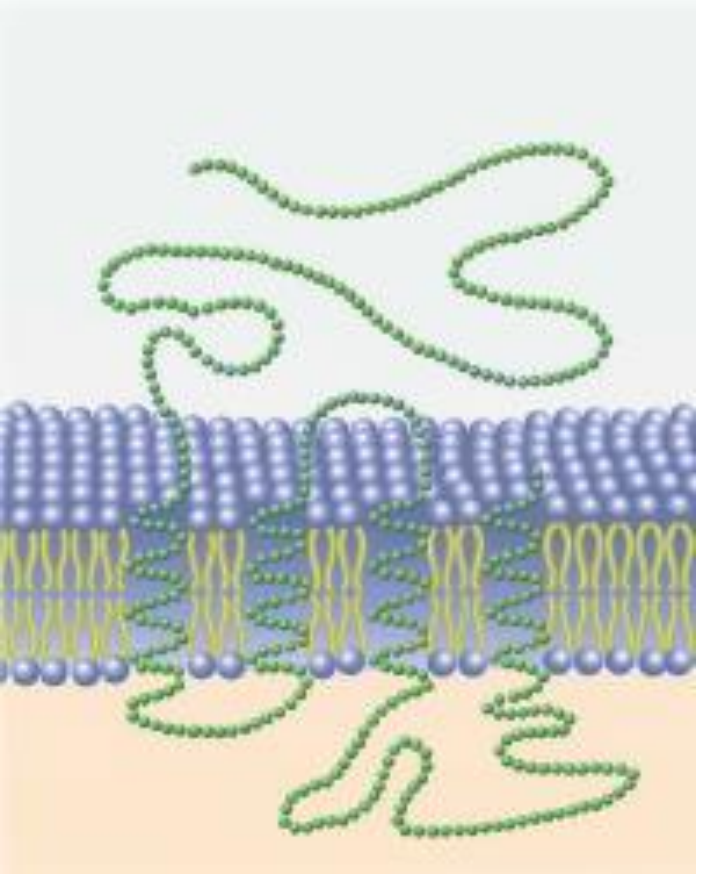

# Lipids

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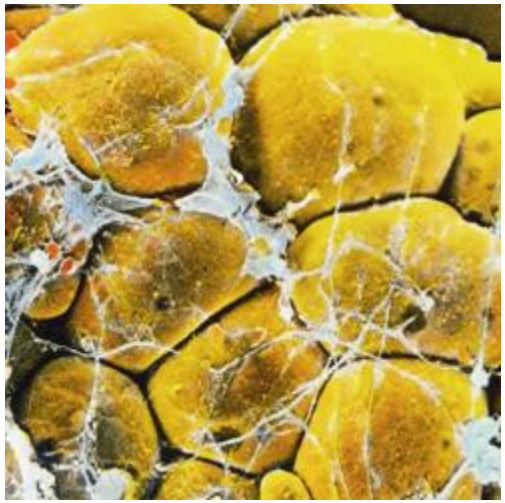
Images were taken Campbell textbook or McMurryetal

# Lipids- Definition

- Naturally occurring organic molecules that are nonpolar and therefore dissolve in nonpolar organic solvents but not in water.
- Many lipids have hydrocarbon or modified hydrocarbon structure, properties, and behavior

# Major role of lipids

- Energy storage from metabolism of food within fat cells (adipocytes).
- Separate the inside and outside of the cells as part of all cell membranes.
- Chemical messengers in the endocrine system and elsewhere.



Adipocytes

# Lipid families

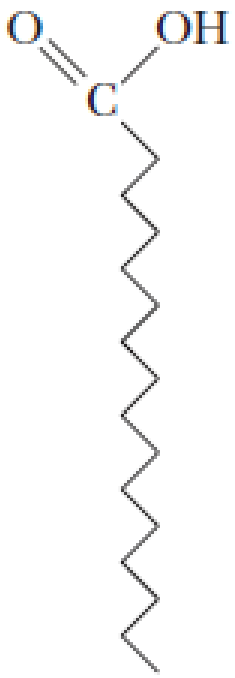
# Fatty Acids

-Are long, unbranched hydrocarbon chains with a carboxylic acid group at one end.

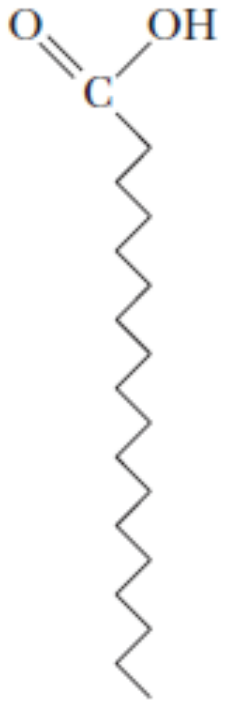
-Most have even numbers of carbon atoms.

-May or may not contain carbon carbon double bonds.

**-Saturated fatty acids (**without double bonds)




Palmitic acid

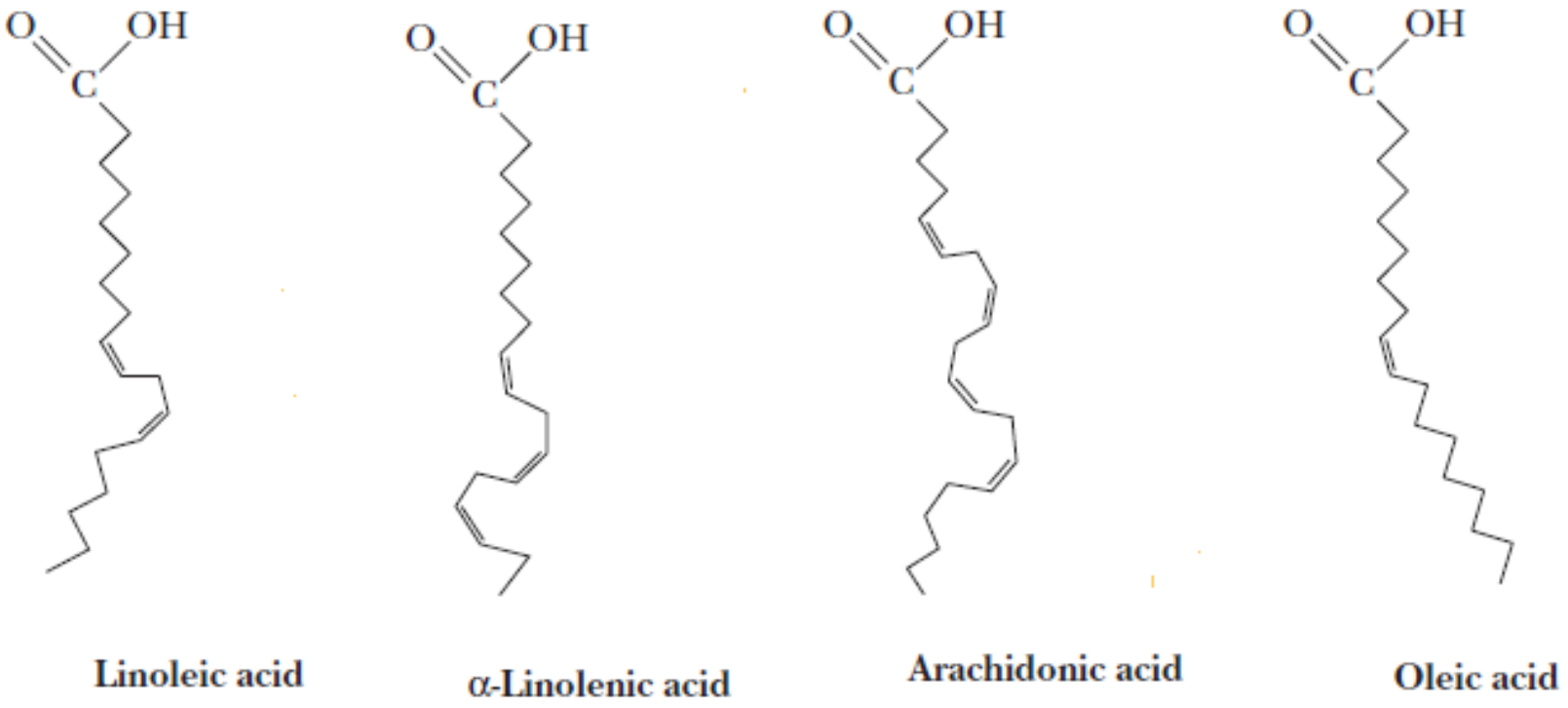



Stearic acid

# Fatty Acids

**-Unsaturated fatty acids (**with double bonds)

- The stereochemistry at the double bond is usually cis rather than trans




**Monounsaturated versus polyunsaturated fatty acids**

# Common fatty acids

**Table 8.1**

**Typical Naturally Occurring Saturated Fatty Acids**

| Acid | Number of Carbon Atoms | Formula | Melting Point (°C) |
|---|---|---|---|
| Lauric | 12 | $CH_3(CH_2)_{10}CO_2H$ | 44 |
| Myristic | 14 | $CH_3(CH_2)_{12}CO_2H$ | 58 |
| Palmitic | 16 | $CH_3(CH_2)_{14}CO_2H$ | 63 |
| Stearic | 18 | $CH_3(CH_2)_{16}CO_2H$ | 71 |
| Arachidic | 20 | $CH_3(CH_2)_{18}CO_2H$ | 77 |

**Table 8.2**

**Typical Naturally Occurring Unsaturated Fatty Acids**

| Acid | Number of Carbon Atoms | Degree of Unsaturation* | Formula | Melting Point (°C) |
|---|---|---|---|---|
| Palmitoleic | 16 | 16:1—$\Delta^9$ | $CH_3(CH_2)_5CH{=}CH(CH_2)_7CO_2H$ | –0.5 |
| Oleic | 18 | 18:1—$\Delta^9$ | $CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H$ | 16 |
| Linoleic | 18 | 18:2—$\Delta^{9,12}$ | $CH_3(CH_2)_4CH{=}CH(CH_2)CH{=}CH(CH_2)_7CO_2H$ | –5 |
| Linolenic | 18 | 18:3—$\Delta^{9,12,15}$ | $CH_3(CH_2CH{=}CH)_3(CH_2)_7CO_2H$ | –11 |
| Arachidonic | 20 | 20:4—$\Delta^{5,8,11,14}$ | $CH_3(CH_2)_4CH{=}CH(CH_2)_4(CH_2)_2CO_2H$ | –50 |

*Degree of unsaturation refers to the number of double bonds. The superscript indicates the position of double bonds. For example, Δ9 refers to a double bond at the ninth carbon atom from the carboxyl end of the molecule.

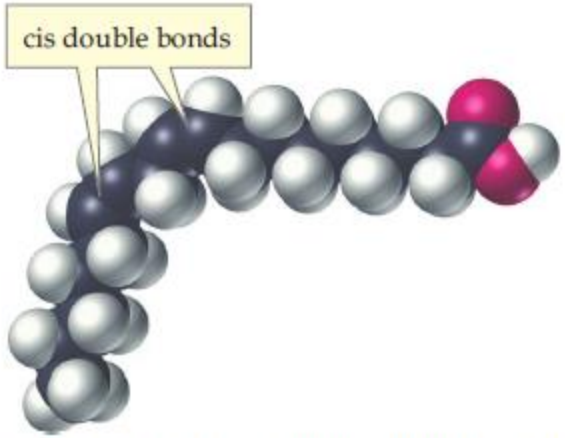
# Properties of Fats and Oils

- Melting point decreases with the presence of  more double bonds a fatty acid has.
- Vegetable **oils are lower melting than animal fats** because oils have more unsaturated fatty acids than animal **fats.**

*A saturated fat has only single C-C bonds and appears straight*

Stearic acid, an 18-carbon saturated fatty acid

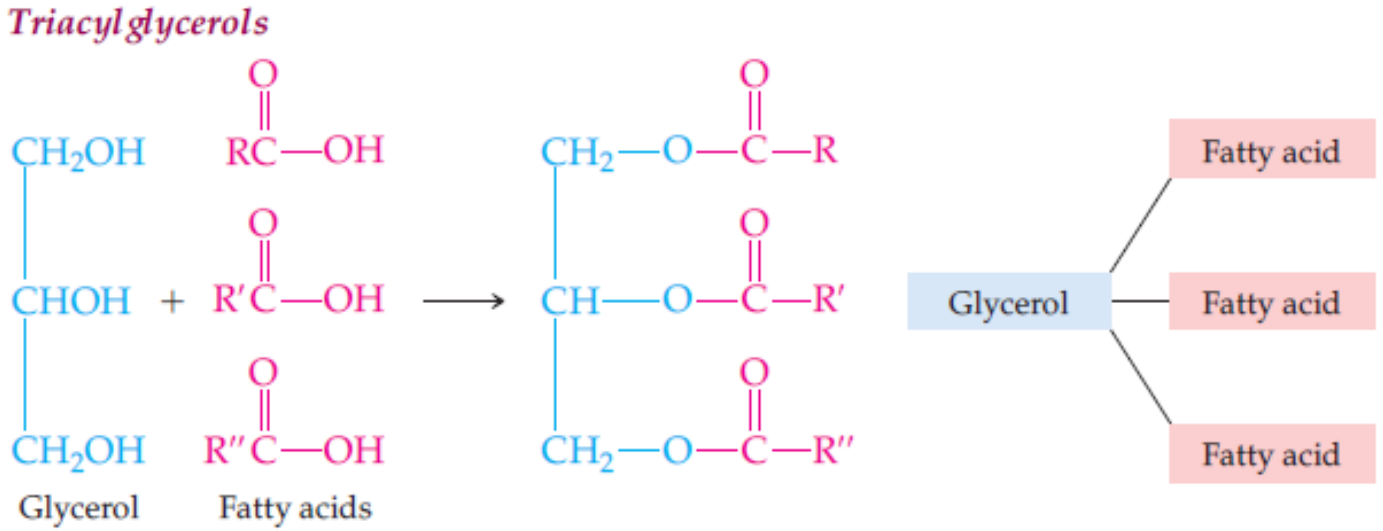
*Unsaturated fats bend due to cis double bonds*



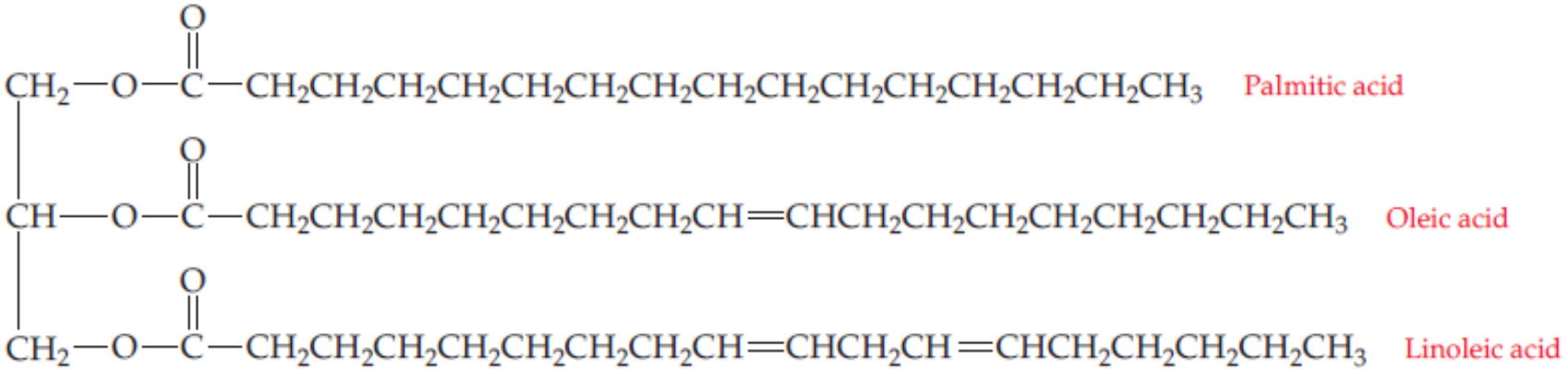

Linoleic acid, an 18-carbon unsaturated fatty acid

# Triacylglycerols

- All fats and oils are composed of triesters of glycerol with three fatty acids.
- Glycerol (glycerine) is 1,2,3-propanetriol
- The 3 fatty acids can be the same or different.



# Example of a triacylglycerol



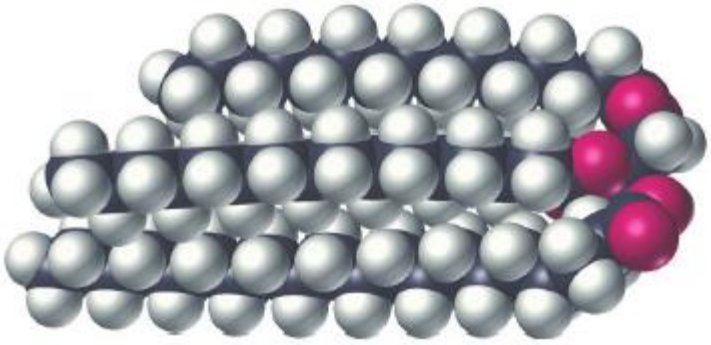
# Oil and fat are mixtures of triacylglycerols

TABLE 24.2 Approximate Composition of Some Common Fats and Oils*

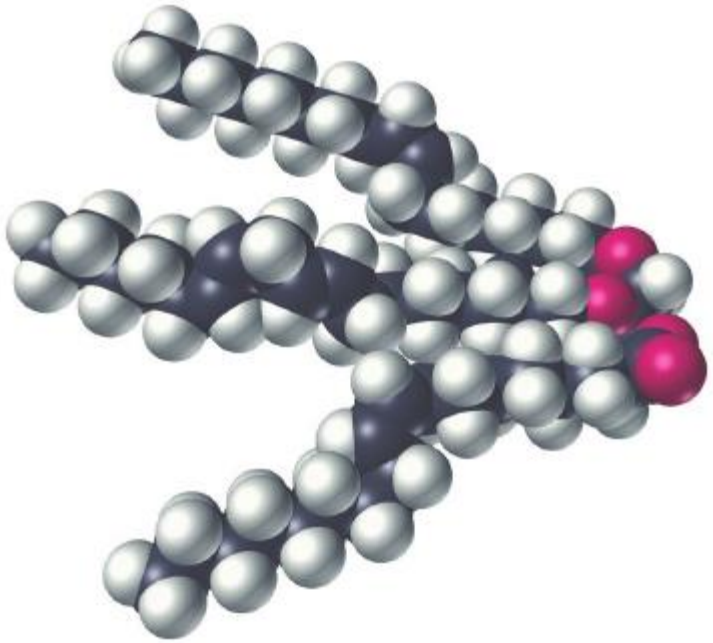
| | SATURATED FATTY ACIDS (%) | | | | UNSATURATED FATTY ACIDS (%) | |
|---|---|---|---|---|---|---|
| SOURCE | $C_{12}$ LAURIC | $C_{14}$ MYRISTIC | $C_{16}$ PALMITIC | $C_{18}$ STEARIC | $C_{18}$ OLEIC | $C_{18}$ LINOLEIC |
| **Animal Fat** | | | | | | |
| Lard | — | 1 | 25 | 15 | 50 | 6 |
| Butter | 2 | 10 | 25 | 10 | 25 | 5 |
| Human fat | 1 | 3 | 25 | 8 | 46 | 10 |
| Whale blubber | — | 8 | 12 | 3 | 35 | 10 |
| **Vegetable Oil** | | | | | | |
| Corn | — | 1 | 8 | 4 | 46 | 42 |
| Olive | — | 1 | 5 | 5 | 83 | 7 |
| Peanut | — | — | 7 | 5 | 60 | 20 |
| Soybean | — | — | 7 | 4 | 34 | 53 |

**Where totals are less than 100%, small quantities of several other acids are present, with cholesterol also present in animal fats.*

# Triacylglycerols from a fat and an oil



A fat



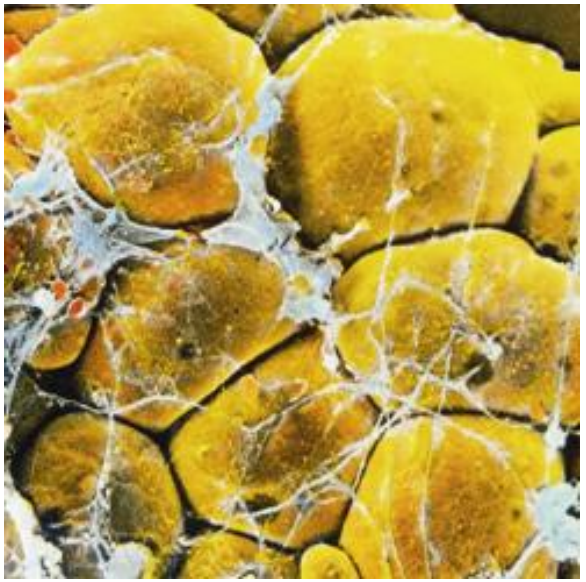
An oil

# Properties of Triacylglycerols

- Uncharged, nonpolar, hydrophobic molecules.
- No ionic charges
- Solid triacylglycerols (fats) high proportion of saturated fatty acid chains
- Liquid triacylglycerols (oils) high proportion of unsaturated fatty acid chains

# Roles of TAGs

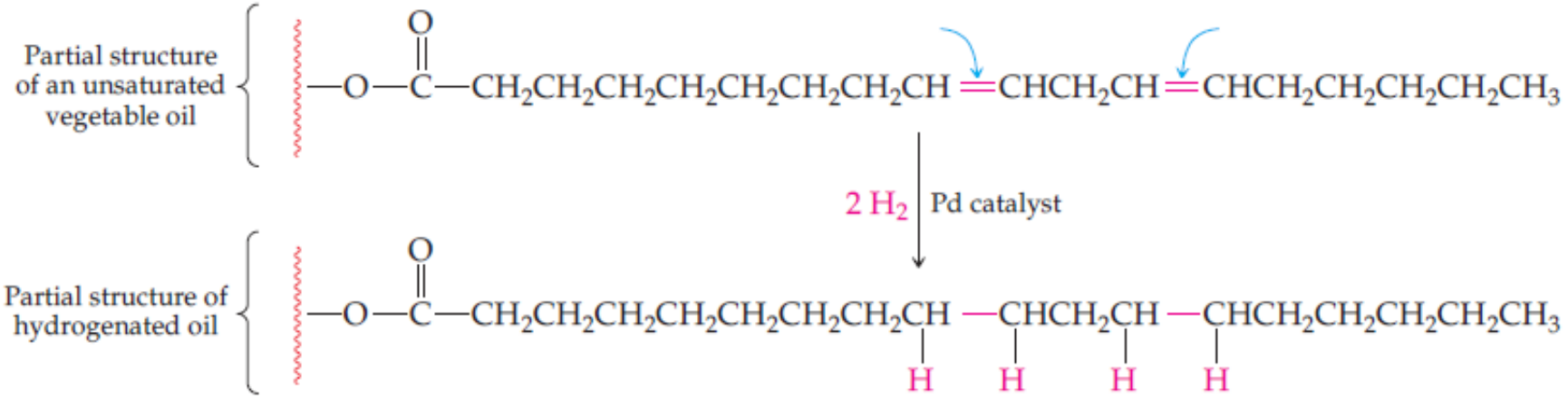
- The primary function of triacylglycerols is long-term storage of energy for the organism



- Adipose tissue provides thermal insulation and protective padding

# Chemical Reactions of TAGs

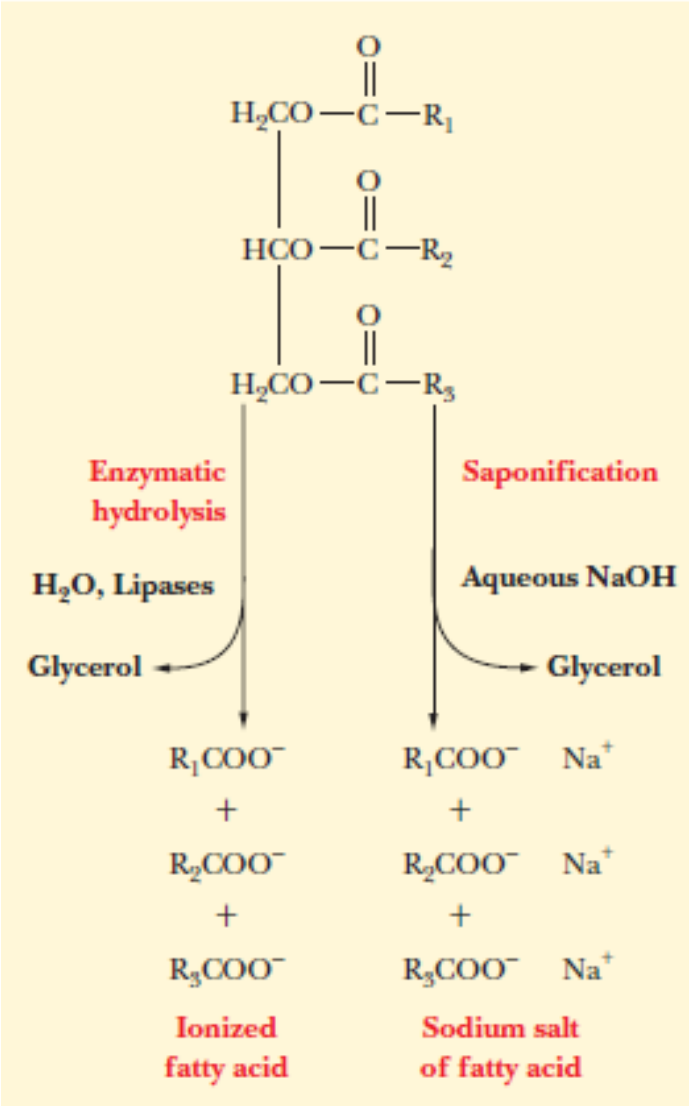
## Hydrogenation




## Margarine

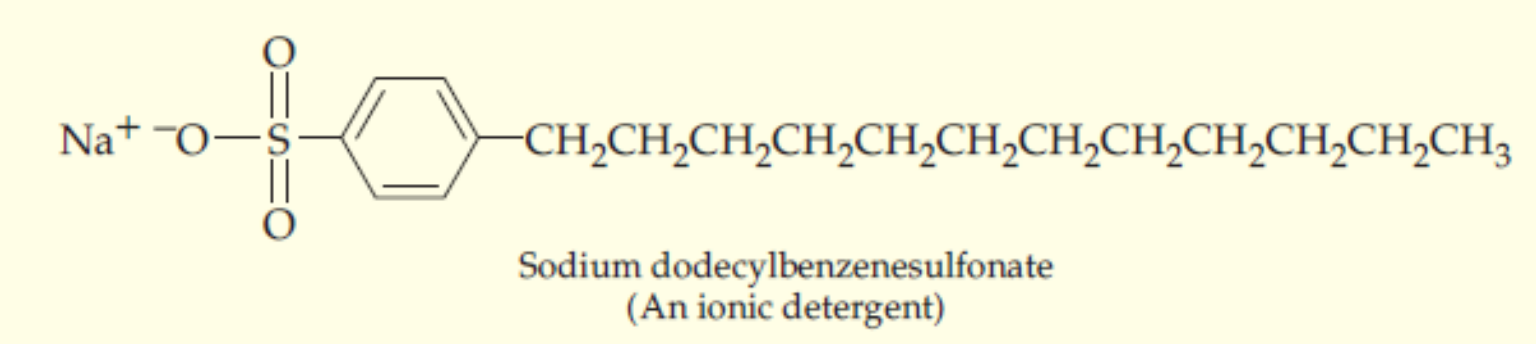
# Hydrolysis of TAGs (Saponification)

- Esters can react with water (hydrolyzed) to form their carboxylic acids and alcohols.
- Lipases catalyze hydrolysis of dietary fats and oils in the body.
- Saponification is the hydrolysis of fats and oils by strong aqueous bases (NaOH or KOH)

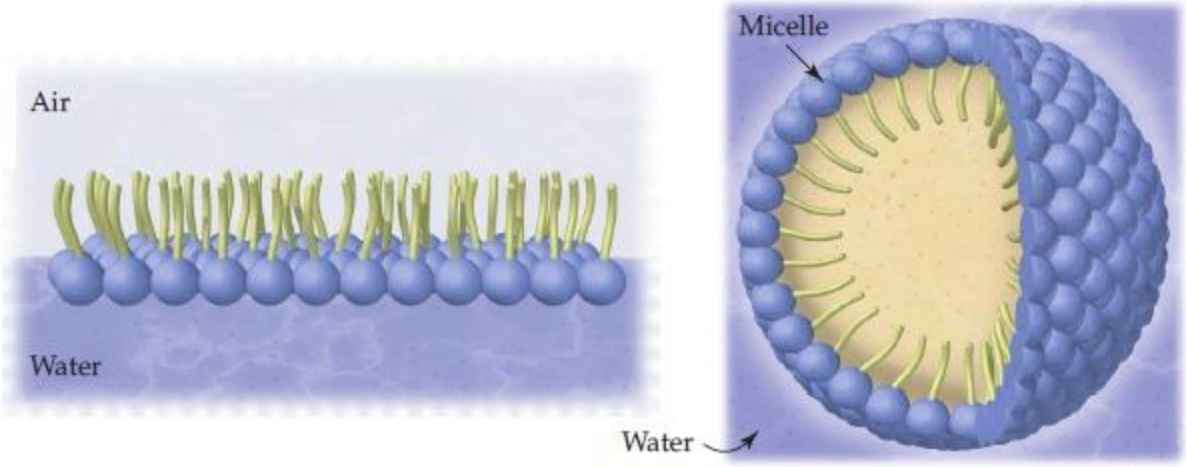


# Detergents

- Anything that washes away dirt

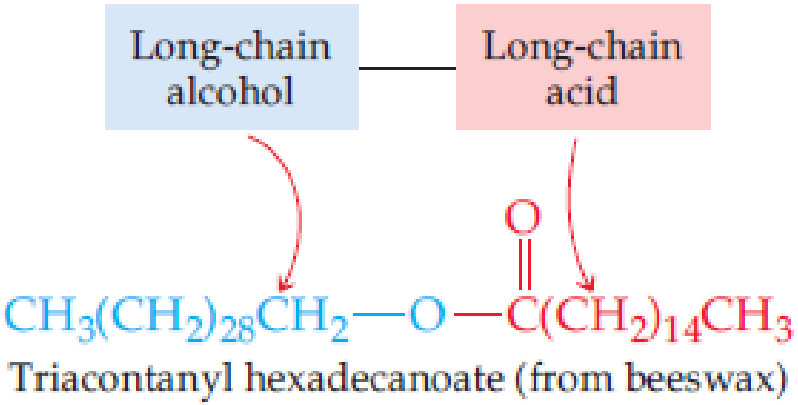


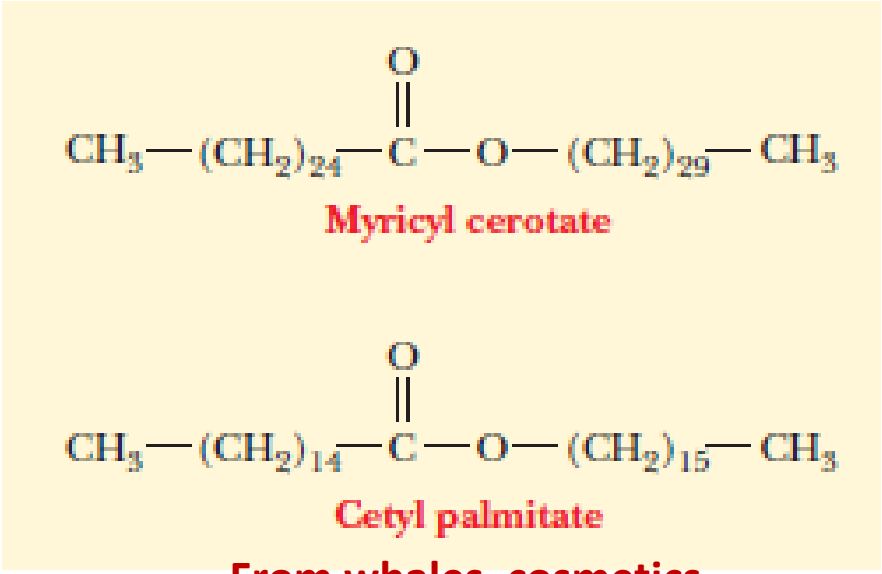

- How do soaps and detergents act?



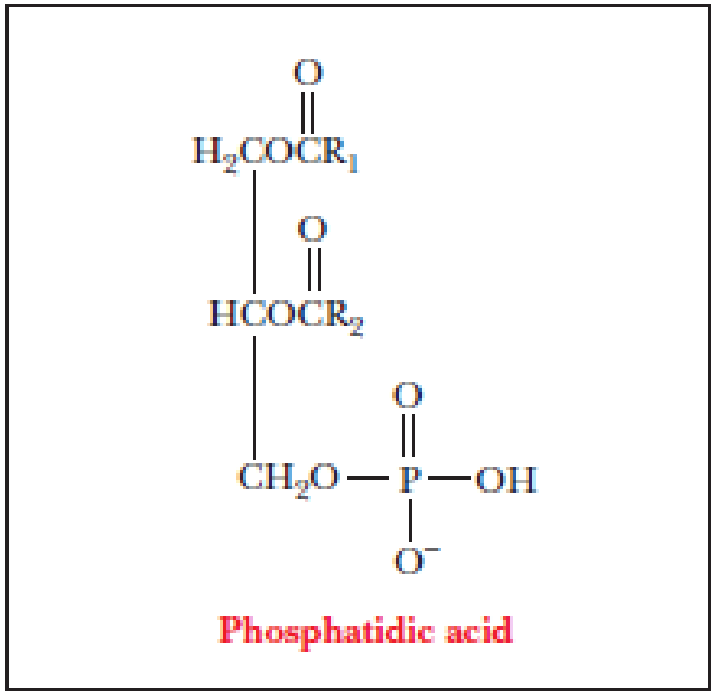
# Waxes

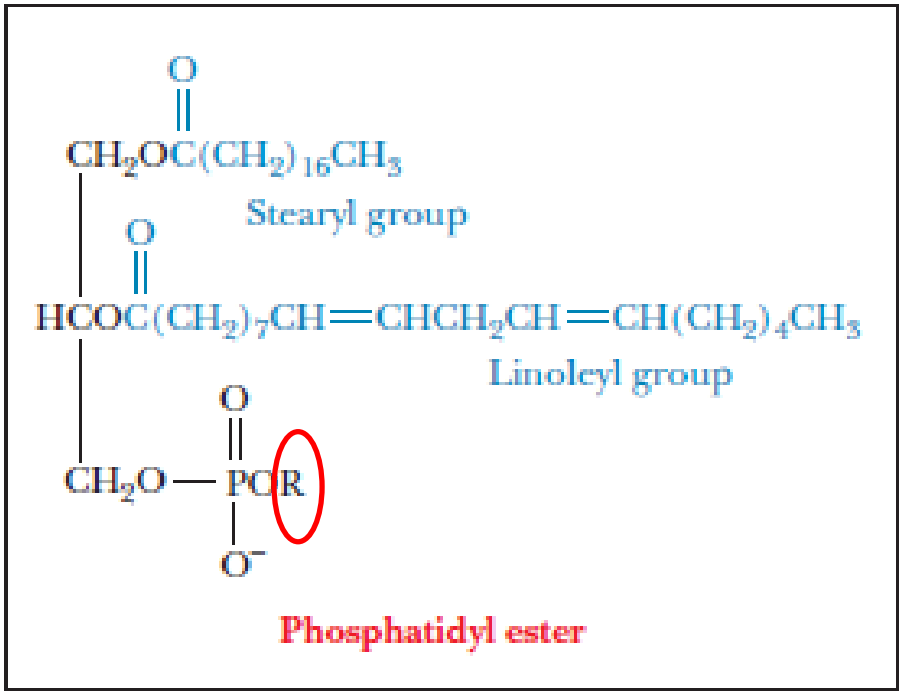
- **Waxes** are complex mixtures of esters of long-chain carboxylic acids and long chain.
- Beeswax, protective coatings on most fruits, aquatic birds feathers, etc



# Phosphoglycerols (Phosphatidyl esters) (Glycerophospholipids)




Phosphoric acid is triprotic and thus can form more than one ester linkage.

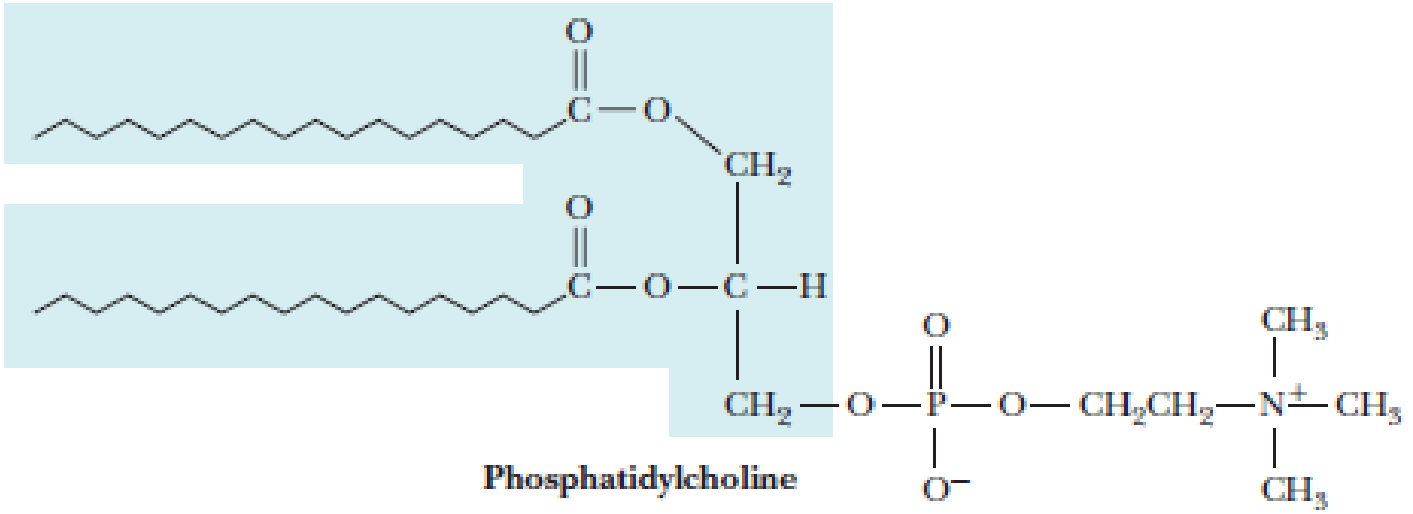
Different R groups result in different types of phosphoglycerols

# Types of Phosphoglycerols

-The nature of the second alcohol esterified to the phosphoric acid determine the type of phosphoglycerol.

-Phosphoacylglycerols are important components of biological membranes.

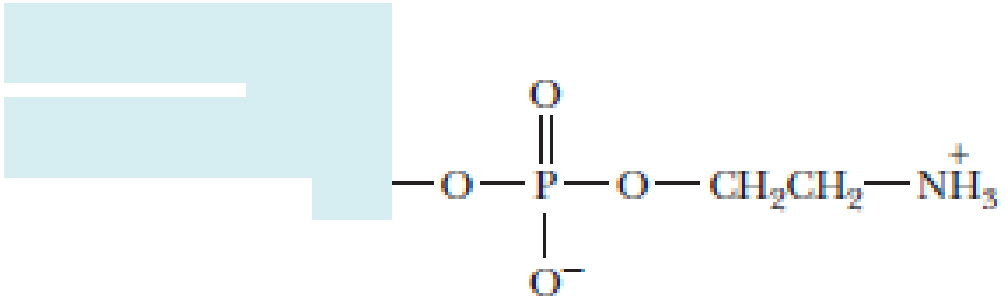
**Phosphatidylcholine (lecithin)**




Phosphatidylcholine

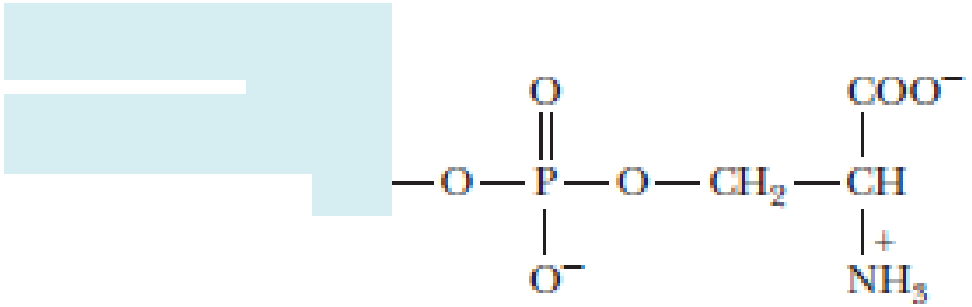
# Types of Phosphoglycerols

**Phosphatidylethanolamine (**cephalin)



Phosphatidylethanolamine

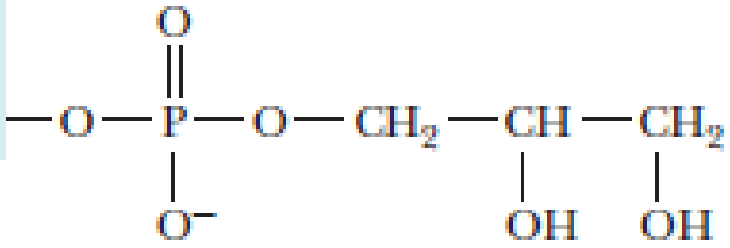
**Phosphatidylserine**



Phosphatidylserine

# Types of Phosphoglycerols

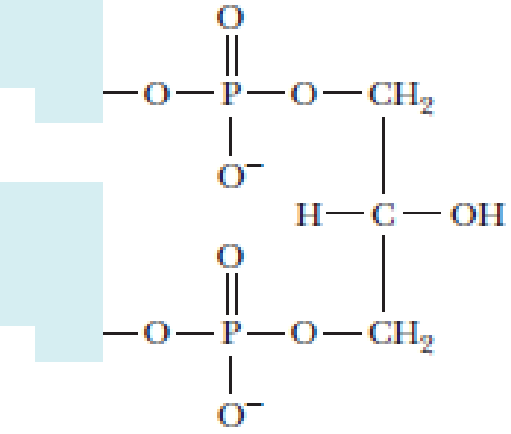
## Phosphatidylglycerol



Phosphatidylglycerol

## Diphosphatidylglycerol (Cardiolipin)

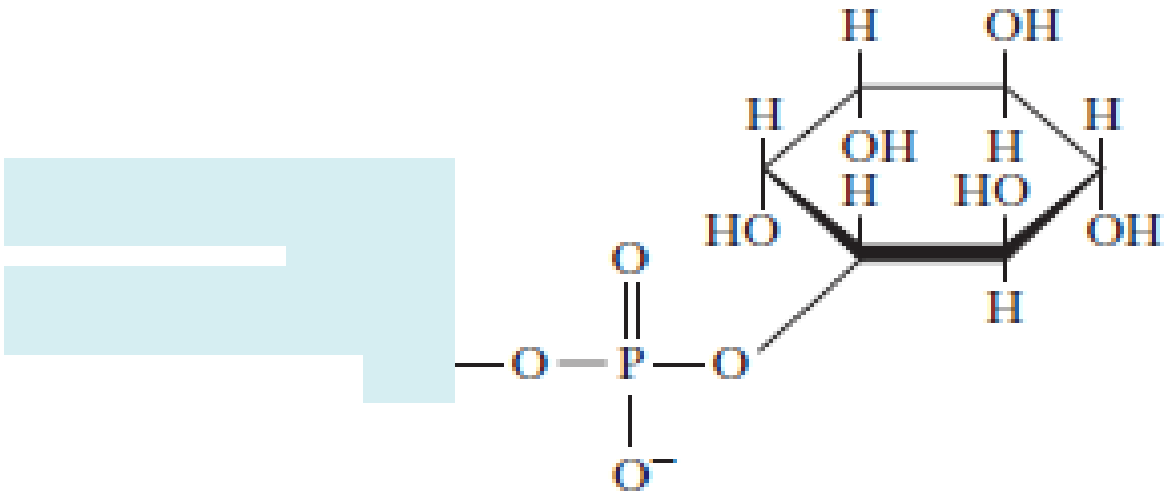
found almost exclusively in the inner mitochondrial membrane



Diphosphatidylglycerol (Cardiolipin)

# Types of Phosphoglycerols

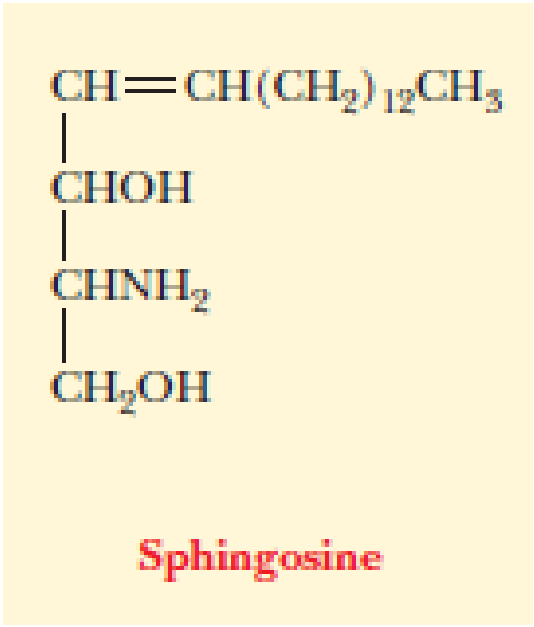
Phosphatidylinositol



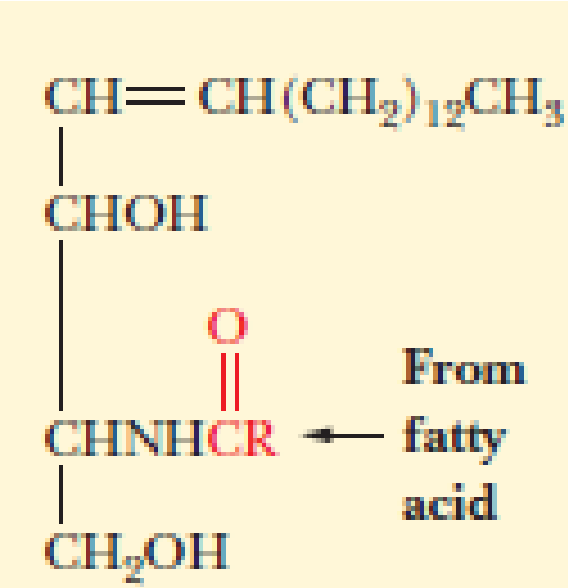

**Phosphatidylinositol**

# Sphingolipids

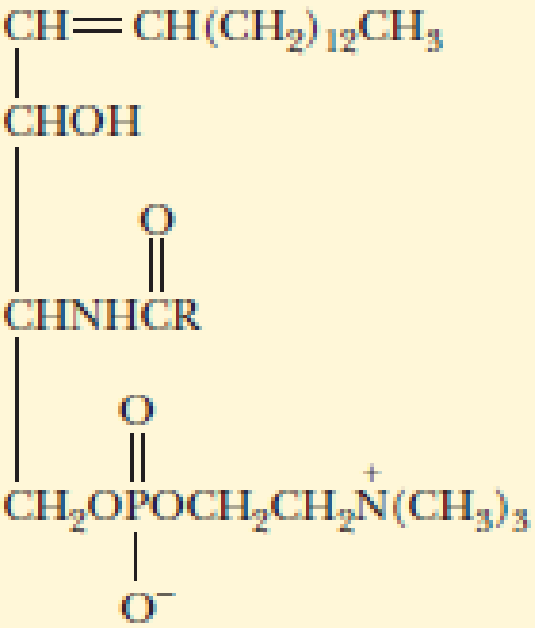
- Abundant in the nervous system




Sphingosine



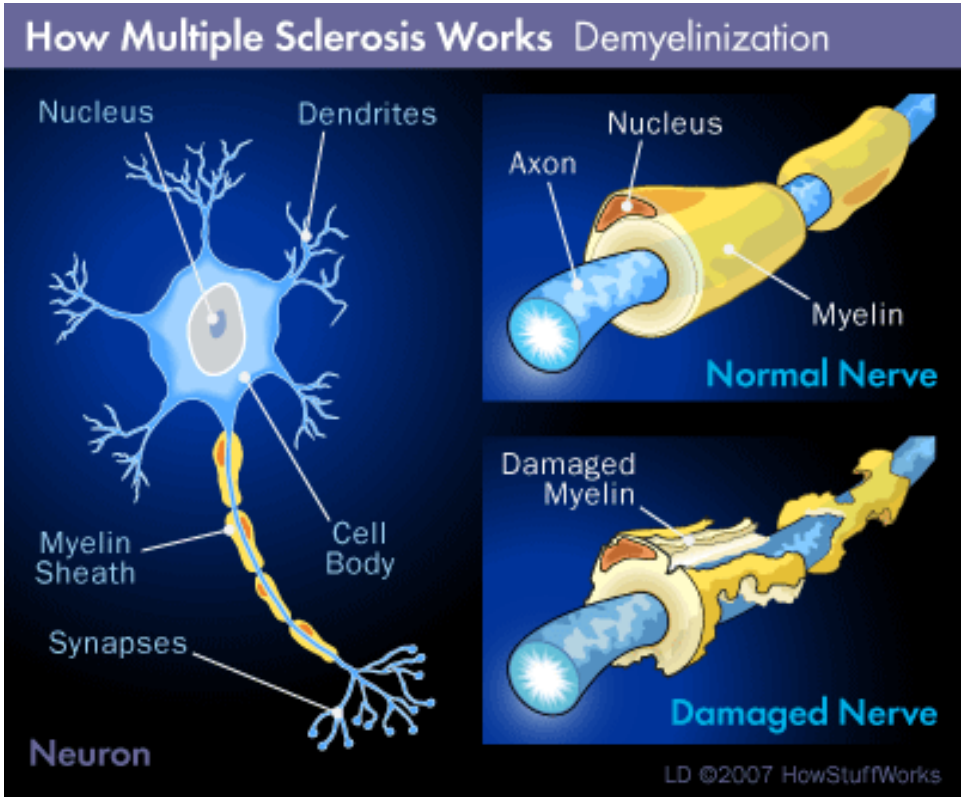

A ceramide
(*N*-acylsphingosine)




A sphingomyelin

# Sphingomyelin and multiple sclerosis (MS)

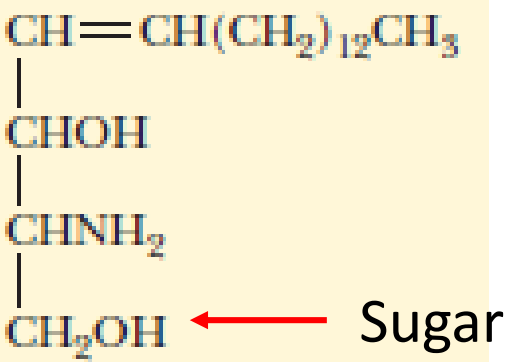
- Myelin sheath consists of many layers of plasma membrane (rich in lipids not proteins) that have been wrapped around the nerve cell.
- Loss of myelin leads to the slowing and eventual cessation of the nerve impulse.
- In MS, the myelin sheath is progressively destroyed by sclerotic plaques that affect the brain and spinal cord.
- Weakness, lack of coordination, and speech and vision problems

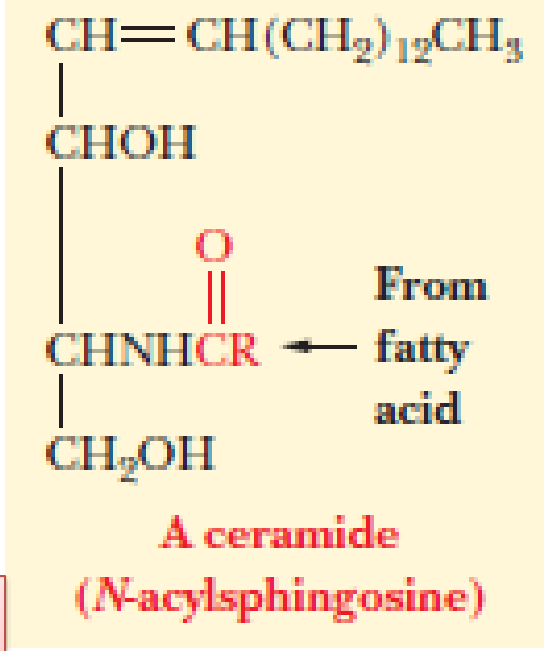


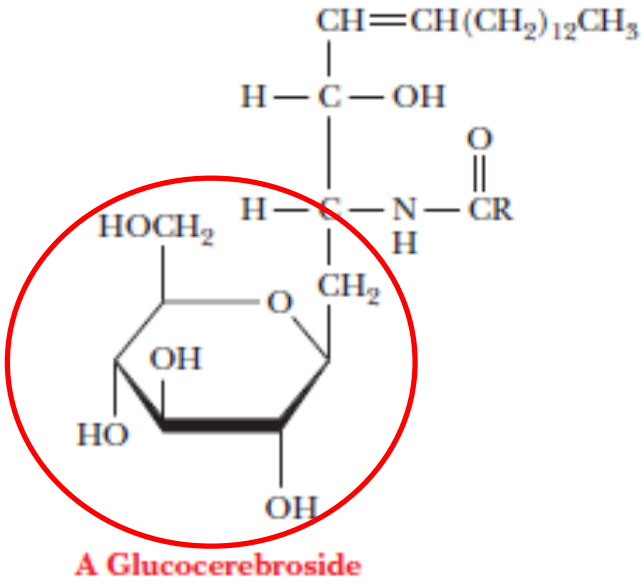



health.howstuffworks.com

# Sphingolipids-Glycolipids



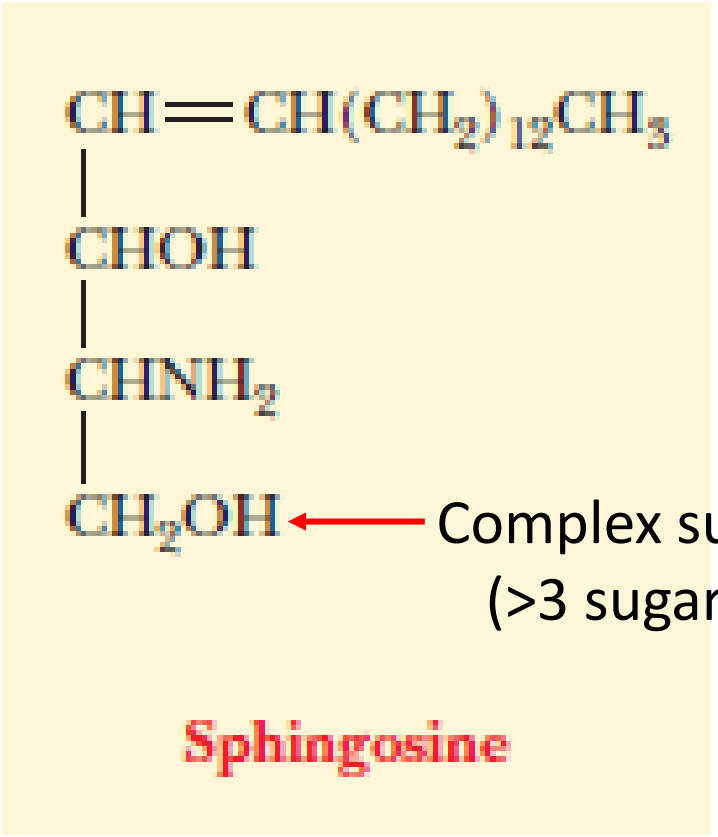

Glycolipids act as markers on cell membranes and play a role in tissue and organ specificity

**Types of cerebrosides**

Ceramide + glucose = glucocerebroside

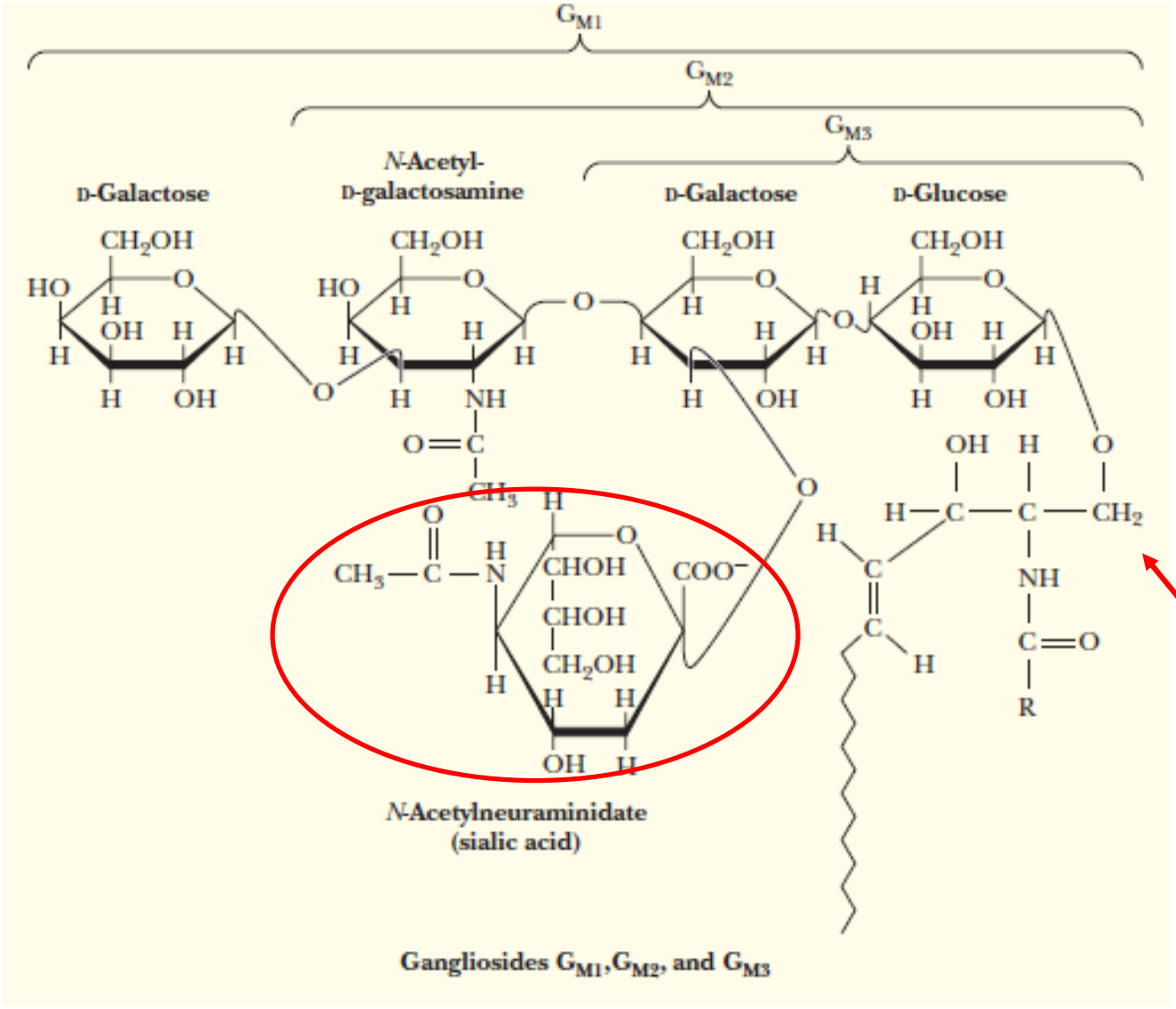
Ceramide + galactose= galactocerebroside

# Glycolipids-Gangliosides



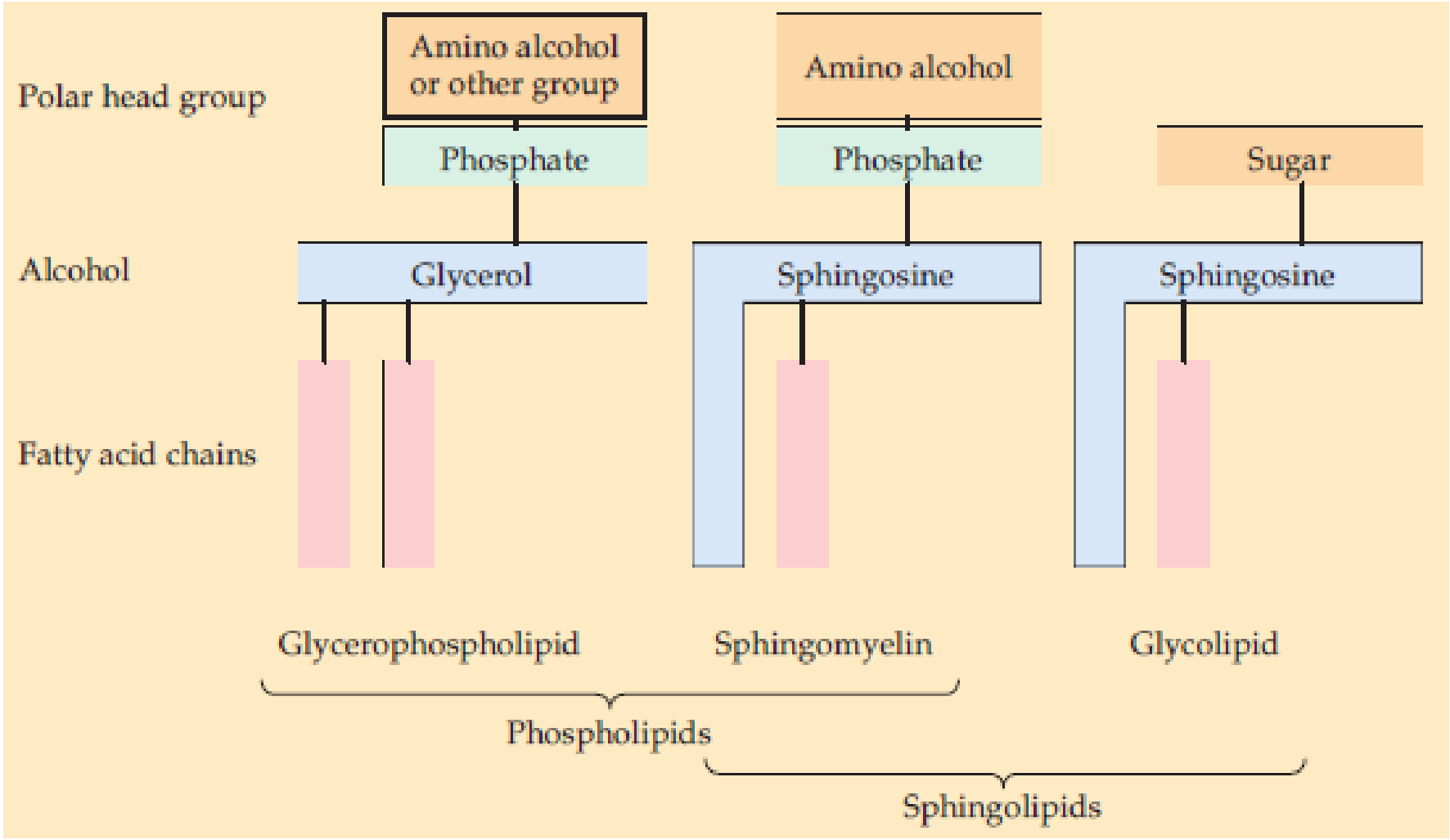

Gangliosides are present in large quantities in nerve tissues

# Glycolipids-Gangliosides



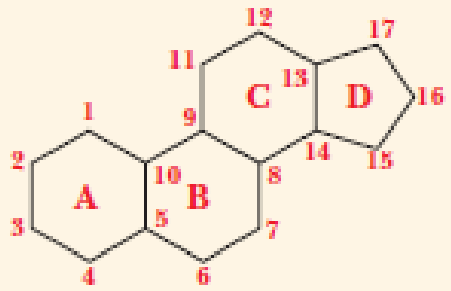

**Sphingosine**

# Membrane lipids

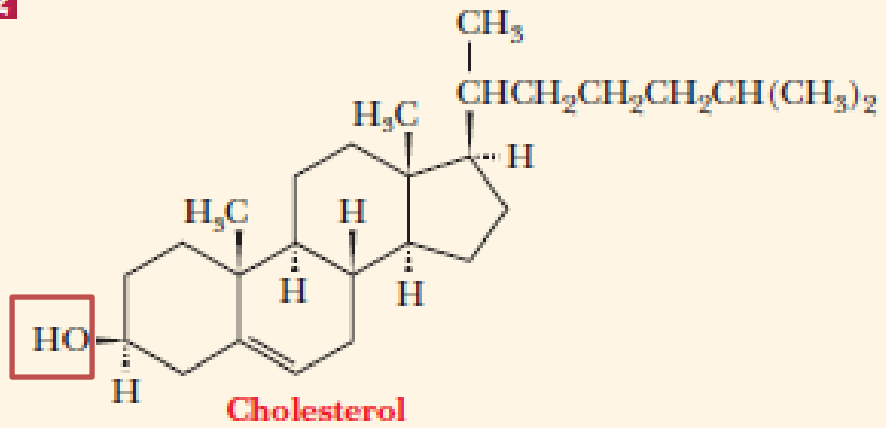


# Steroids

**1**

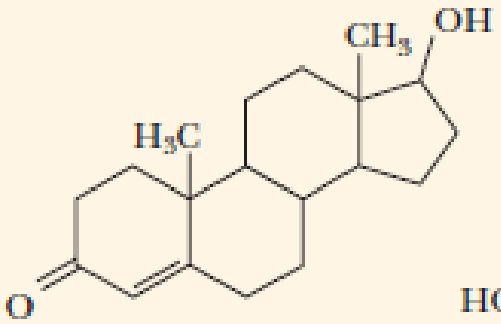



**2**

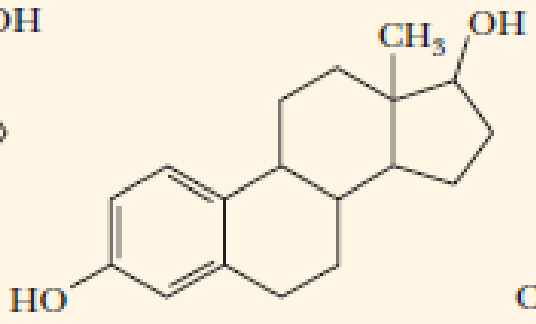



Cholesterol

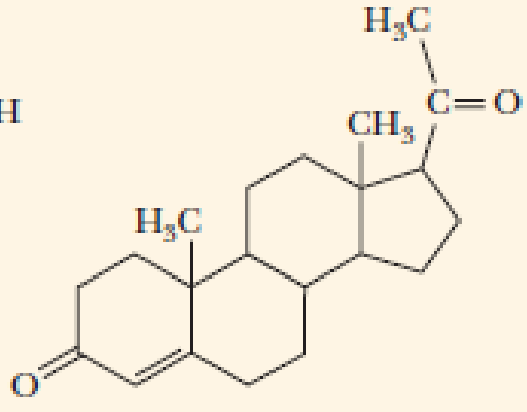
**3** **Sex hormones**




Testosterone




Estradiol

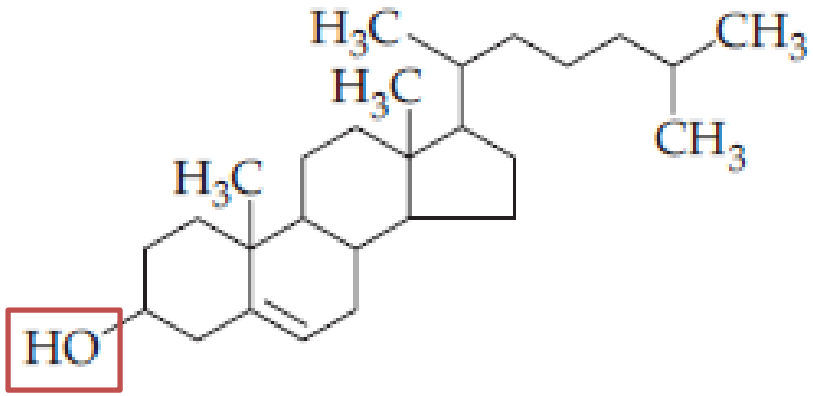



Progesterone

# Cell Membrane Lipids

## Cholesterol

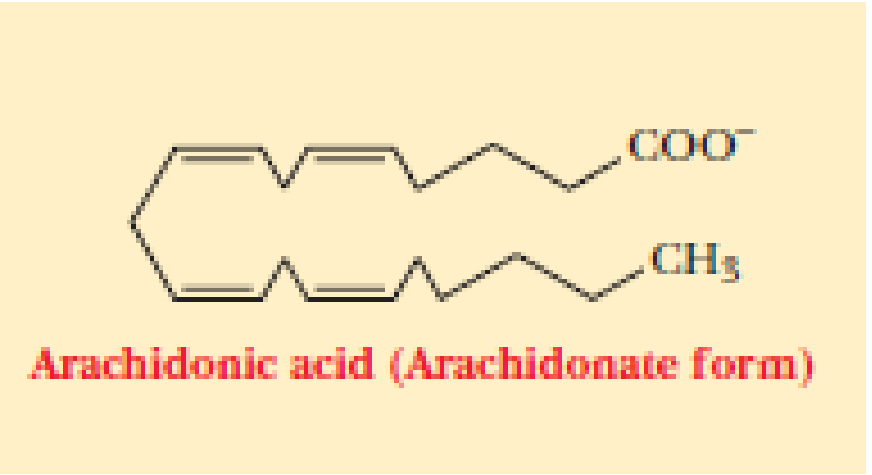
- A steroid
- 4 fused rings- flat shape
- Membrane fluidity
- A component of cell membranes
- A precursor of other steroids and of vitamin D3.




- Is modified in liver cells to produce bile acids, essential in the digestion of dietary fats.
- 800 mg/day
- Has a role in the development of atherosclerosis

# Eicosanoids: Prostaglandins and Leukotrienes

- Local hormones (paracrine)
- Arachidonic acid derivatives (20:4)

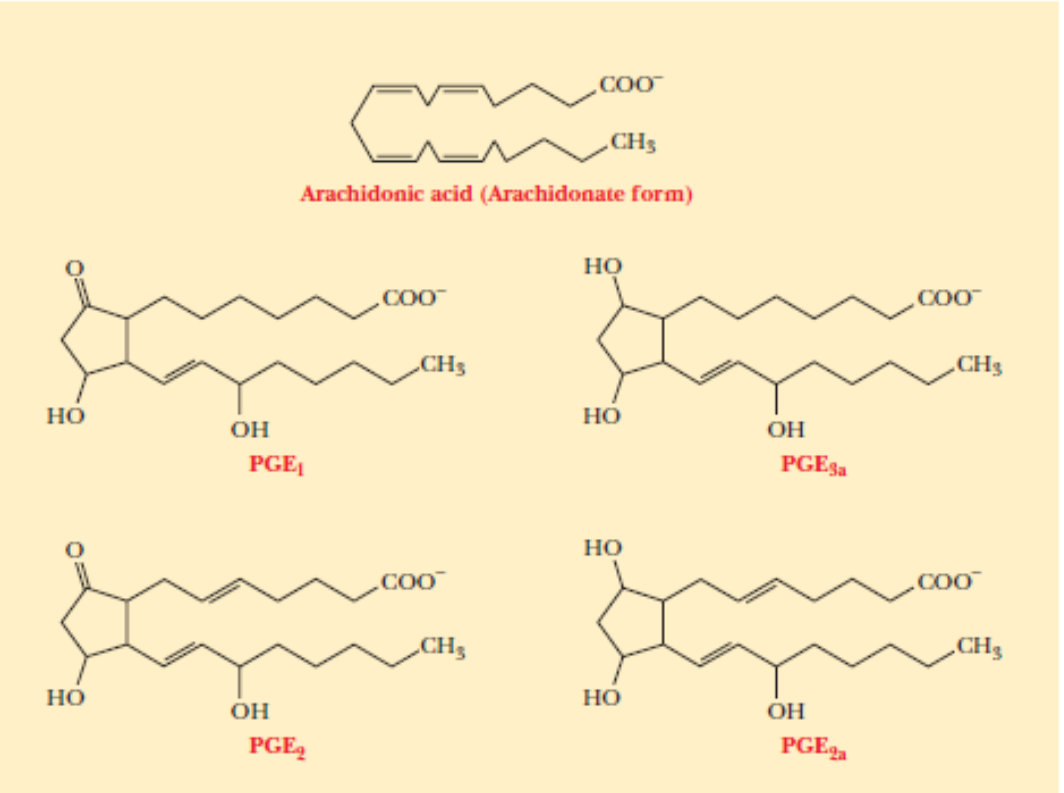


Arachidonic acid (Arachidonate form)

# Prostaglandins (PGs)

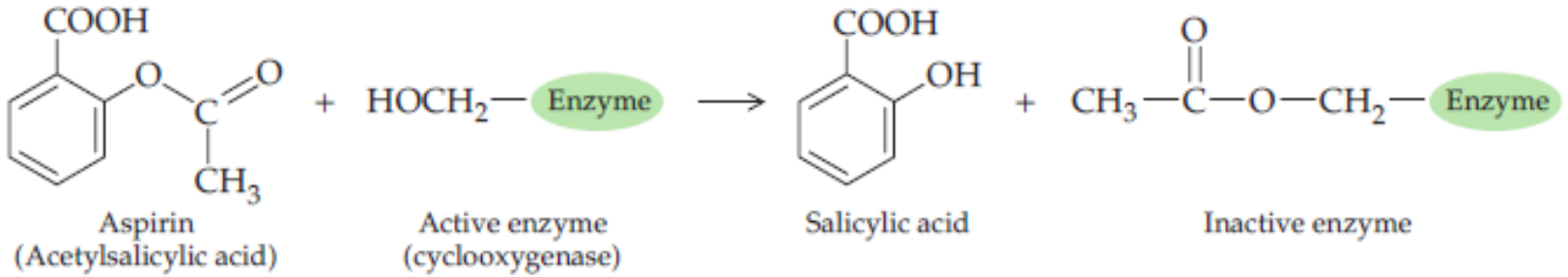
Different PGs differ in the numbers and positions of double bonds and oxygen-containing functional groups.

Functions: Control of blood pressure, stimulation of smooth-muscle contraction, induction of inflammation, and inhibit the aggregation of platelets.




Cortisone and other steroids also have anti-inflammatory effects because of their inhibition of PG synthesis.

# Clinical application




Aspirin inhibits PG synthesis, particularly in blood platelets, accounting for its anti-inflammatory and fever-reducing properties.

Non-steroidal anti-inflammatory drugs (NSAIDS) like aspirin and ibuprofen inhibit COX-1 and COX-2 resulting in PG synthesis inhibition and an anti-inflammatory effect.

Paracetamol (like Panadol) inhibit COX-3 (COX-3 does not activate inflammatory reactions) and only acts as an analgesic and antipyretic

# Leukotrienes (LK)

- Function: constriction of smooth muscle, especially in the lungs.
- In asthma, allergic reactions to pollens increase LK C synthesis resulting in airway constrictions.
- Drugs that inhibit the synthesis of leukotriene C or block its receptors are used in the treatment of asthma

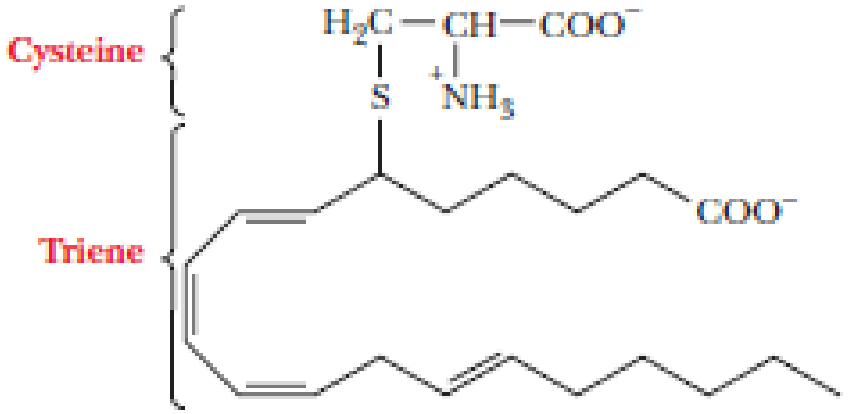



FIGURE 8.35 Leukotriene C.

# Thromboxanes

- Arachidonic acid derivatives.
- They contain cyclic ethers.
- Ex. thromboxane A2 (TxA2) induces platelet aggregation and smooth-muscle contraction.

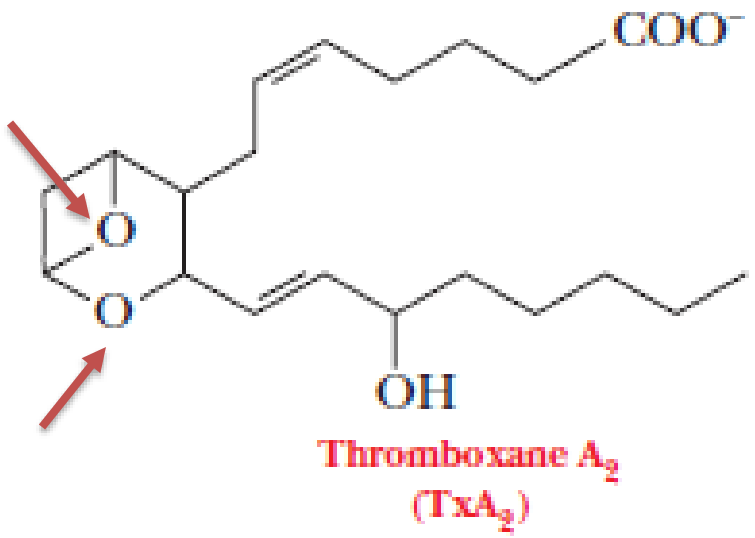
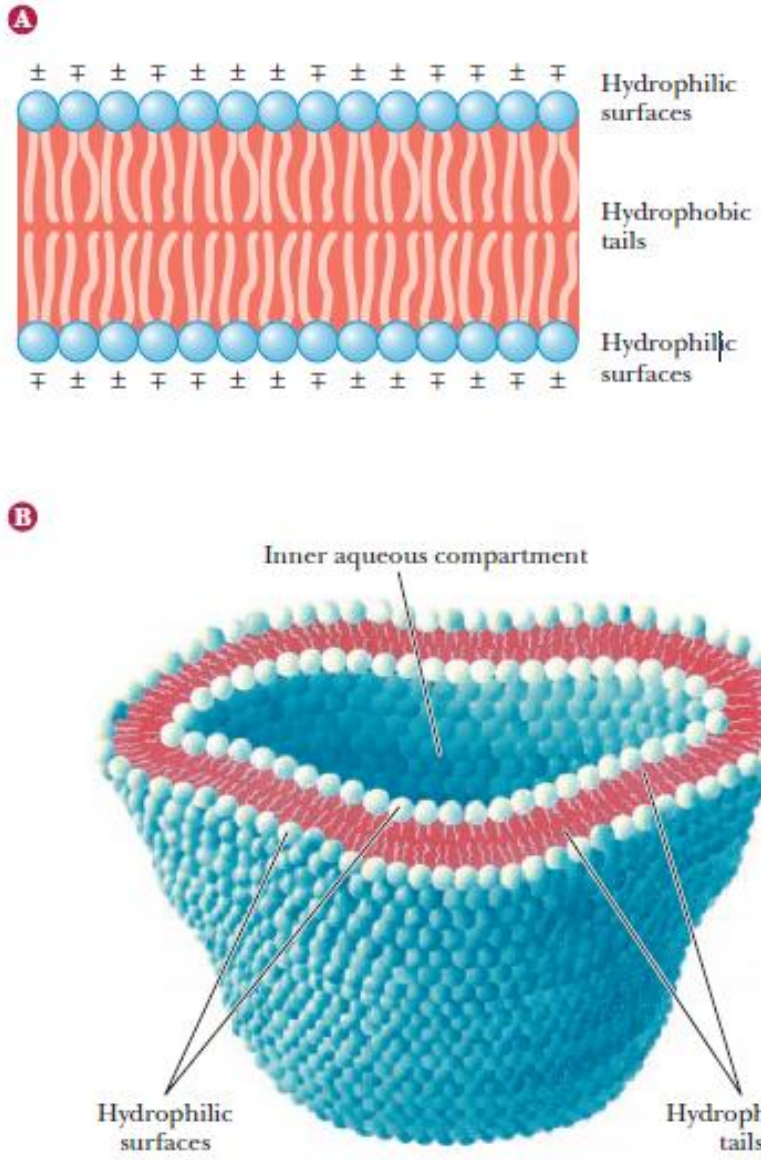



FIGURE 8.36 Thromboxane $A_2$.

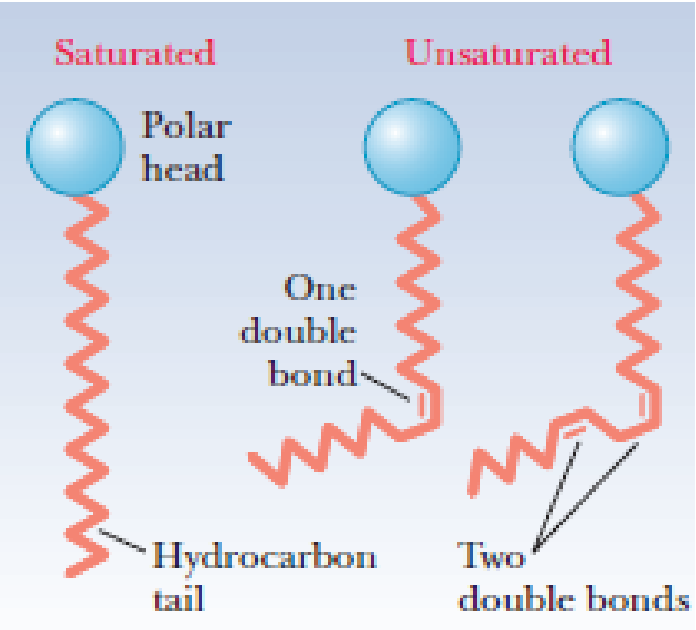
# The lipid bilayer

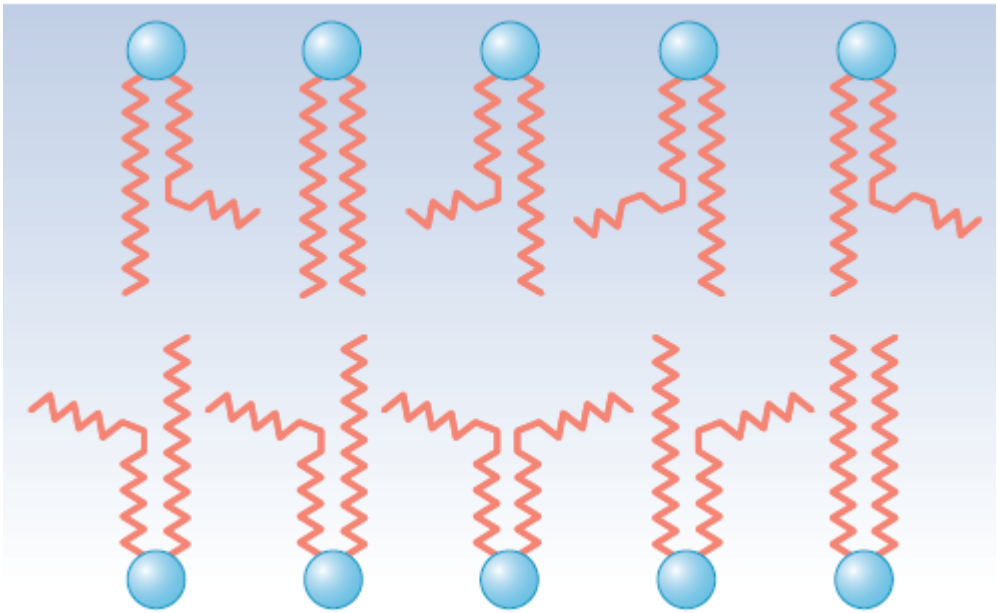
Bulkier molecules (e.g. cerebrosides) tend to occur in the outer layer, and smaller molecules tend to occur in the inner layer.

Because the bilayer is curved, the molecules of the inner layer are more tightly packed



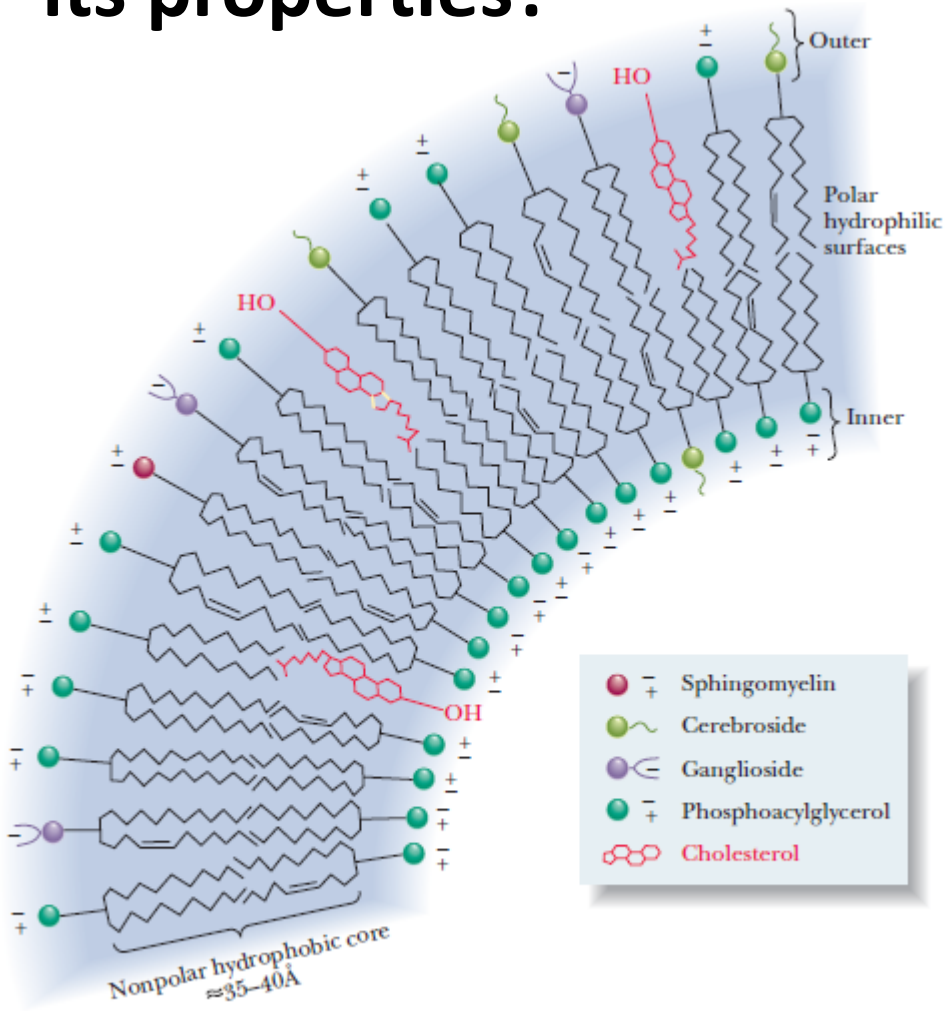
# Fatty acids and membrane fluidity



Highly fluid membrane

# How does the composition of the bilayer affect its properties?



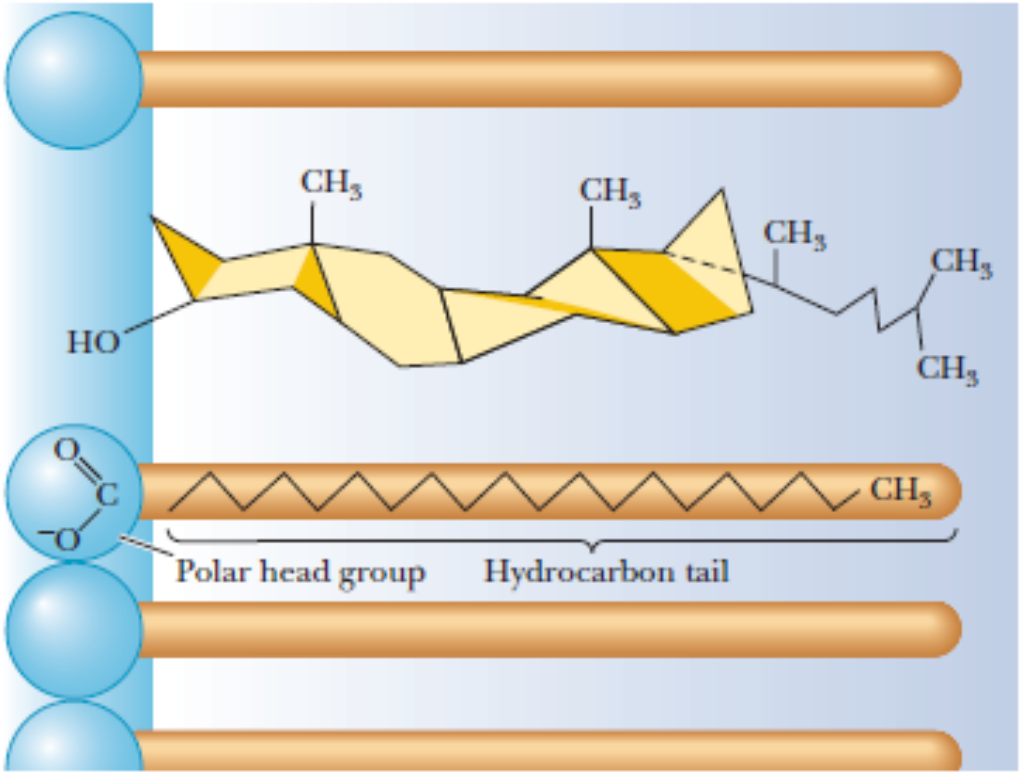

■ FIGURE 8.11 **Lipid bilayer asymmetry.** The compositions of the outer and inner layers differ; the concentration of bulky molecules is higher in the outer layer, which has more room.

-The bilayer's fluidity depends on its composition

-Saturated fatty acids, more packing and rigidity

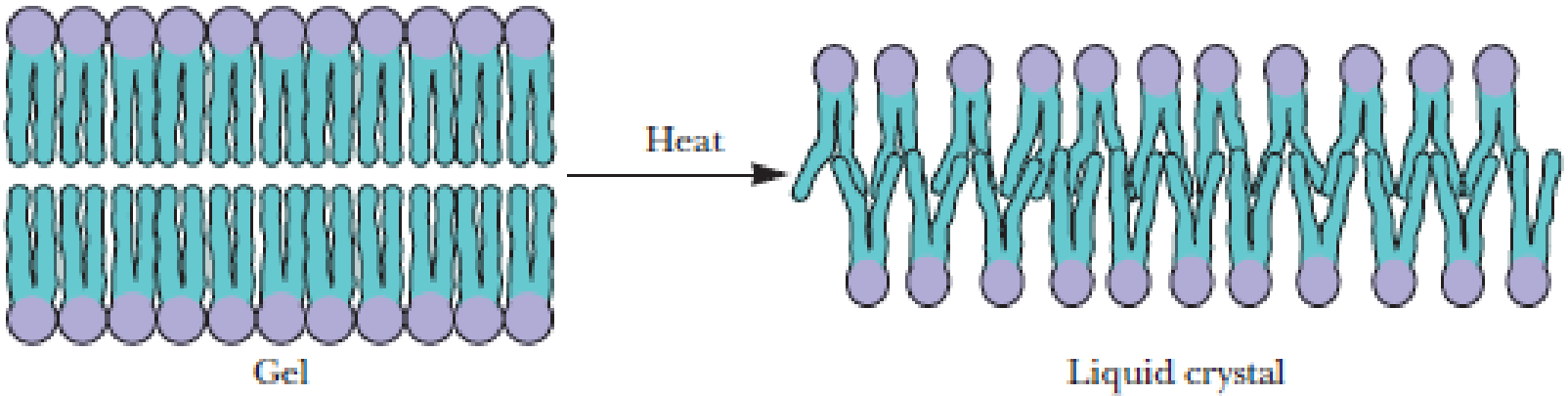
-The lipid bilayer components are always in motion (more movement in more fluid bilayers than rigid ones)

# The effect of cholesterol on membrane fluidity




■ **FIGURE 8.14 Stiffening of the lipid bilayer by cholesterol.** The presence of cholesterol in a membrane reduces fluidity by stabilizing extended chain conformations of the hydrocarbon tails of fatty acids, as a result of van der Waals interactions.

# Membrane gel-to-liquid crystalline phase transition



# Lipid molecule movement within membranes

- Occasional “flip-flop” migration of lipid molecules from one layer of the bilayer to another.

- Lateral motion of lipid molecules within one of the two layers frequently takes place especially in more fluid bilayers.

# Lipid-Soluble Vitamins

- Vitamin A, D, E and K
- Hydrophobic

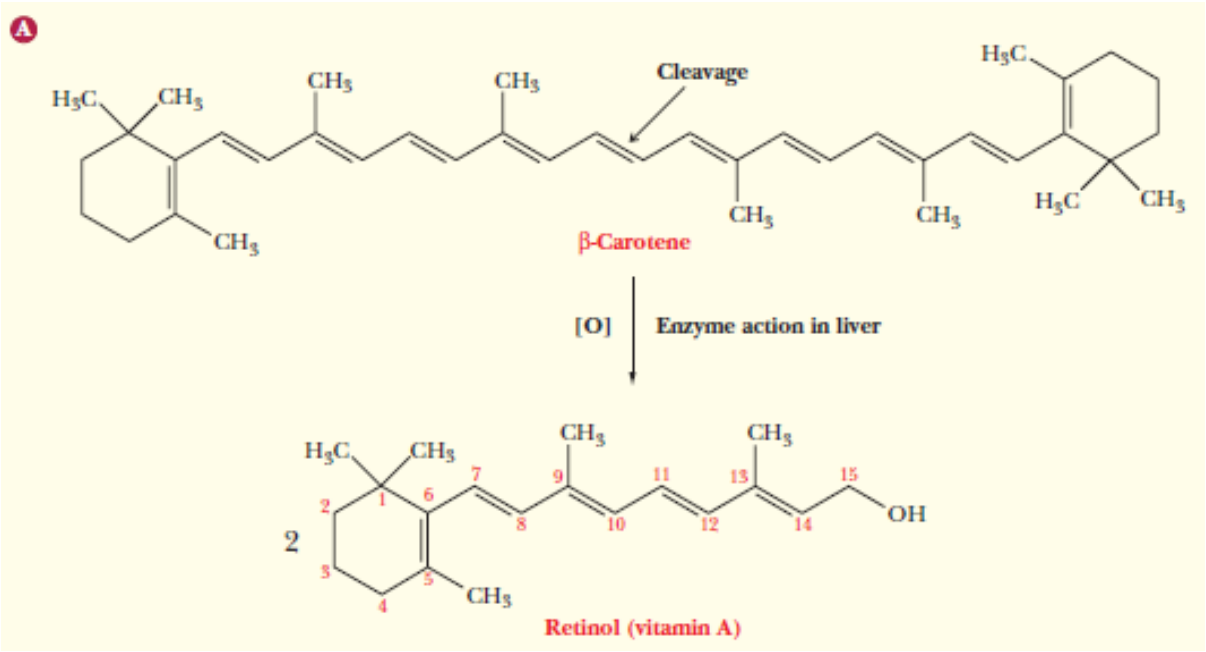
**Table 8.3**

**Lipid-Soluble Vitamins and Their Functions**

| Vitamin | Function |
|---|---|
| Vitamin A | Serves as the site of the primary photochemical reaction in vision |
| Vitamin D | Regulates calcium (and phosphorus) metabolism |
| Vitamin E | Serves as an antioxidant; necessary for reproduction in rats and may be necessary for reproduction in humans |
| Vitamin K | Has a regulatory function in blood clotting |

# Lipid-Soluble Vitamins
# Vitamin A or retinol

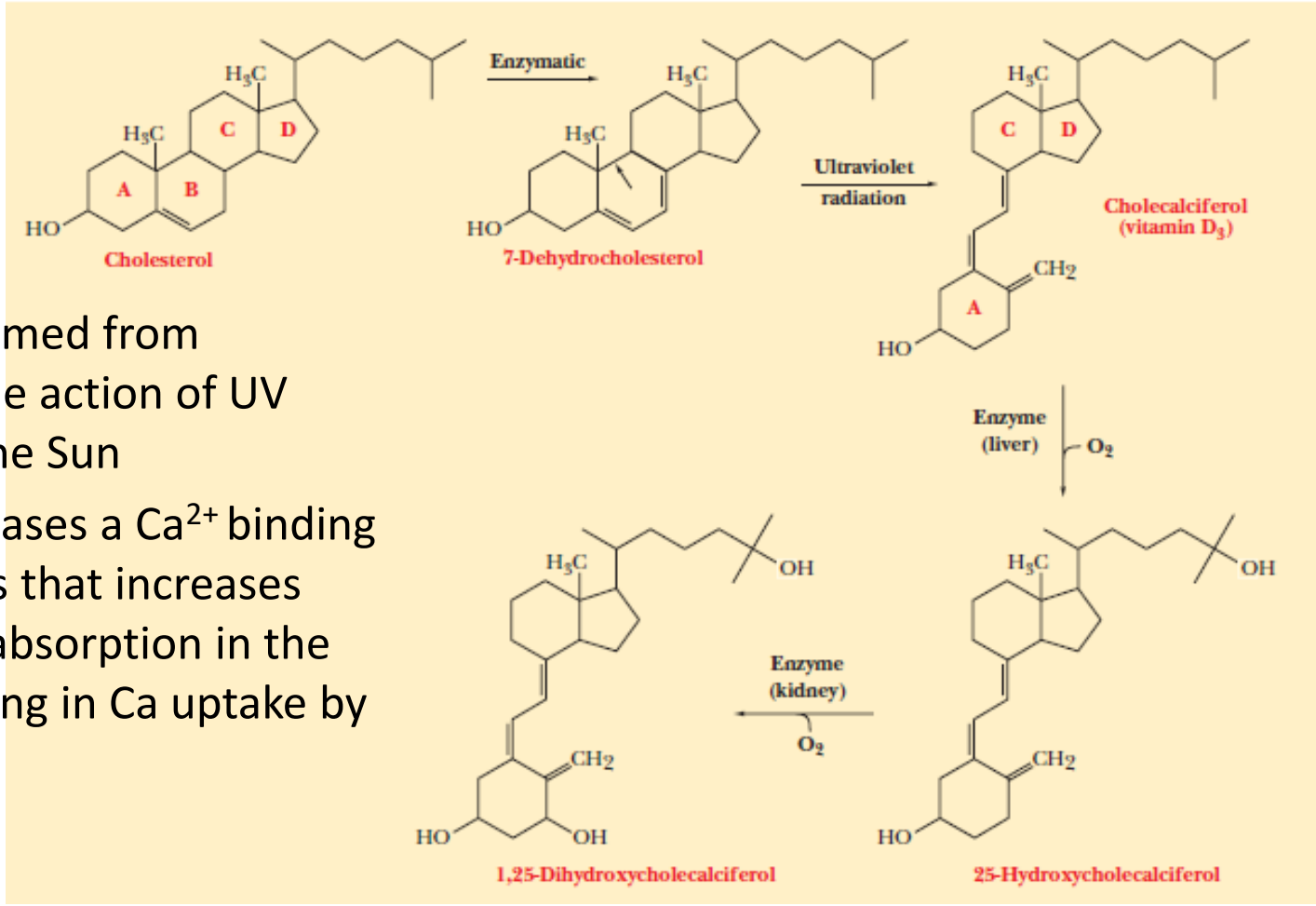
- **β-carotene** is the precursor of **vitamin A**
- **β-carotene is an** unsaturated hydrocarbon




- Vitamin A is oxidized to retinal that reacts with opsin to form rhodopsin

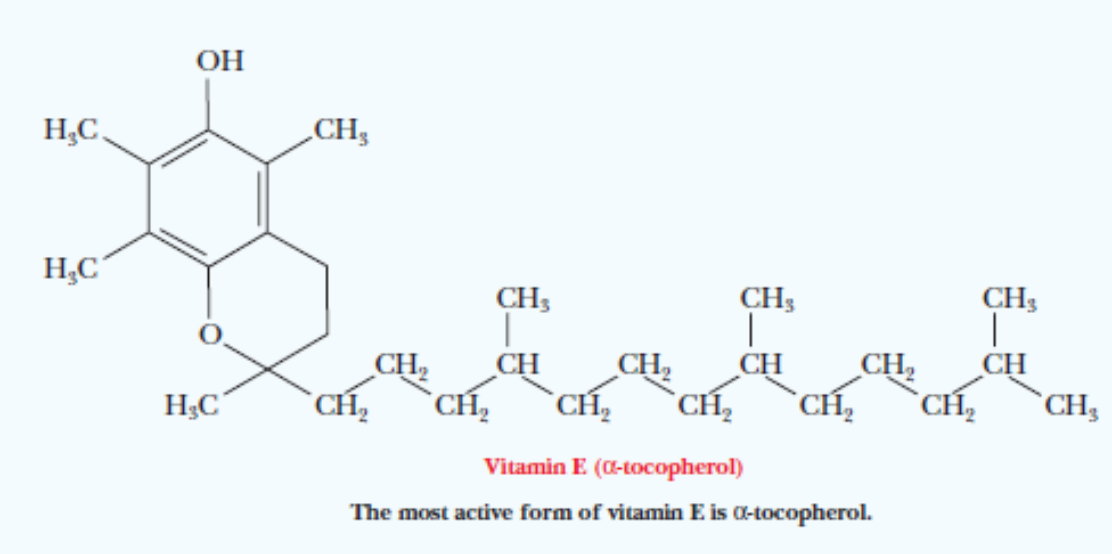
# Lipid-Soluble Vitamins
# Vitamin D

- Has several forms such as, vitamin D3 (cholecalciferol)




- Vitamin D3 is formed from cholesterol by the action of UV radiation from the Sun
- Vitamin D3 increases a $Ca^{2+}$ binding protein synthesis that increases dietary calcium absorption in the intestines resulting in Ca uptake by the bones.
- Rickets

# Lipid-Soluble Vitamins
# Vitamin E

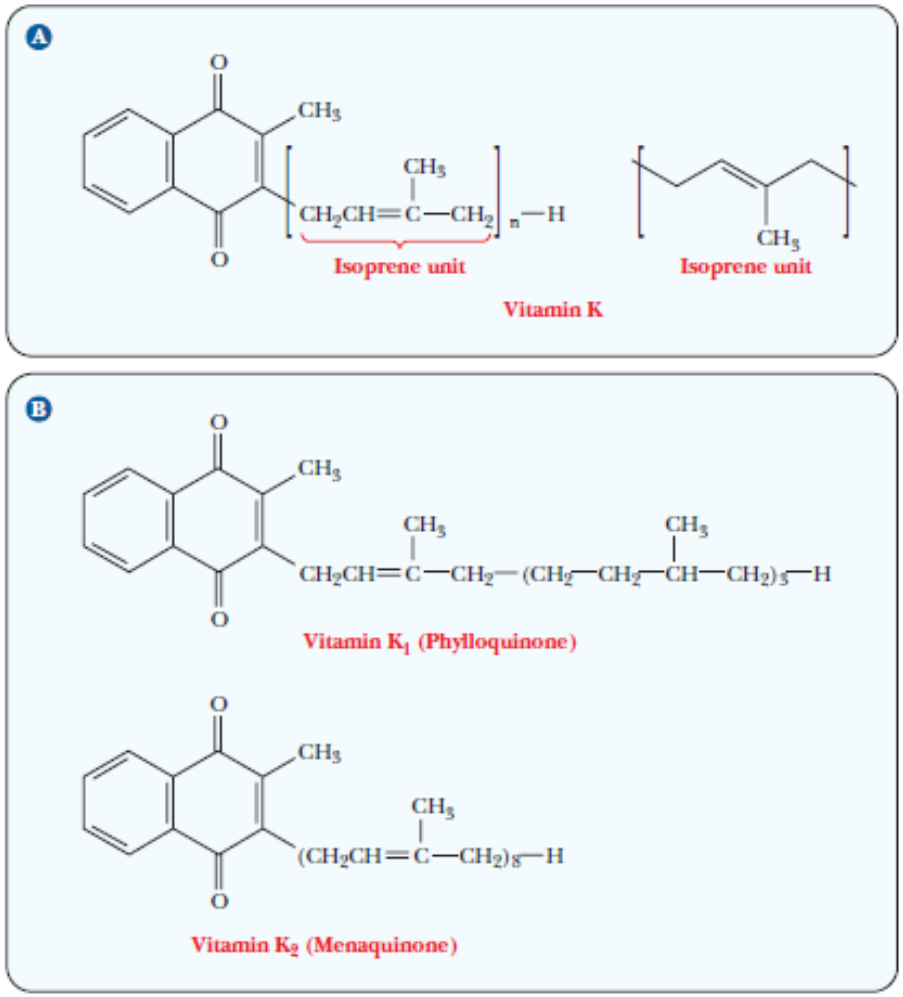



Vitamin E (α-tocopherol)

The most active form of vitamin E is α-tocopherol.

- The most active form of **vitamin E** is **α-tocopherol**
- An **antioxidant (**a good reducing agent) to protect important compounds, such as vitamin A, from degradation and to react with and remove **free radicals.**
- A free radical are very reactive because it has at least one unpaired electron
- Free radicals play a role in the development of cancer and in the aging process.

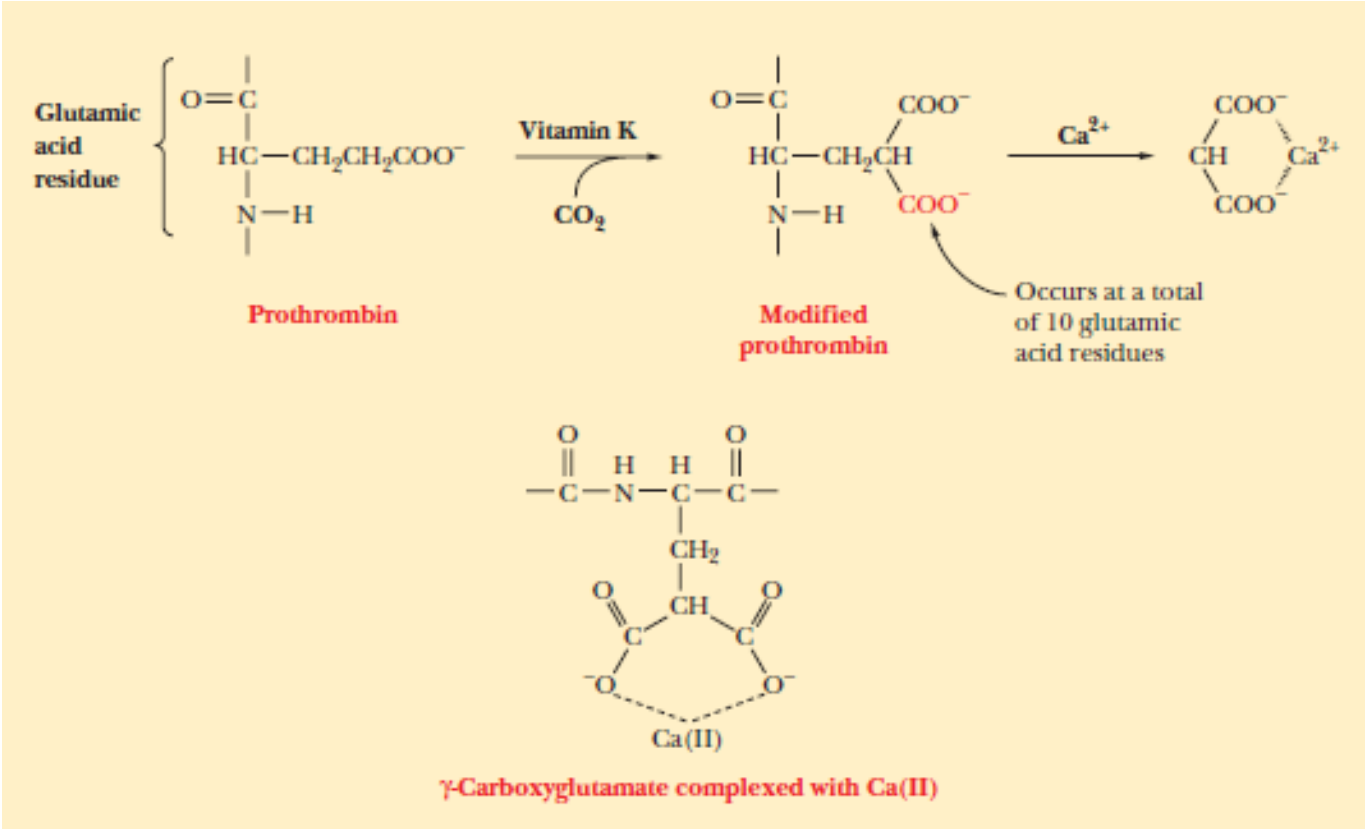
# Lipid-Soluble Vitamins
# Vitamin K




- From the Danish *Koagulation*
- A long unsaturated hydrocarbon side chain consists of repeating isoprene units
- The number of isoprene units determines the exact form of vitamin K.

# Vitamin K and coagulation

- The anticoagulants, dicumarol and warfarin (a rat poison), are vitamin K antagonists



# Plasmalogens

- Plasmalogens
  - Phospholipids with one ether bond
  - important in membranes of heart and brain
  - Signaling
  - Protective against reactive oxygen species