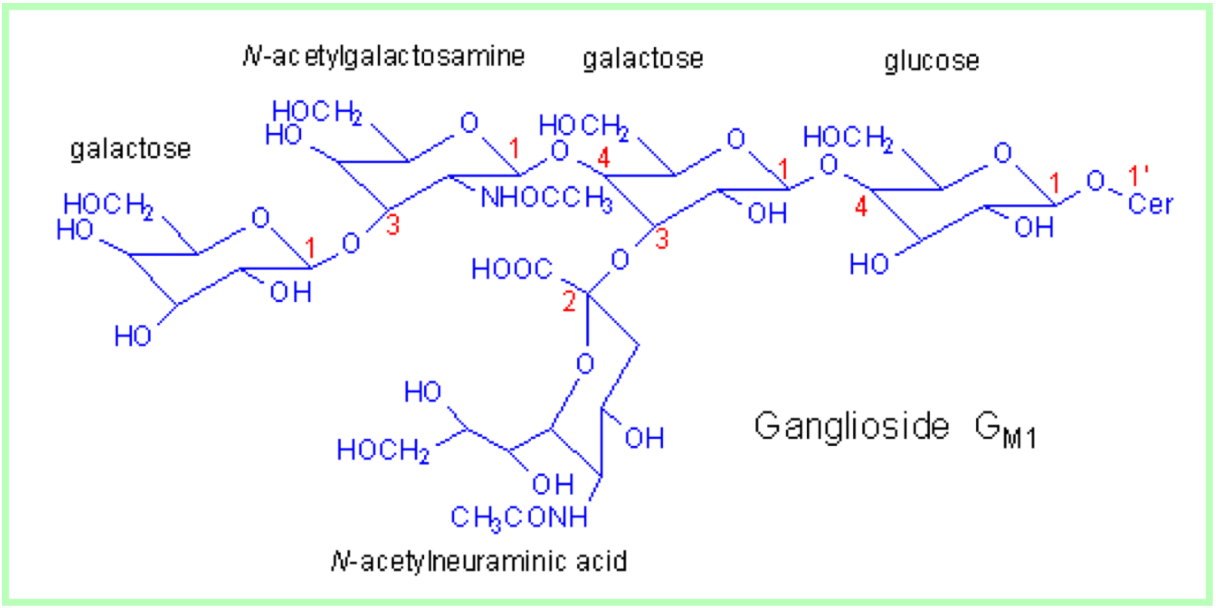





Sphingosine
Ceramide
Sphingomyelin
A cerebroside
Gal
Ceramide
A Ganglioside
(G_{M2})
GalNAc
Gal
Glu
Ceramide
SIA
(b)

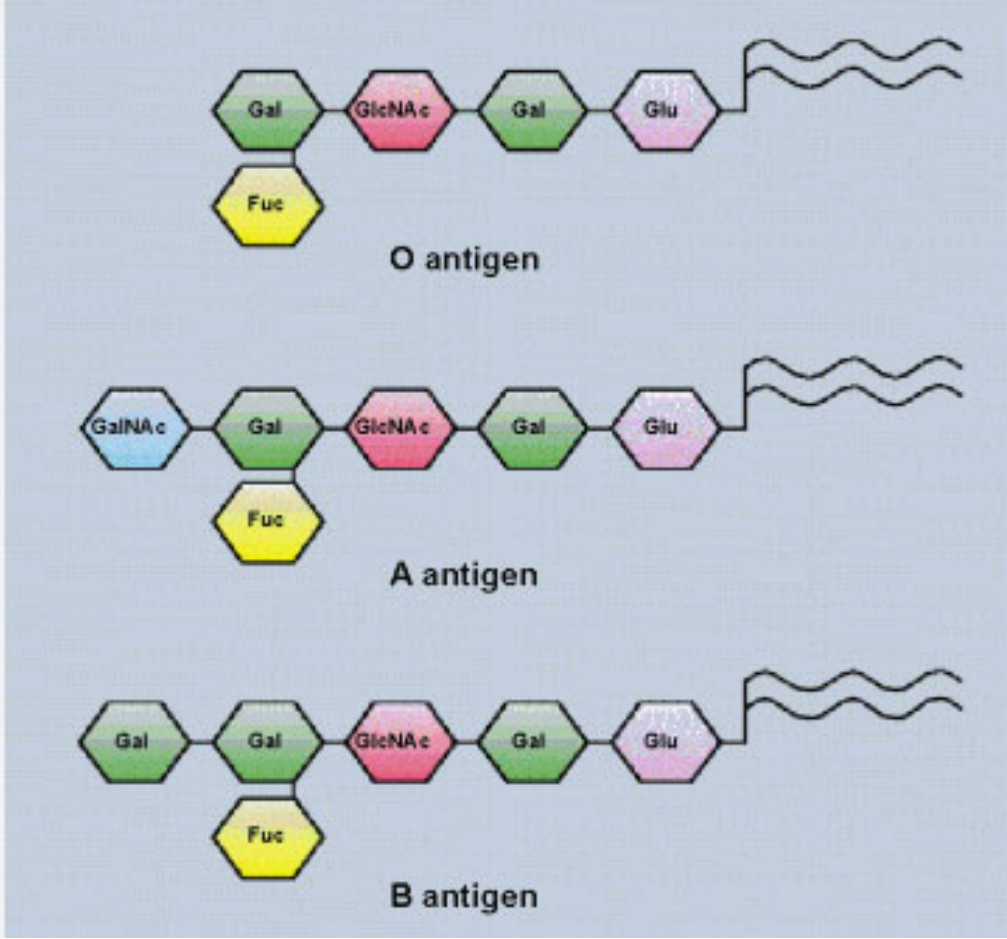
ganglioside เป็น **ceramide** ที่มี **polar head group** เป็น **complex oligosaccharide**, เช่น **sialic acid**

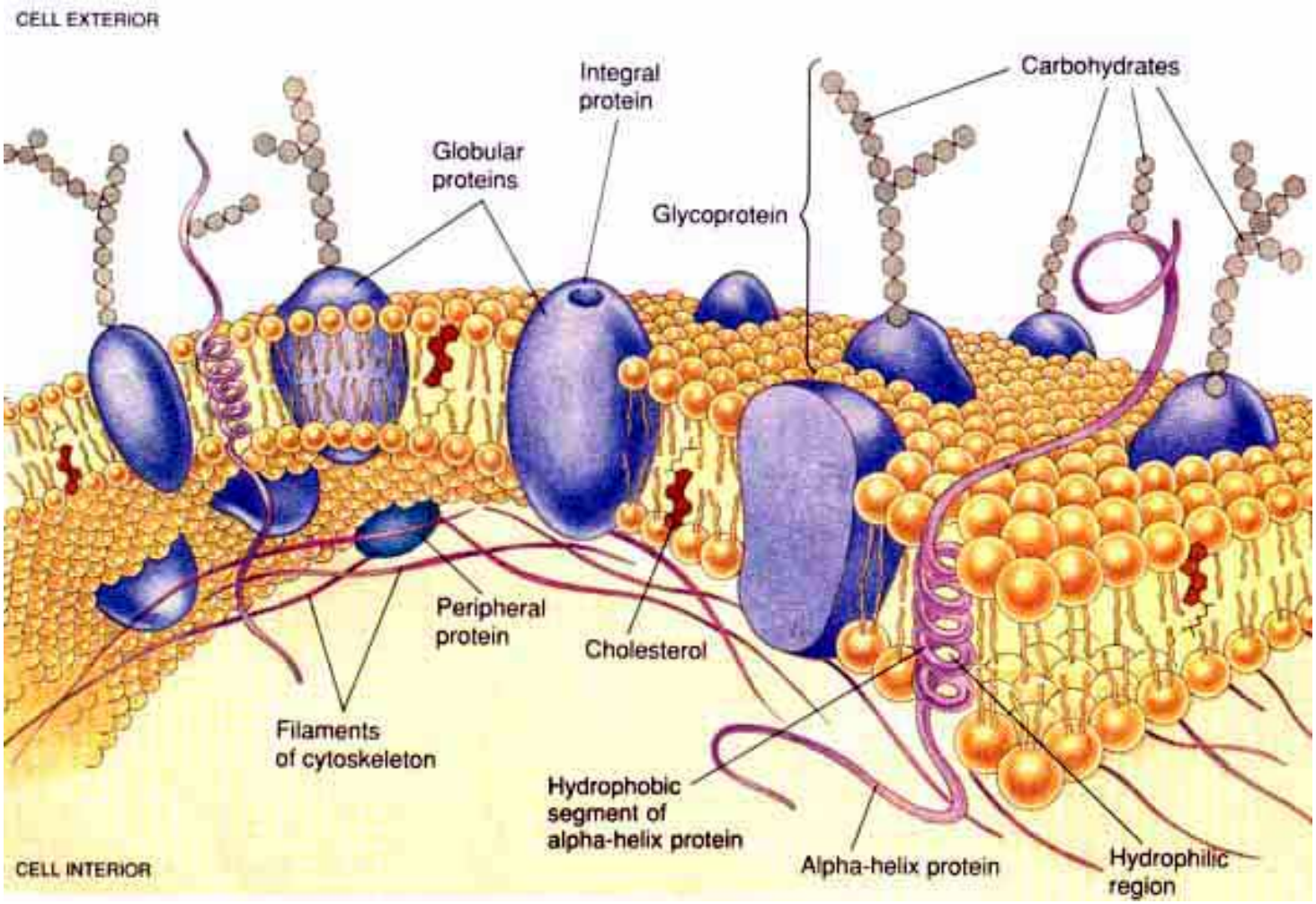




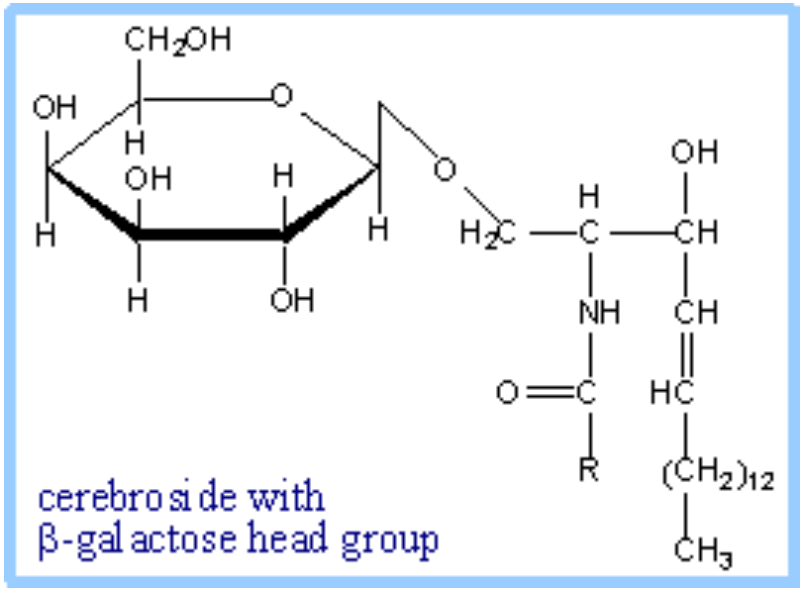
Glycolipids

Antigen at rbc surface



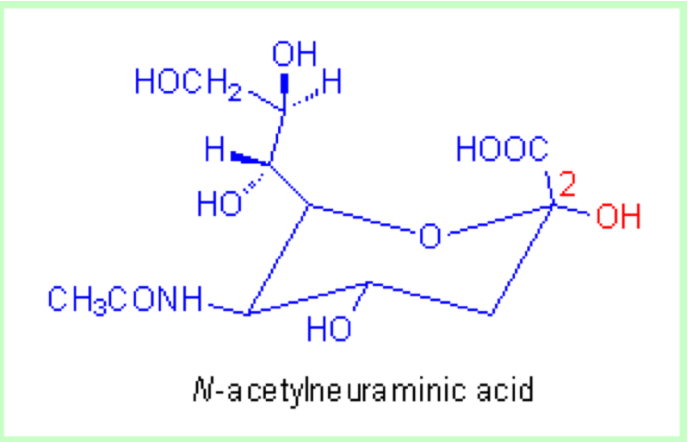


Fluid mosaic model

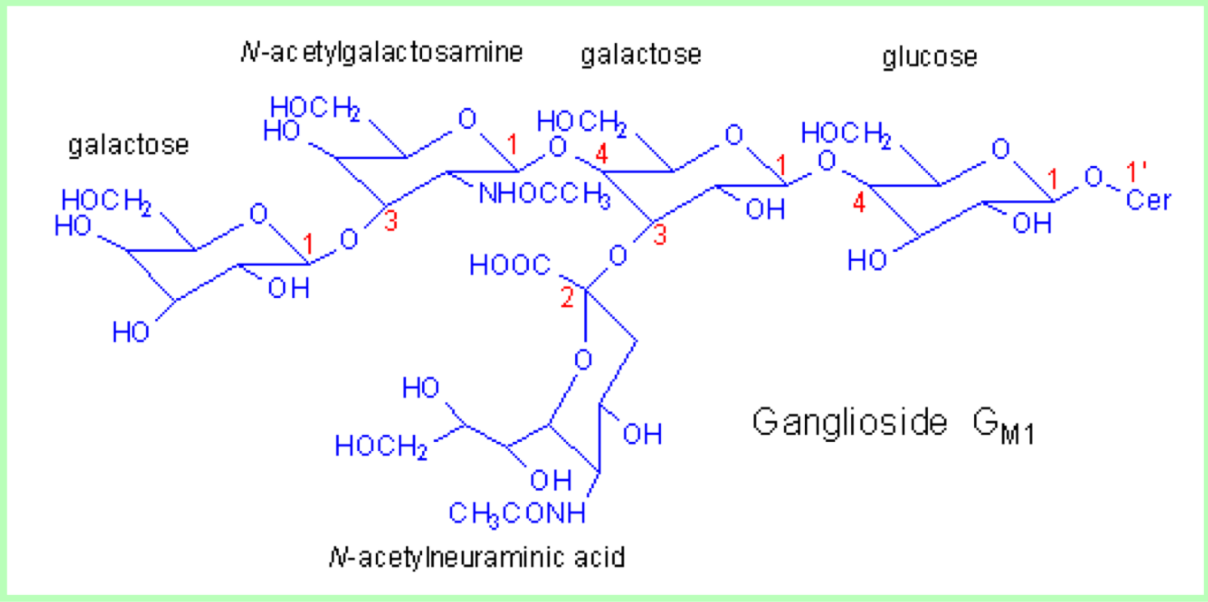


cerebroside is a sphingolipid (ceramide) with a **monosaccharide** such as glucose or galactose as polar head group.

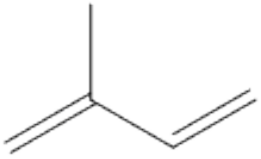
ganglioside is a ceramide with a polar head group that is a complex oligosaccharide, including the acidic sugar derivative sialic acid



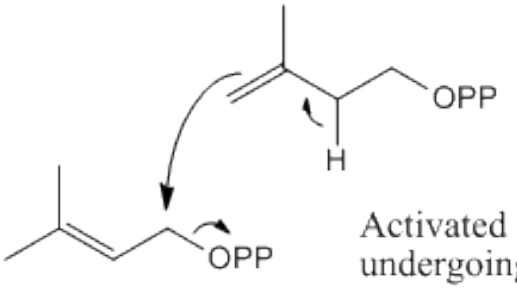
N-acetylneuraminic acid



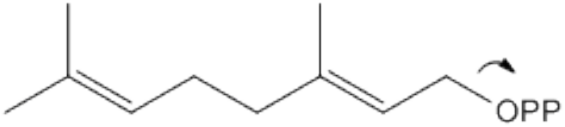
Miscellaneous lipid



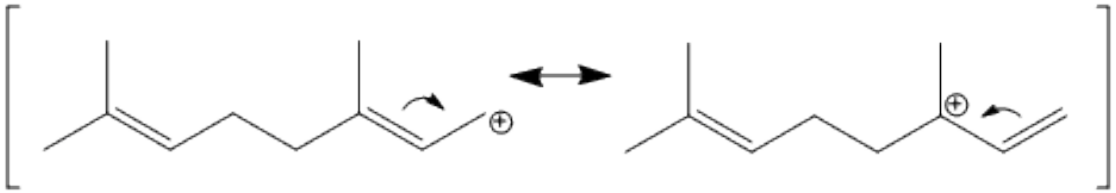
Isoprene

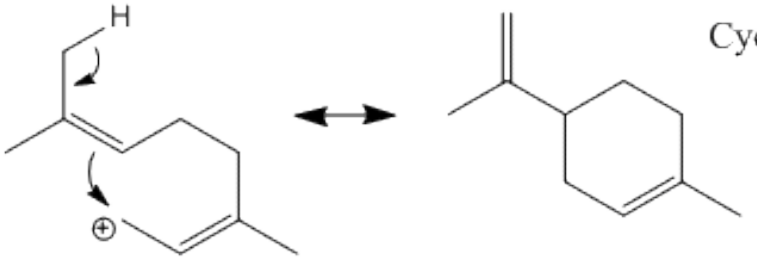


Activated forms of Isoprene undergoing polymerization



Terpene





Cyclization of Terpene

Terpenes

Pine resin

Terpenes

Terpenes are made from the polymerization of isoprene.

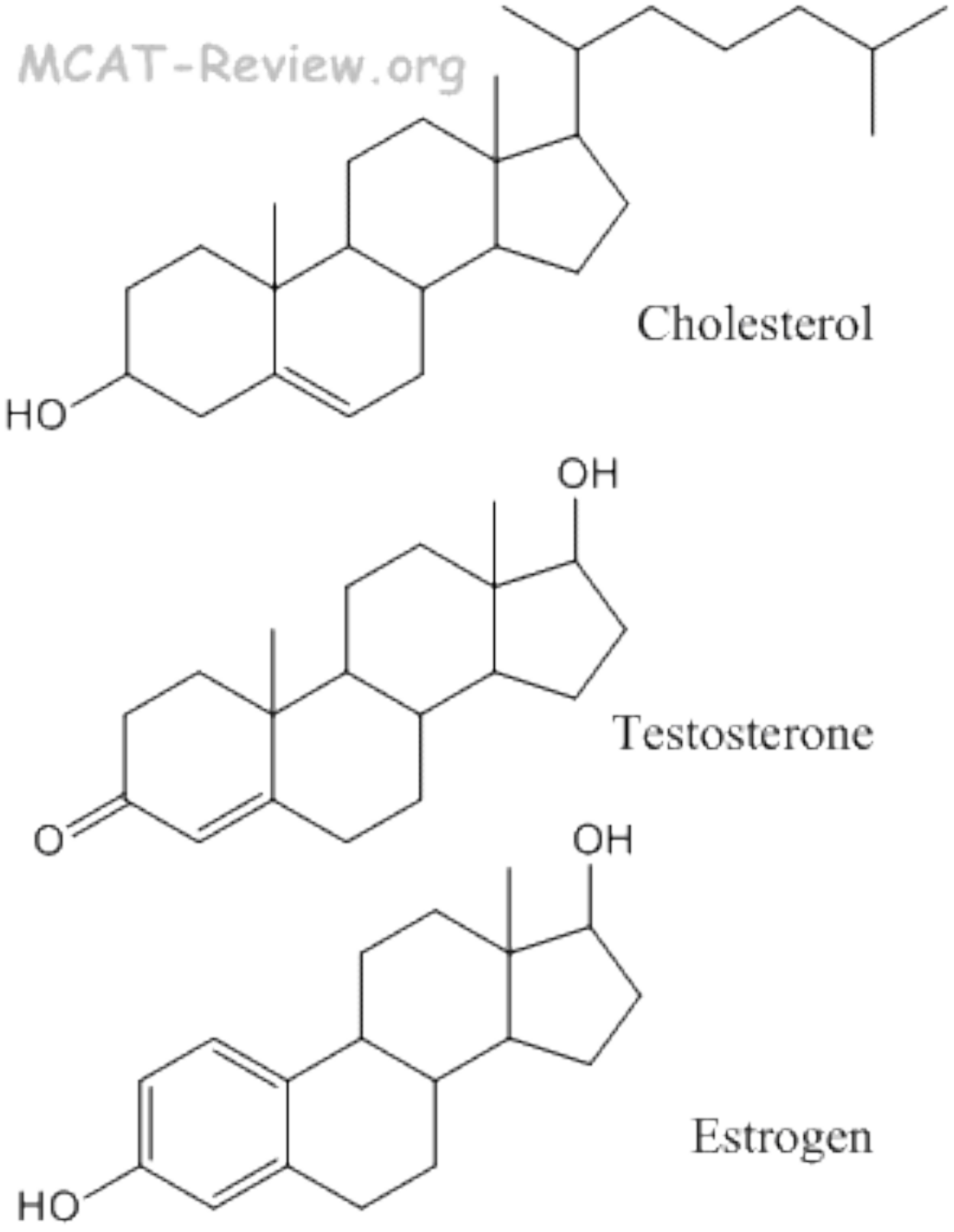
Terpenes contain double bonds, which gives the molecule the ability to undergo cyclization.

Squalene, the precursor of steroids, is a terpene that consists of 6 isoprene subunits. A complex self-cyclization reaction converts squalene to make steroids.

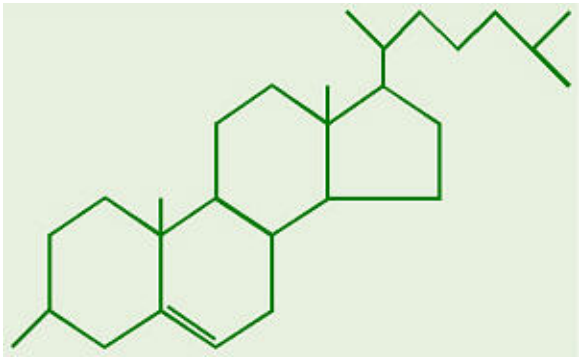
Squalene is classified as a triterpene. Triterpene = 6 isoprene subunits. Diterpene = 4 units. Monoterpene = 2 units.

Steroids

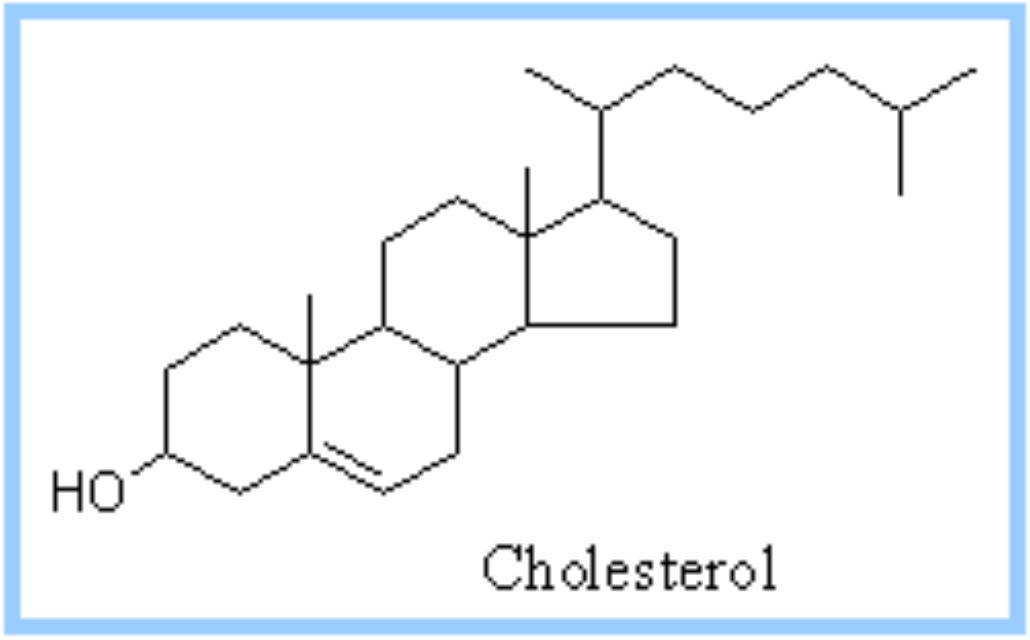
Steroids are made from the cyclization of squalene, which is a terpene.



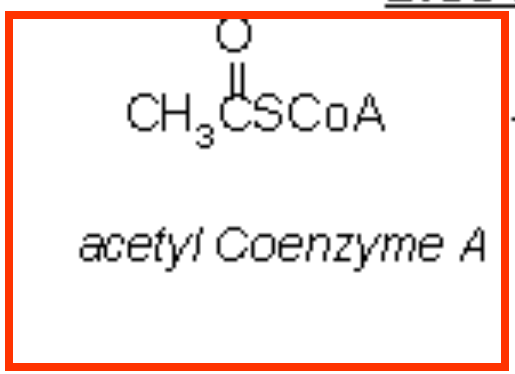
Cholesterol



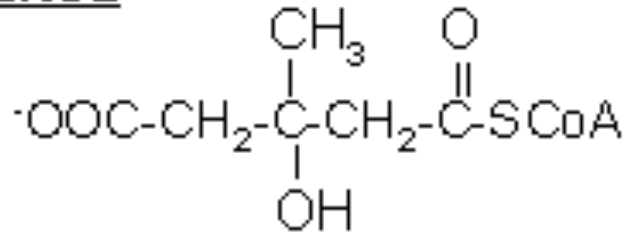
Perhydrocyclopentanophenanthrene ring



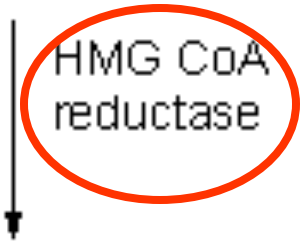
BIOSYNTHESIS OF CHOLESTEROL

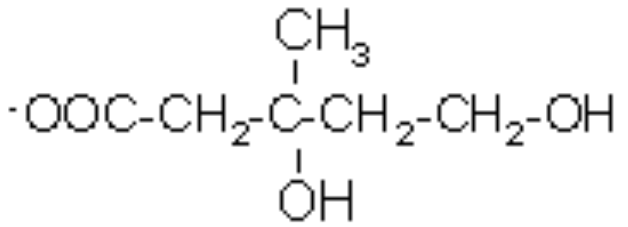


acetyl Coenzyme A



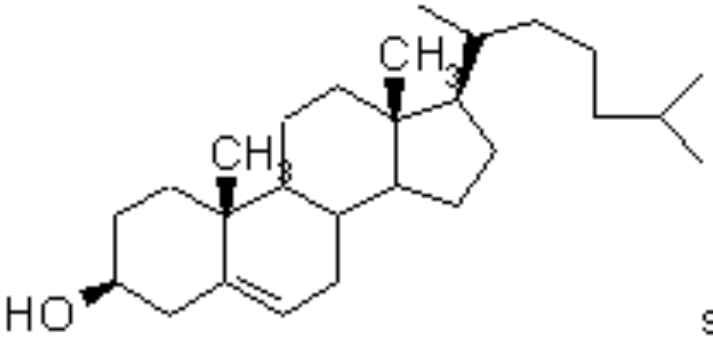
3-hydroxy-3-methyl-glutaryl-CoA



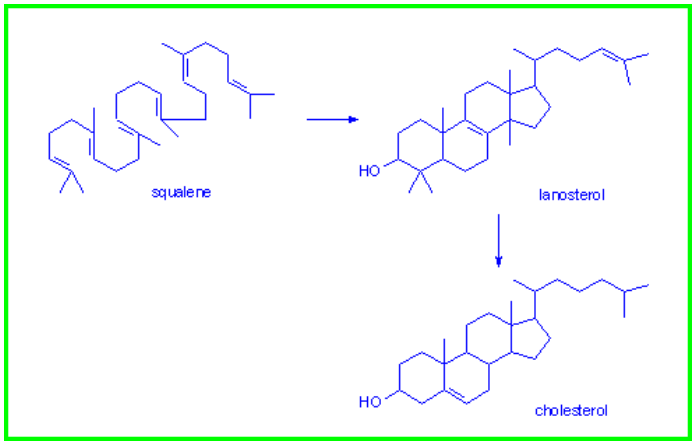


mevalonate

several steps

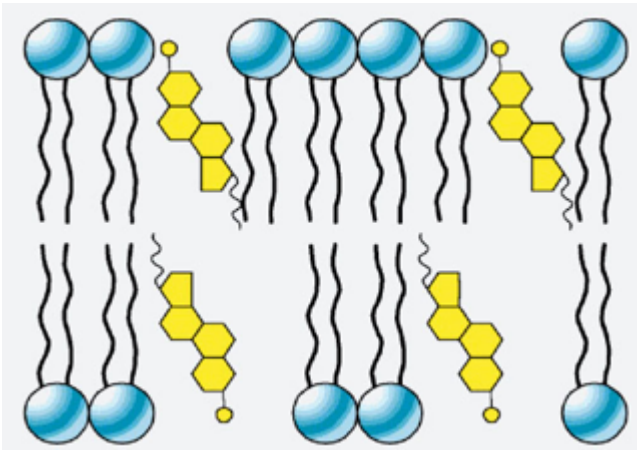


cholesterol

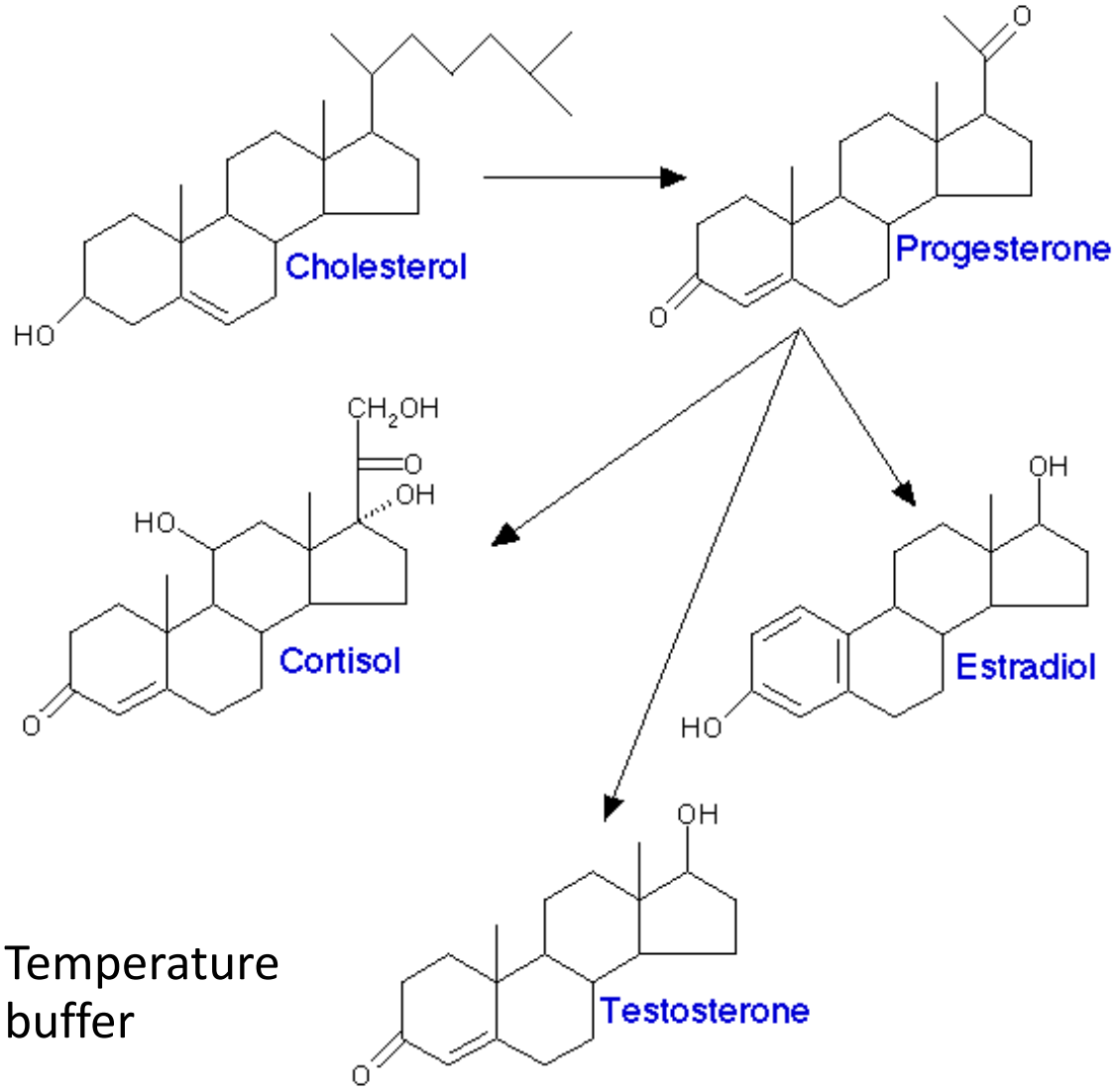


Rich Sources of Cholesterol

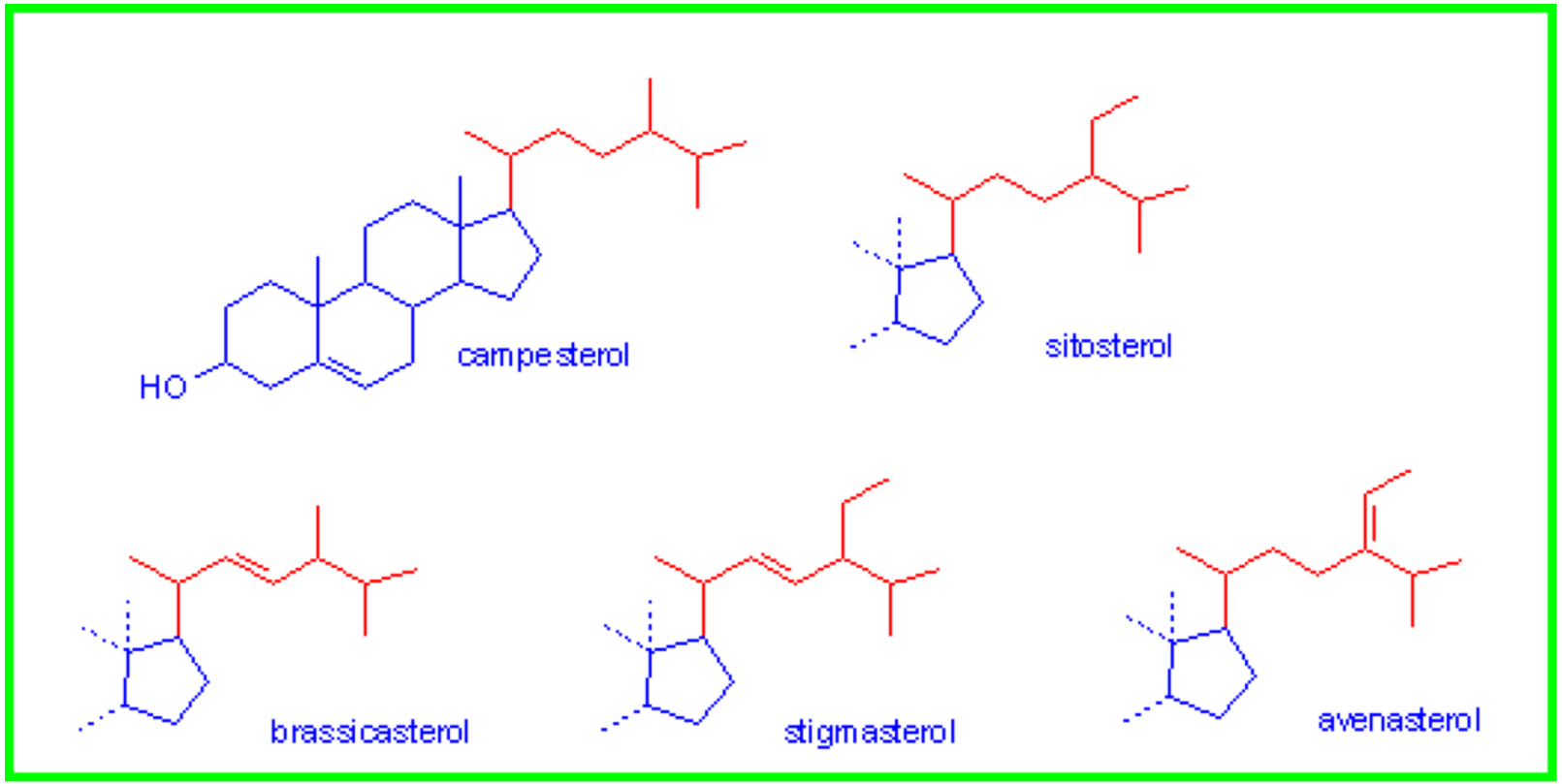
Poor Sources of Cholesterol



Temperature buffer



Plant sterols



Eicosanoids

eicosa = 20

like hormones, have profound physiological effects at very, very low concentrations.

(1) The inflammatory response (rheumatoid arthritis).

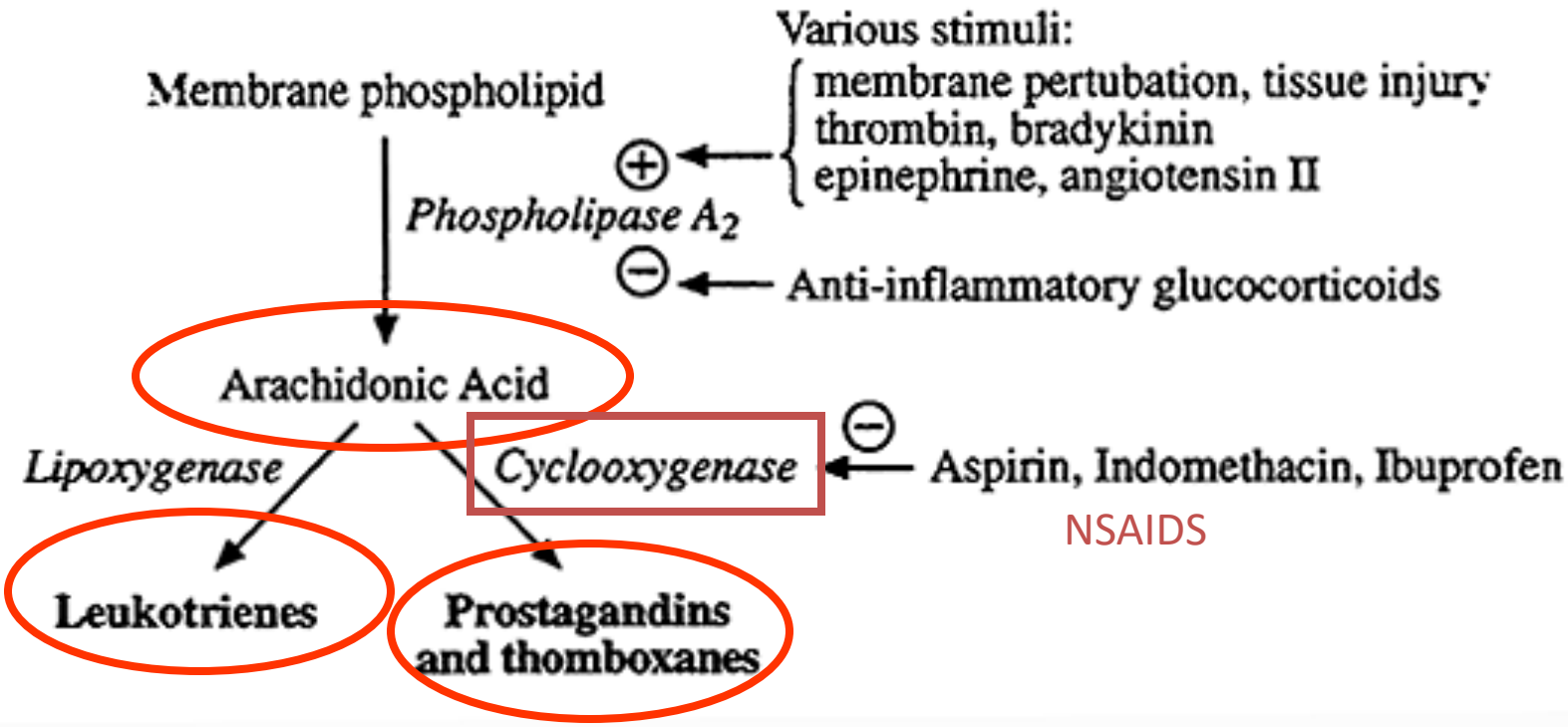
(2) The production of pain and fever.

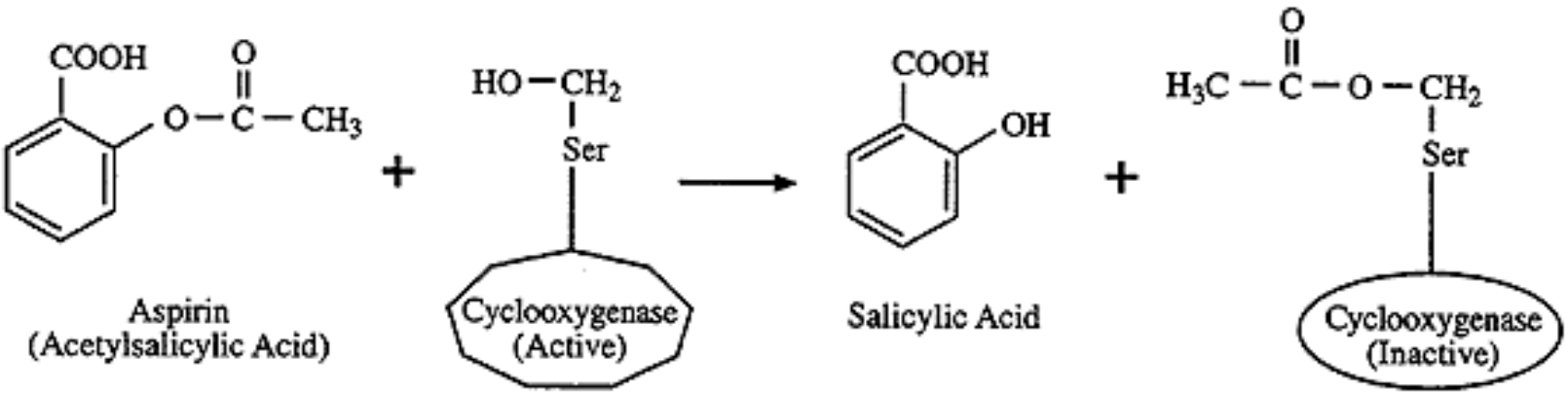
(3) The regulation of blood pressure.

(4) The induction of blood clotting.

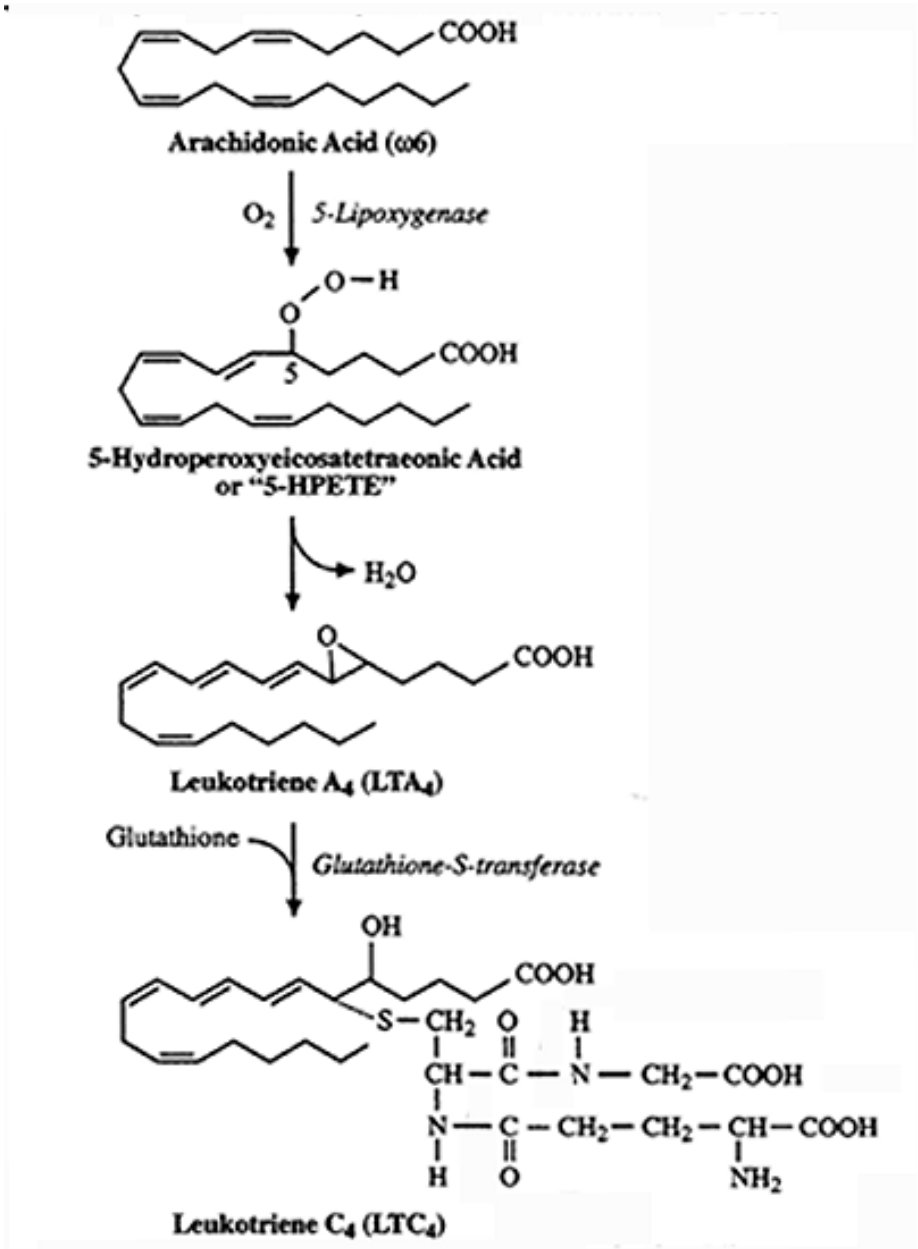
(5) The control of several reproductive functions such as the induction of labor.

(6) The regulation of the sleep / wake cycle.

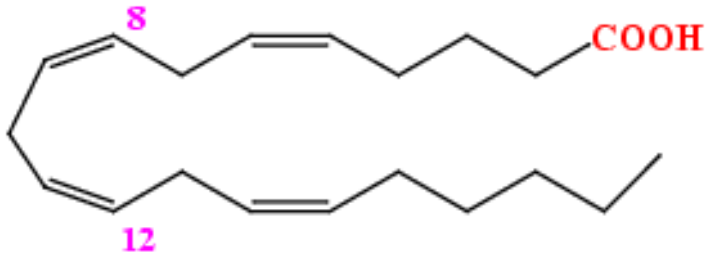

Various stimuli:
membrane pertubation, tissue injury
thrombin, bradykinin
epinephrine, angiotensin II
Membrane phospholipid
Phospholipase A2
Anti-inflammatory glucocorticoids
Arachidonic Acid
Lipoxygenase
Cyclooxygenase
Aspirin, Indomethacin, Ibuprofen
NSAIDS
Leukotrienes
Prostagandins and thomboxanes


COOH
O
O — C — CH3
HO — CH2
Ser
Cyclooxygenase (Active)
COOH
OH
H3C — C — O — CH2
Ser
Cyclooxygenase (Inactive)
Aspirin (Acetylsalicylic Acid)
Salicylic Acid

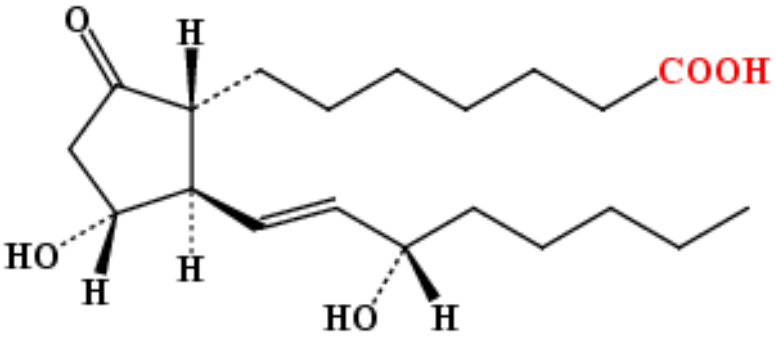
Leukotrienes



Prostaglandin

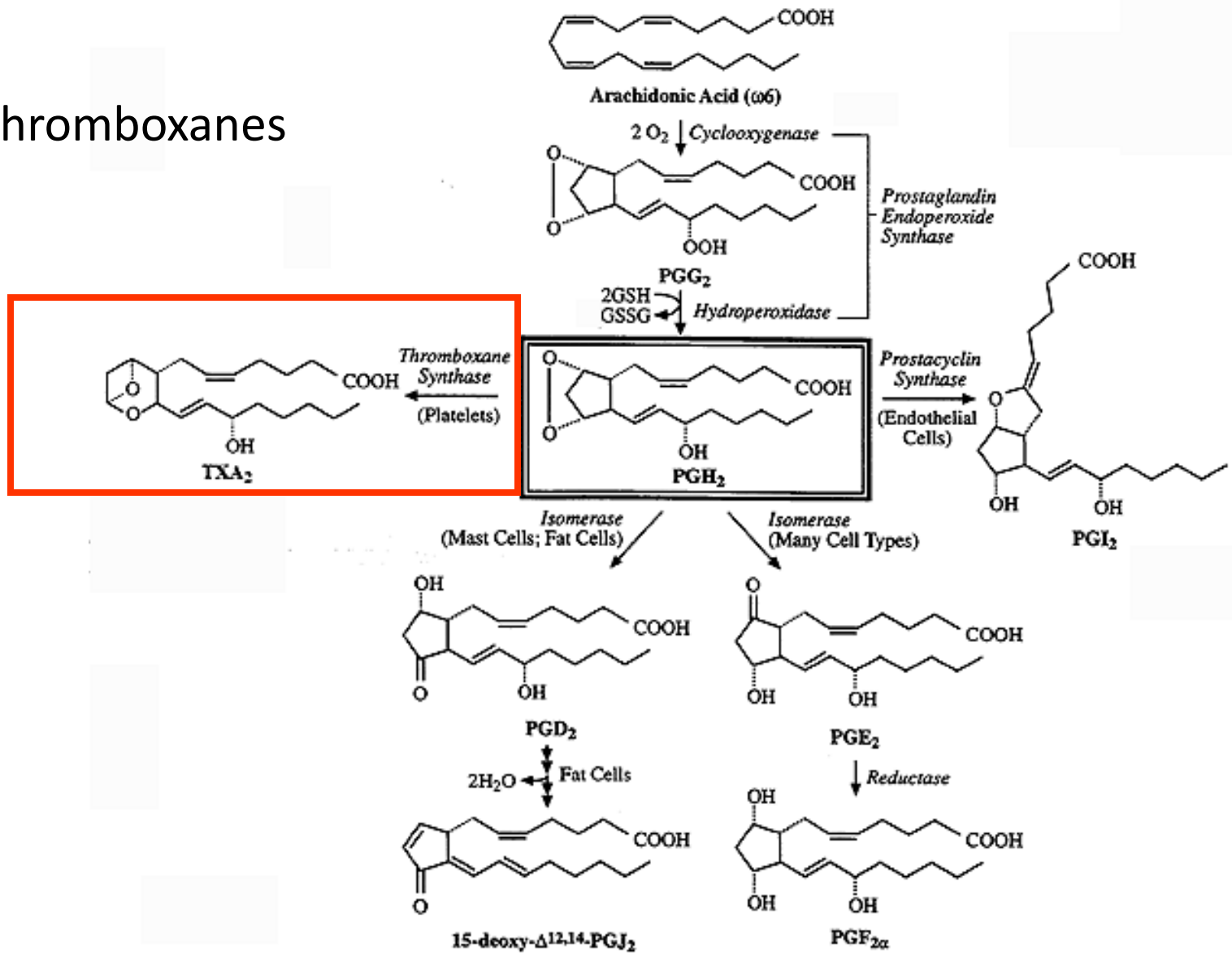


arachidonic acid



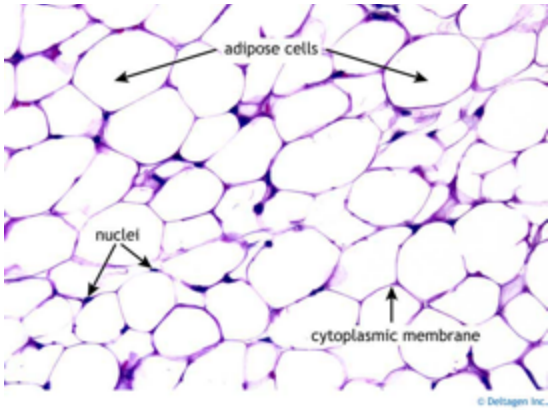
a prostaglandin

Thromboxanes



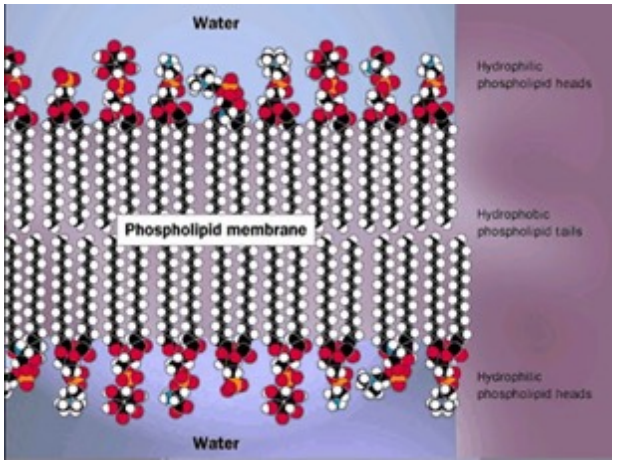
Role of lipids

1. **Energy storage - triacylglycerol**

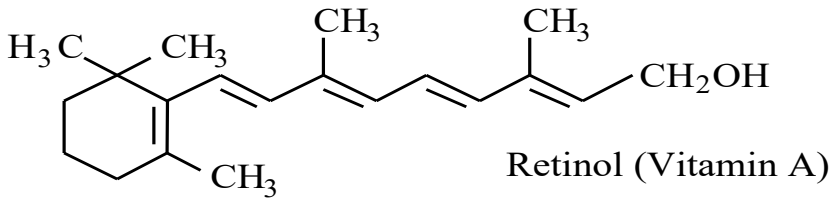


Adipose tissue

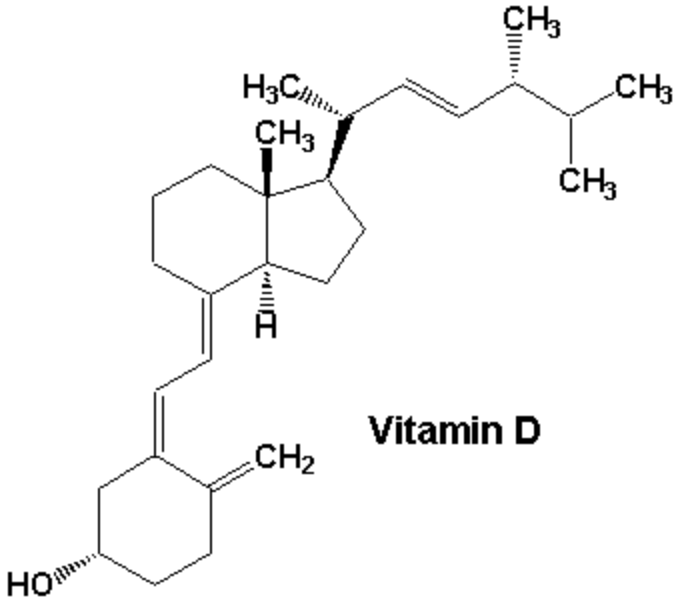
2. **Composition of biological membrane -phospholipid**



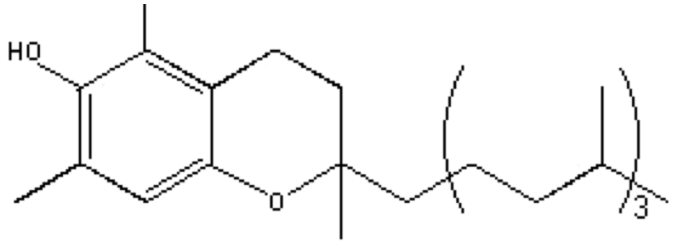
3. **Transport nonpolar compounds -vit A D E K**



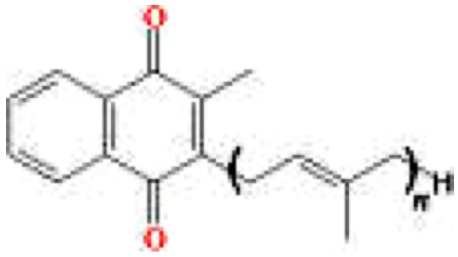
Retinol (Vitamin A)



Vitamin D



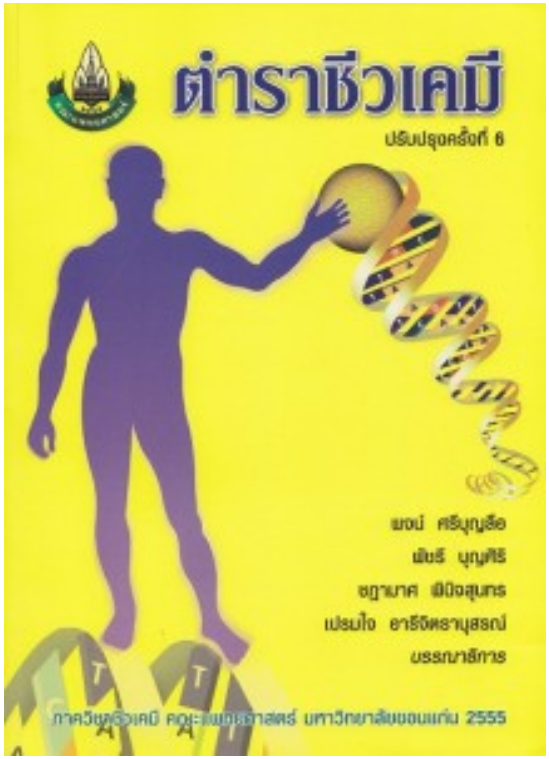
alpha-tocopherol

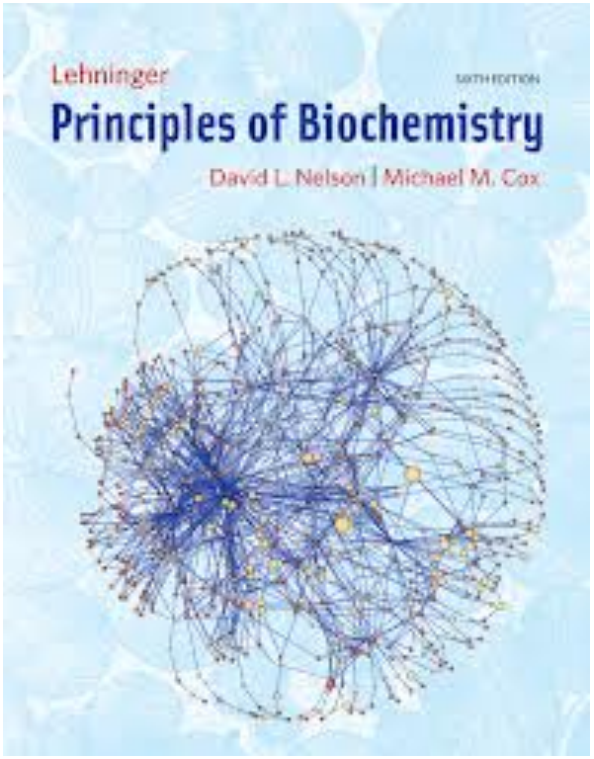


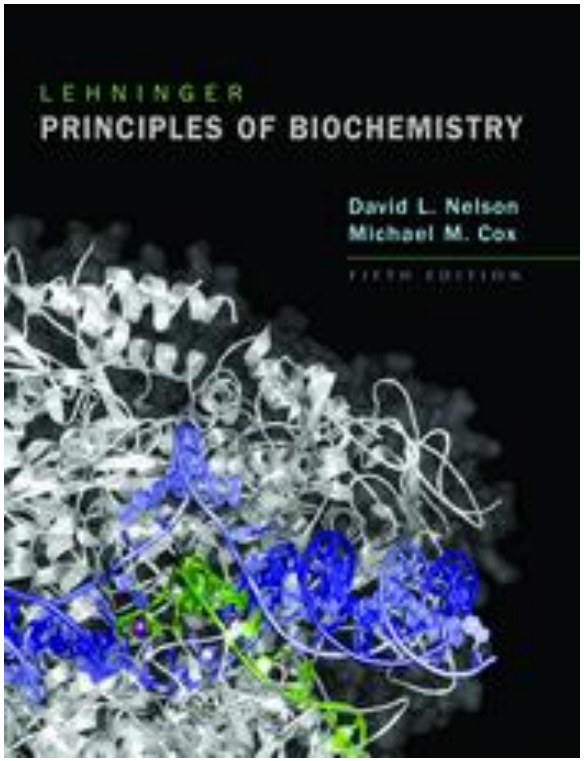
4. **Insulators**

5. **Signals, hormones**

References







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