# Heterocyclic Organic Chemistry

## CHEM 341

**Credit hrs.: (2+0)**

*King Saud University*

College of Science, Chemistry Department

CHAPTER 7: Lipids

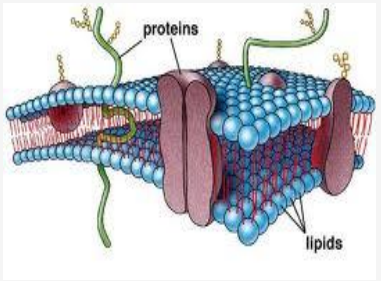
# Lipids

- Lipids are biological molecules that are insoluble in water but soluble in nonpolar solvents (nonpolar).
- The word lipid comes from the Greek lipos, which means "fat."
- Lipids are the waxy, greasy, or oily compounds found in plants and animals.

- wax coating that protects plants

- used as energy storage
- insulation against cold

- structural components (cell membranes)



# Classification of Lipids

## Lipids are divided into:

### Saponifiable (Hydrolyzable) lipids

- They contain esters,
- They can undergo saponification (*hydrolysis under basic conditions*)

**Simple lipids**

contain two components (*fatty acid and an alcohol*)

- **Triglycerides (Fats & oils)**
- **Waxes**

**Complex lipids**

contain more than two components (*fatty acids, an alcohol, and other components*)

- **phosphoglycerides**
- **Sphingolipids.**

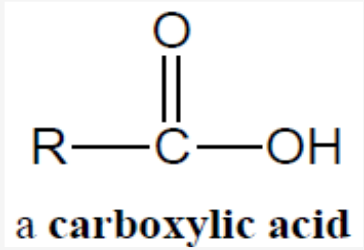
### Nonsaponifiable (Nonhydrolyzable) lipids

- They do not contain ester groups,
- They cannot be saponified (*cannot be cleaved into smaller molecules by aqueous hydrolysis*)

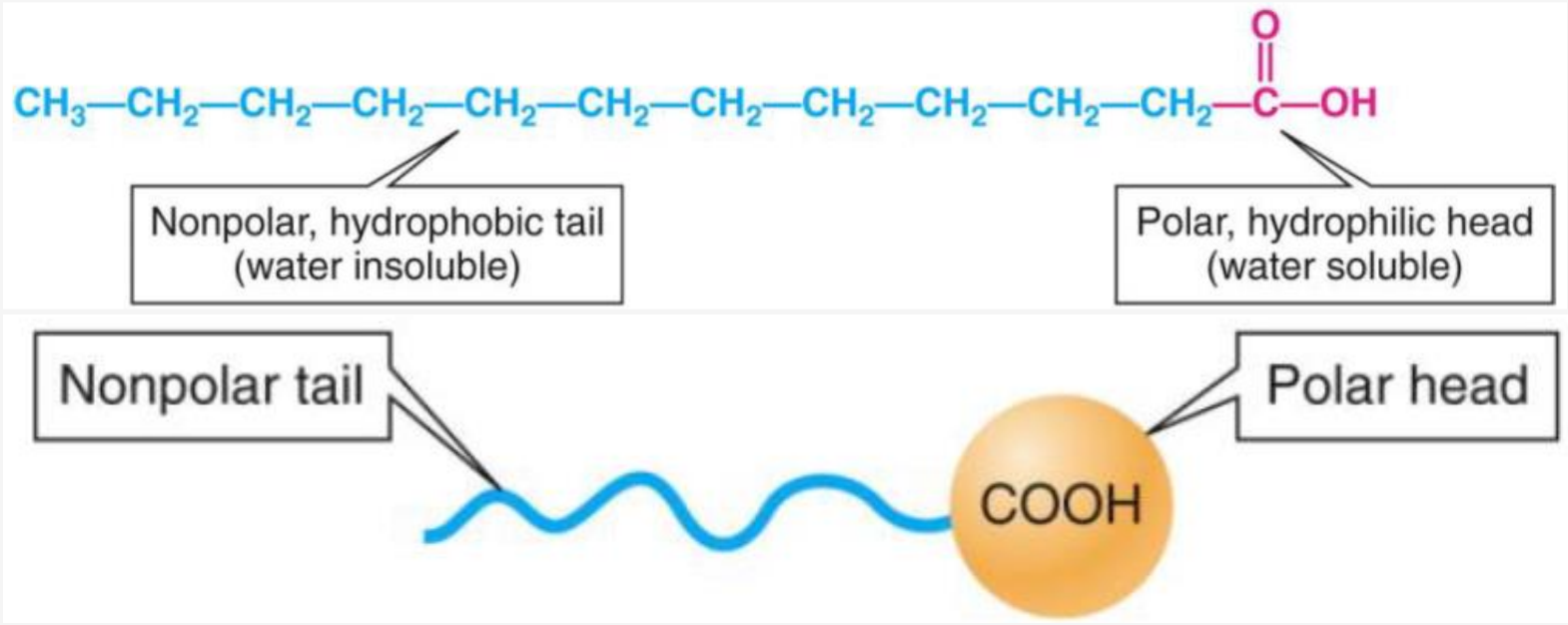
- **steroids**
- **prostaglandins**

# Fatty Acids

- **Fatty acids** are long-chain unbranched carbon attached to a carboxyl group (-COOH).



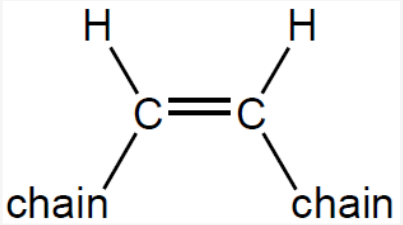
a carboxylic acid



# Fatty Acids

## Characteristics of Fatty Acids:

- They are usually have straight chains (no branches) that are about 10 to 20 carbon atoms in length.
- They usually have an even number of carbon atoms (counting the carboxyl carbon).
- **The carbon chains may be**;
  - **saturated** (all single bonds) or
  - **unsaturated** (containing double bonds).
- i.e. **Functional groups** are only the *carboxyl group* and the *double bonds*.
- The double bonds are usually in *cis* configurations:



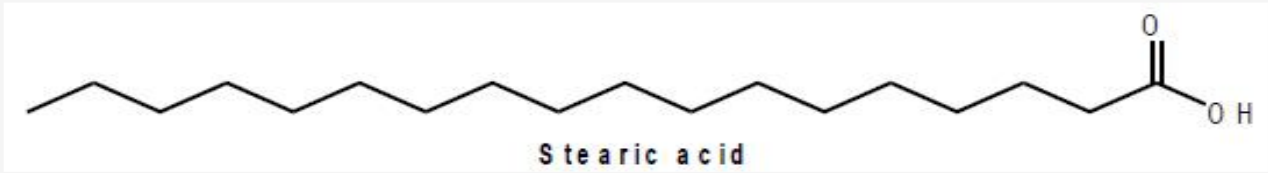
# Fatty Acids

## Saturated and Unsaturated Fatty Acids

- **Saturated fatty acids** have no double bonds in their long hydrocarbon chains.

**Stearic acid:** $CH_3(CH_2)_{16}COOH$

Stearic Acid
(m.p. 71°C)




They are solids at room temperature.

**Stearic acid** is found in palm oil, which is frequently used in handmade soap.

# Fatty Acids

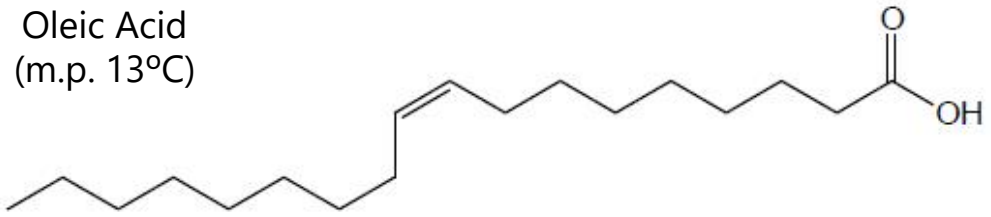
## Saturated and Unsaturated Fatty Acids

- **Unsaturated fatty acids** have 1 or more double bonds (generally *cis*) in their long hydrocarbon chains.
  - **Oleic acid** (*one double bond*), and
  - **Linoleic acid** (*two double bonds*)
  - All have 18 carbons in the chain, but their melting points are different

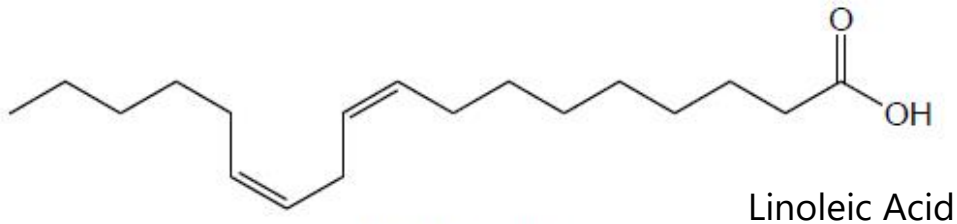
- Oleic acid is derived mainly from "olive" oil. sesame oil, Sunflower, shea butter, coconut oil, … etc.

- Linoleic acid is found in soybean oil

Oleic Acid
(m.p. 13°C)




Oleic acid



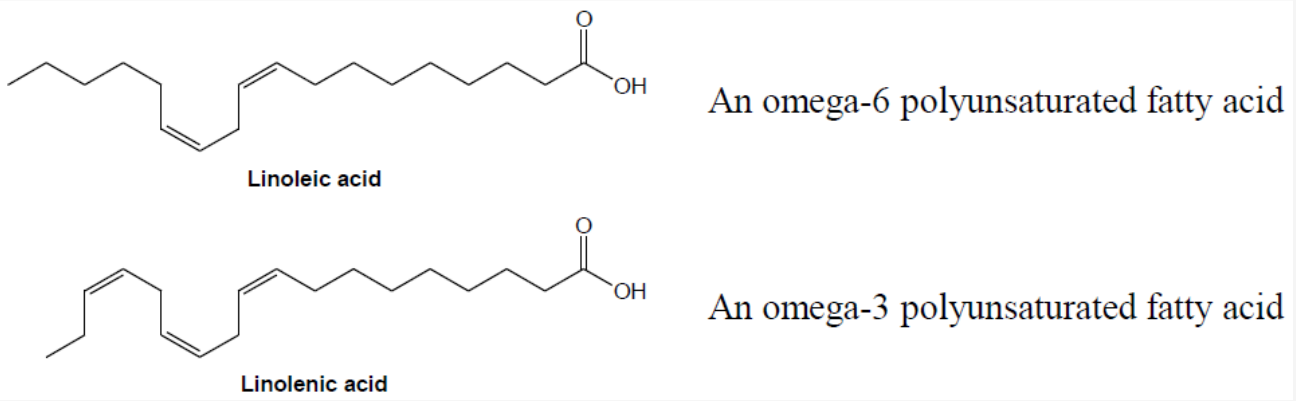

Linoleic acid

Linoleic Acid
(m.p. -5°C)

# Fatty Acids

## Essential Fatty Acids

- Most of the fatty acids we need can be synthesized in the body.
- Two fatty acids, *linoleic acid* and *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.
- Both are found in plant and fish oils.
- In the body, they are used to produce hormone-like substances that regulate blood pressure, blood clotting, blood lipid levels, the immune response, and inflammatory reactions.



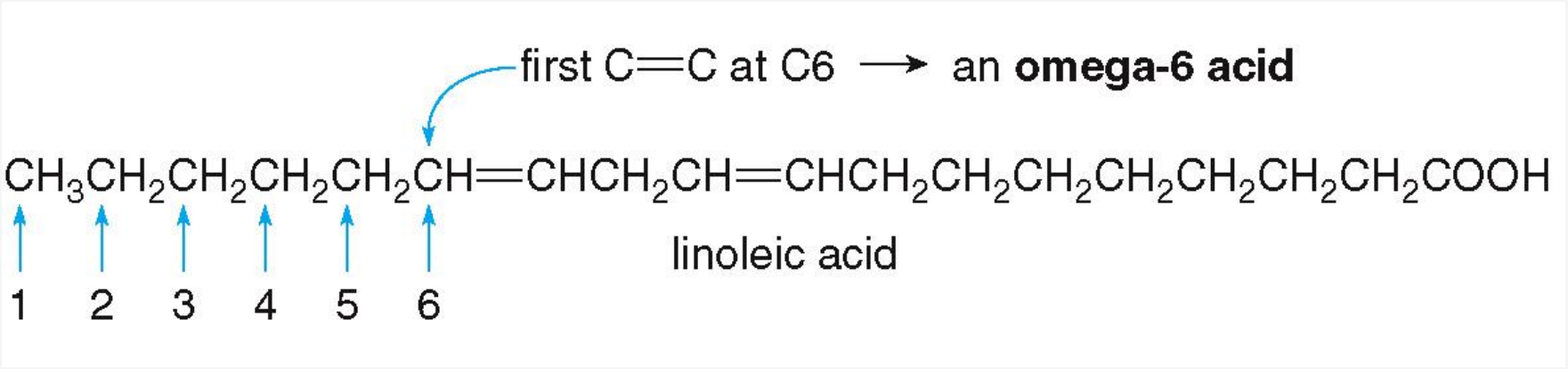
# Fatty Acids

## Essential Fatty Acids

- All fatty acids that bear the "omega" label are unsaturated, containing one or more double bonds.

Omega-n acids  n: the position of the first double bond

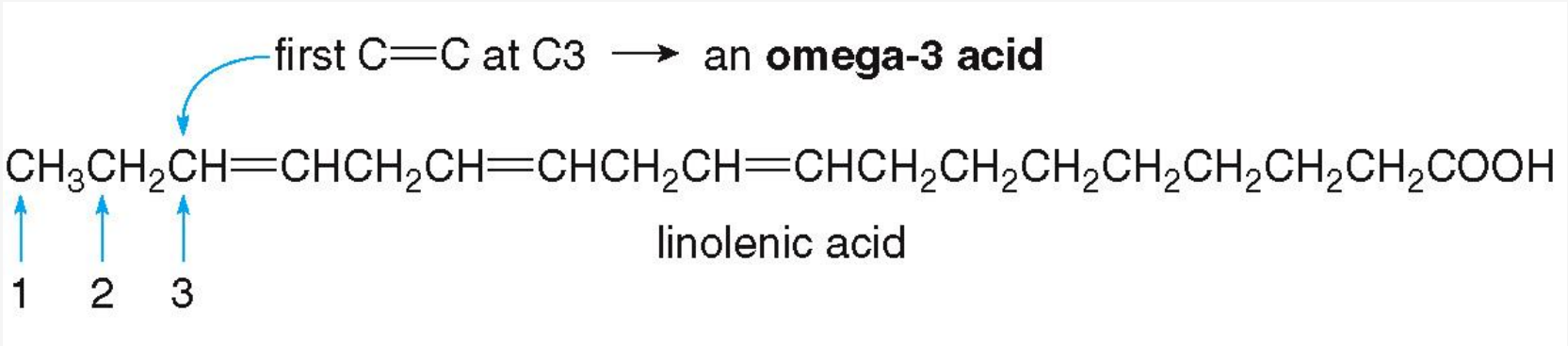
Linoleic acid is called an omega-6 acid, because of the position of the first C=C in the nonpolar chain.




# Fatty Acids

## Essential Fatty Acids

Linolenic acid is called an omega-3 acid, because of the position of the first C=C in the nonpolar chain.





# Fatty Acids

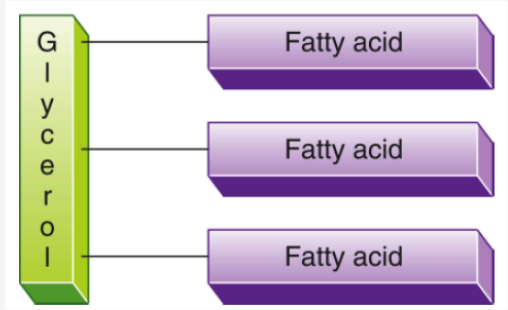
## Some Important Fatty Acids

| #C's | Name | Formula | MP | Common Sources |
|---|---|---|---|---|
| **Saturated** | | | | |
| 14 | Myristic acid | $CH_3(CH_2)_{12}COOH$ | 54°C | Butterfat, coconut oil, nutmeg oil |
| 16 | Palmitic acid | $CH_3(CH_2)_{14}COOH$ | 63°C | Lard, beef fat, butterfat, cottonseed oil |
| 18 | Stearic acid | $CH_3(CH_2)_{16}COOH$ | 70°C | Lard, beef fat, butterfat, cottonseed oil |
| 20 | Arachidic acid | $CH_3(CH_2)_{18}COOH$ | 76°C | Peanut oil |
| **Monounsaturated** | | | | |
| 16 | Palmitoleic acid | $CH_3(CH_2)_5CH{=}CH(CH_2)_7COOH$ | -1°C | Cod liver oil, butterfat |
| 18 | Oleic acid | $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$ | 13°C | Lard, beef fat, olive oil, peanut oil |
| **Polyunsaturated** | | | | |
| 18 | Linoleic acid | $CH_3(CH_2)_4(CH{=}CHCH_2)_2(CH_2)_6COOH$ | -5°C | Cottonseed oil, soybean oil, corn oil, linseed oil |
| 18 | Linolenic acid | $CH_3CH_2(CH{=}CHCH_2)_3(CH_2)_6COOH$ | -11°C | Linseed oil, corn oil |
| 20 | Arachidonic acid | $CH_3(CH_2)_4(CH{=}CHCH_2)_4(CH_2)_2COOH$ | -50°C | Corn oil, linseed oil, animal tissues |
| 20 | Eicosapentaenoic acid | $CH_3CH_2(CH{=}CHCH_2)_5(CH_2)_2COOH$ | | Fish oil, seafoods |
| 22 | Docosahexaenoic acid | $CH_3CH_2(CH{=}CHCH_2)_6CH_2COOH$ | | Fish oil, seafoods |

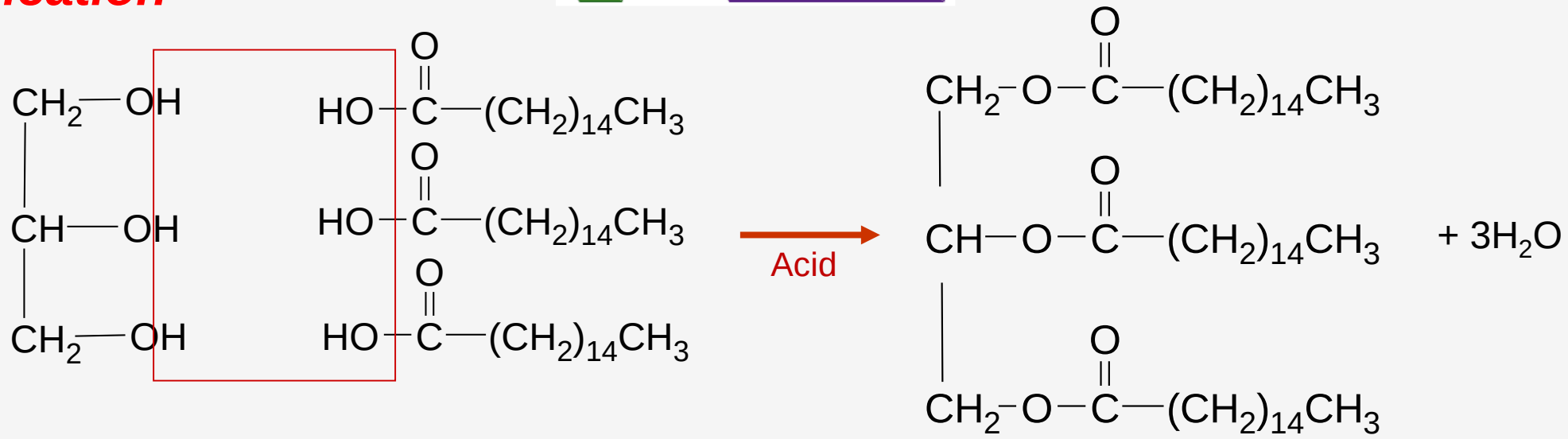
# Triglycerides



- 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*:



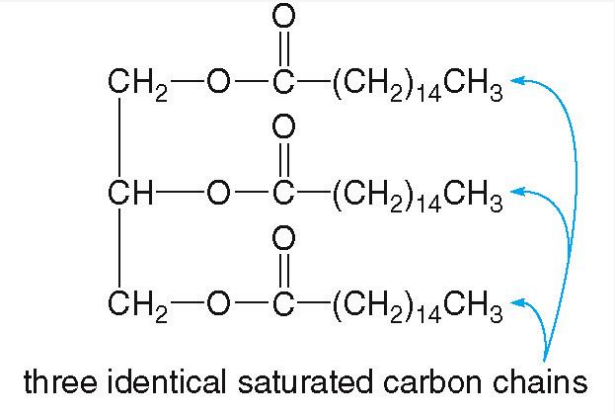

## *Esterification*



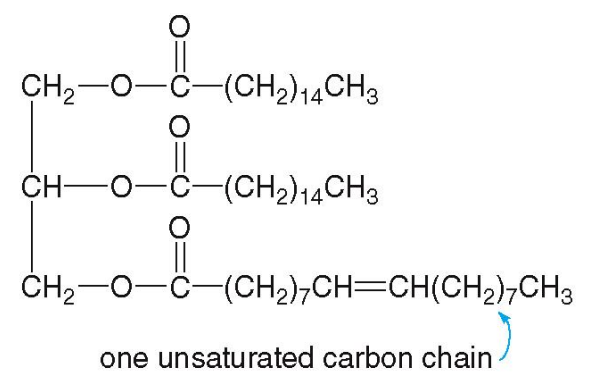
# Triglycerides

## Simple lipids

- Simple triacylglycerols have three identical fatty acid side chains.



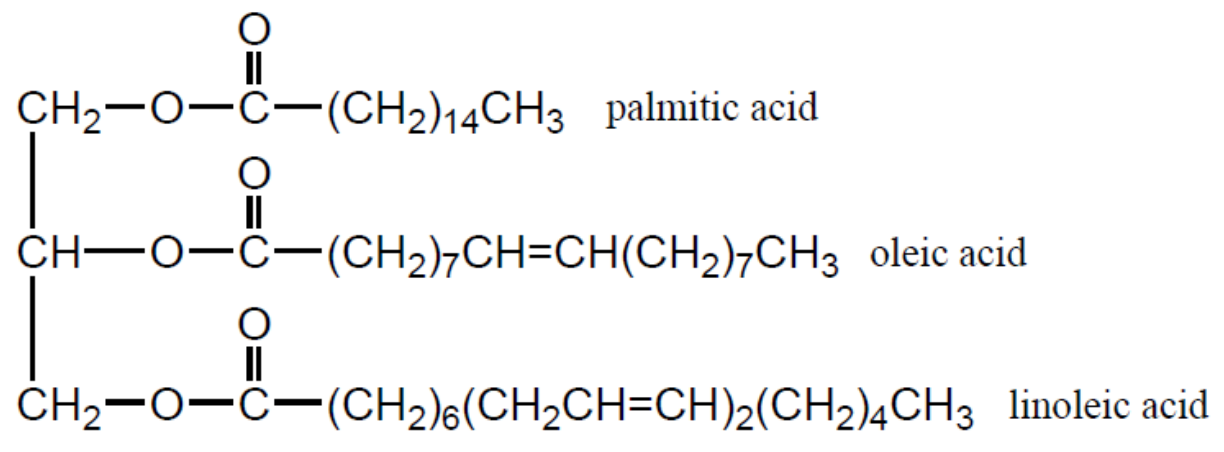

- Mixed triacylglycerols have two or three different fatty acids.



# Fats & oils

# Simple lipids

- The fatty acids in a triglyceride molecule are usually not all the same;
- Natural triglycerides are often mixtures of different triglyceride molecules.




## Fats are

- triglycerides that are solids at room temp.
- usually derived from animals
- mostly saturated fatty acids

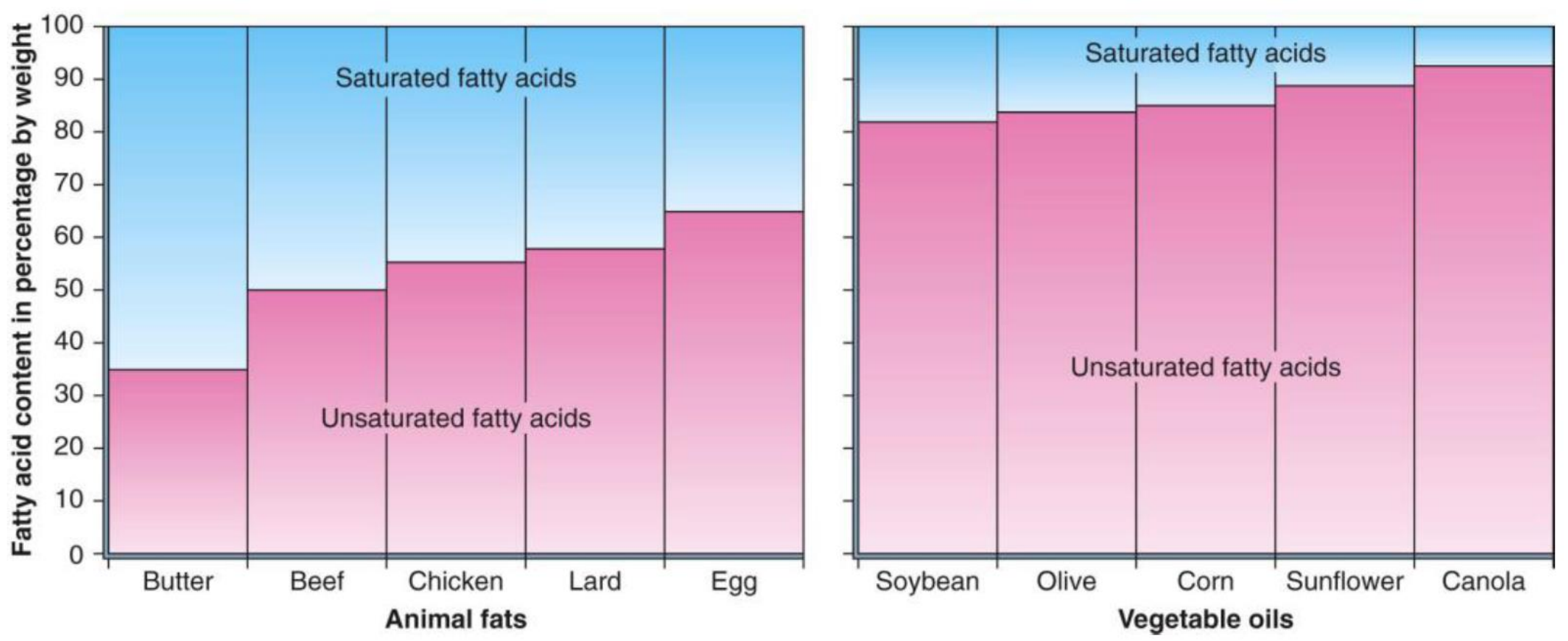

## Oils are

- triglycerides that are liquids at room temp.
- usually derived from plants or fish
- mostly unsaturated fatty acids

# Fats & oils

## Simple lipids

**A comparison of saturated and unsaturated fatty acids in some foods.**



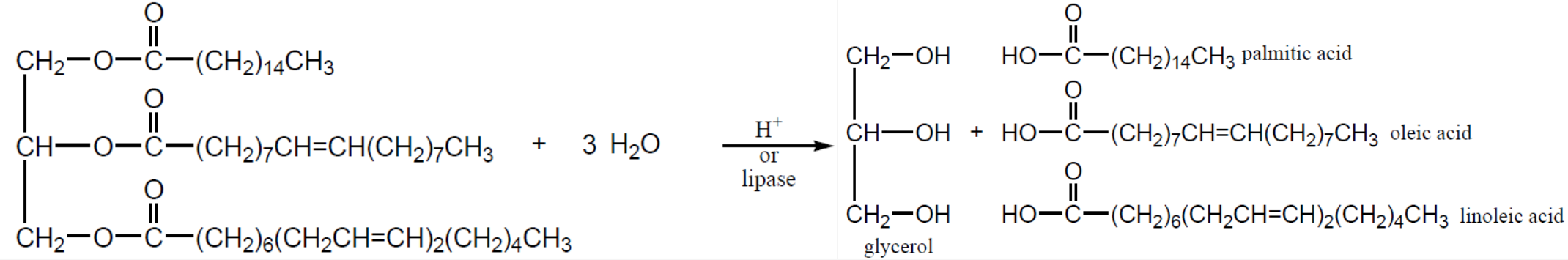
# Fats & oils

# Simple lipids

## Chemical Properties of Fats and Oils

### Hydrolysis of Triglycerides

Triglycerides can be broken apart with water and an acid catalyst (*hydrolysis*), or by digestive enzymes called lipases:



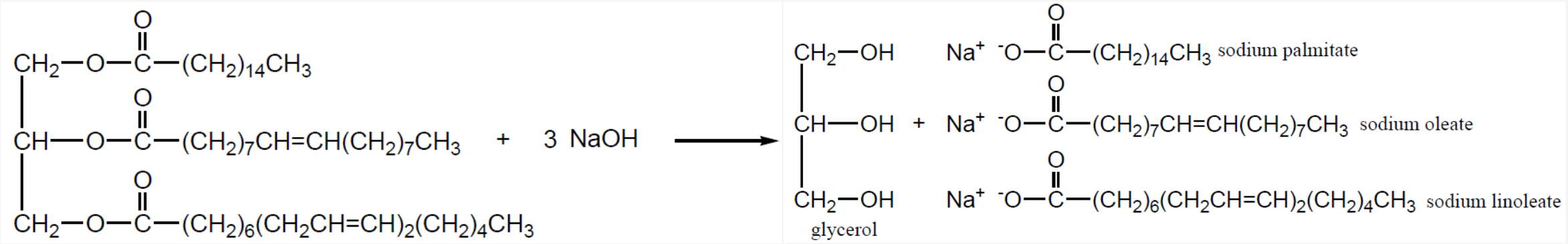
# Fats & oils

# Simple lipids

## Chemical Properties of Fats and Oils

### *Saponification of Triglycerides (Basic Hydrolysis)*

Triglycerides react with strong bases (NaOH or KOH) to form the carboxylate salts of the fatty acids, called soaps:



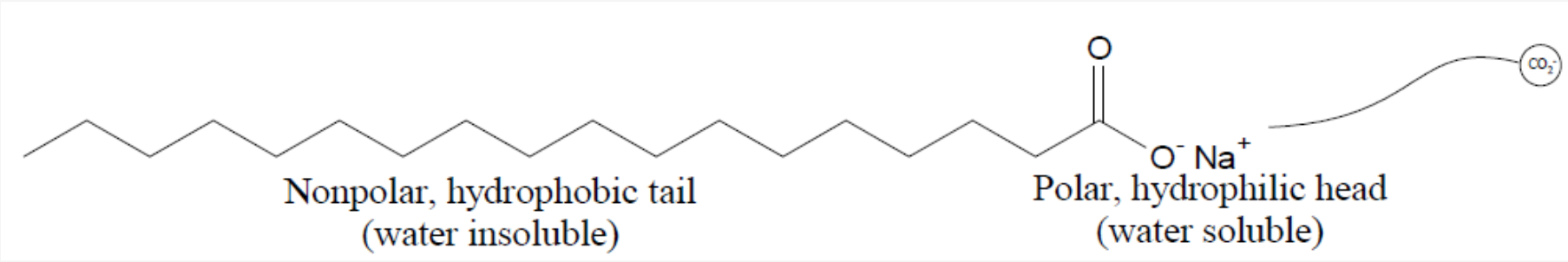
# Fats & oils

**Simple lipids**

## Chemical Properties of Fats and Oils

### *Soaps*

- NaOH produces a "hard" soap, commonly found in bar soaps;
- KOH produces a "soft" soap, such as those in shaving creams and liquid soaps.
- These salts combine two solubility characteristics:
  - a long, nonpolar, water-insoluble (*hydrophobic*) hydrocarbon "tail."
  - a charged, water-soluble (*hydrophilic*) "head."



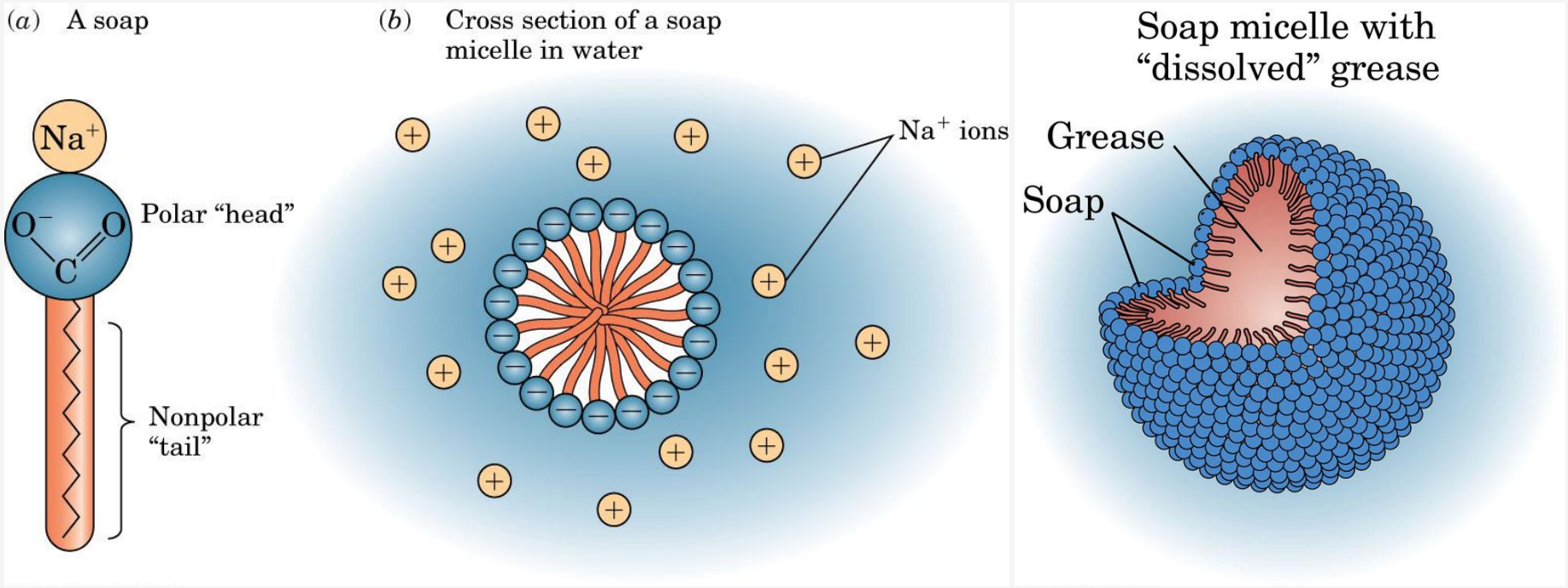
# Fats & oils

# Simple lipids

## Chemical Properties of Fats and Oils

### *Soaps*

In water, the "tails" become tangled, leaving the charged heads sticking out into the solution, forming a structure called a **micelle**.



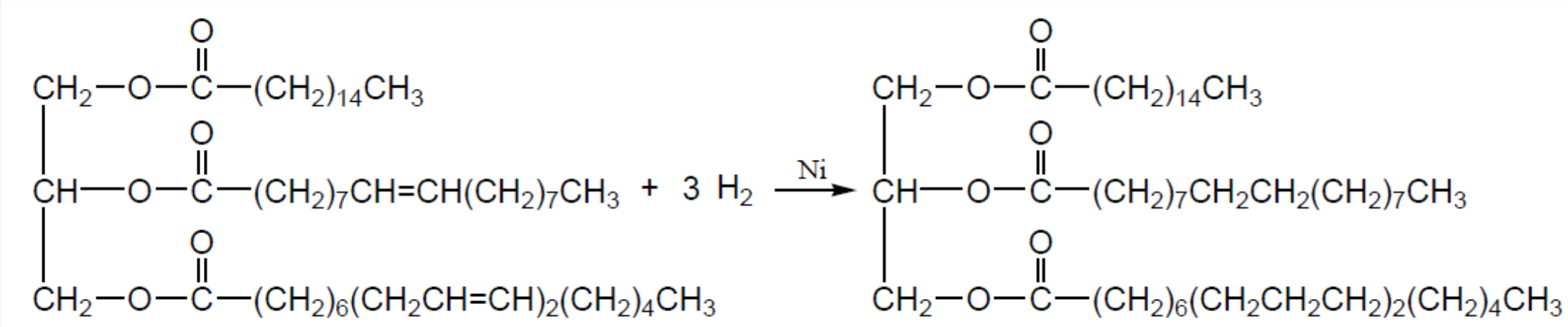
# Fats & oils

# Simple lipids

## Chemical Properties of Fats and Oils

### Hydrogenation

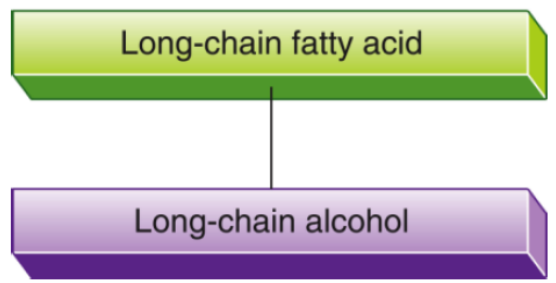
- Alkenes are converted into alkanes with hydrogen gas ($H_2$) and a catalyst (Pt, Ni, or some other metal).
- This process is used to convert unsaturated vegetable oils, which are liquids at room temp., to saturated fats, which are solids at room temp.

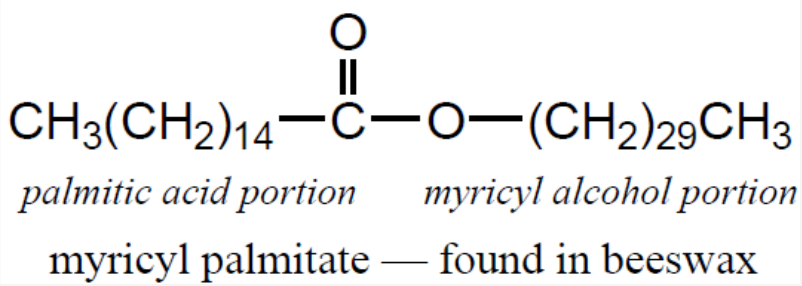


# Waxes

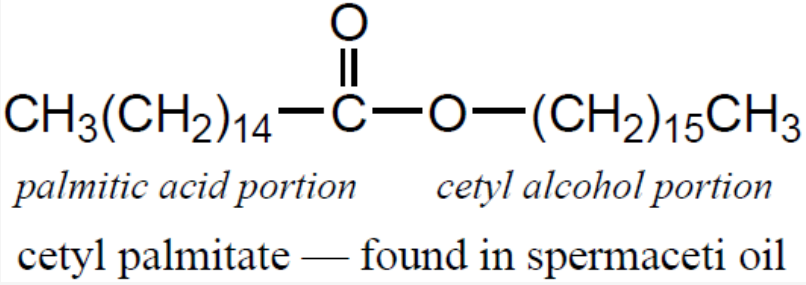


**Waxes** *are simple lipids contain a fatty acid joined to a long-chain (12-32 carbons) alcohol*:



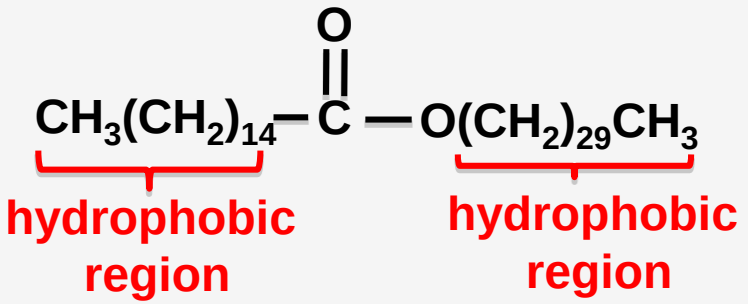

myricyl palmitate — found in beeswax




cetyl palmitate — found in spermaceti oil

Because of their long nonpolar C chains, waxes are very hydrophobic.

Beeswax
(myricyl palmitate)



# Waxes

## Simple lipids

- Waxes are insoluble in water, and not as easily hydrolyzed as fats and oils.
- Waxes often occur in nature as protective coatings on feathers, fur, skin, leaves, and fruits.
- Waxes are used commercially to make cosmetics, candles, ointments, and protective polishes.

Beeswax

Lanolin from wool →

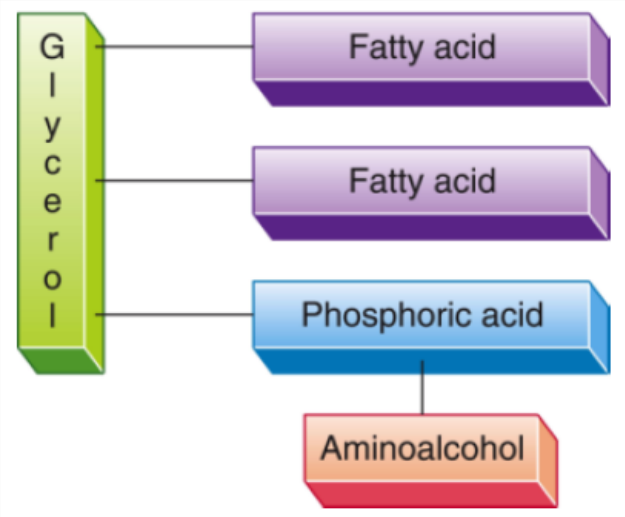

lotions

# Phospholipids

# Complex lipids

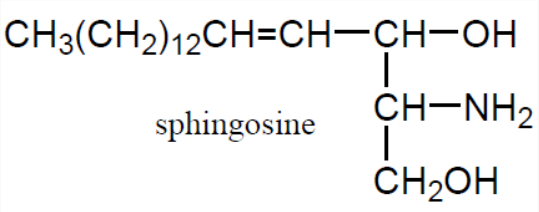
- Phospholipids are lipids that contain a P atom.
- There are two common types:

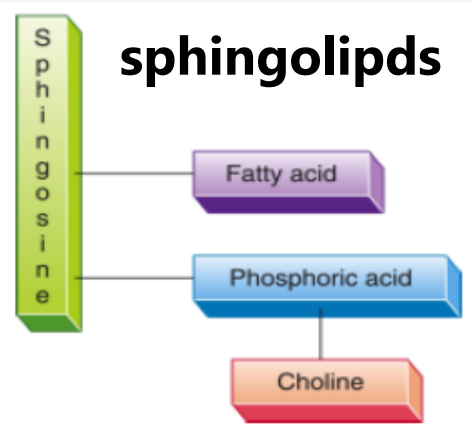
## Phosphoglycerol




## Sphingolipids

Sphingolipids are complex lipids that contain sphingosine instead of glycerol.



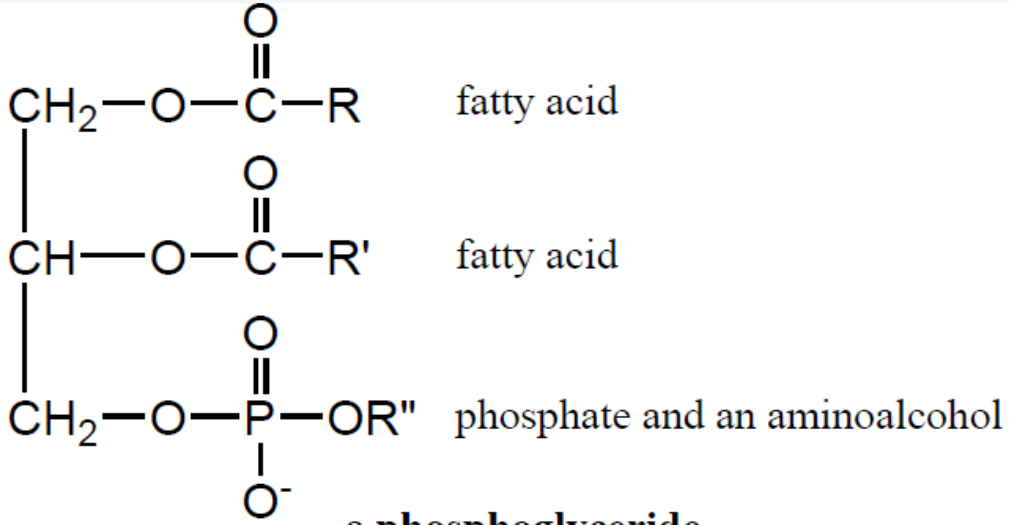



# Phospholipids

# Complex lipids

## Phosphoglycerols

- Phosphoglycerols are complex lipids that are *major components of cell membranes*.
- Structurally, they resemble a triacylglycerol, except the third fatty acid has been replaced with a phosphodiester bonded to an alcohol.



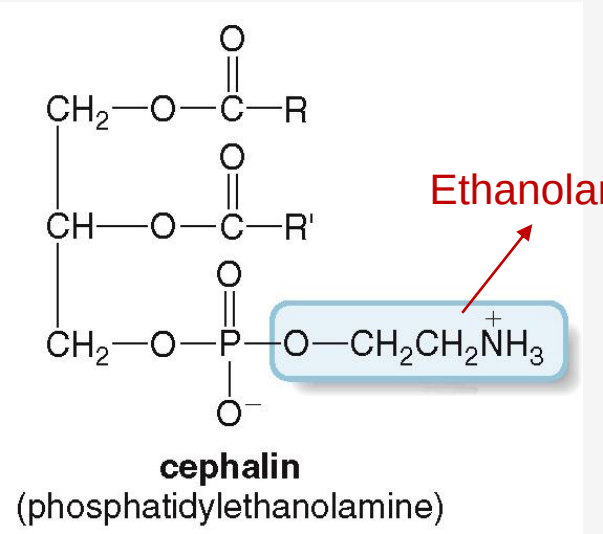

a **phosphoglyceride**

# Phospholipids

# Complex lipids

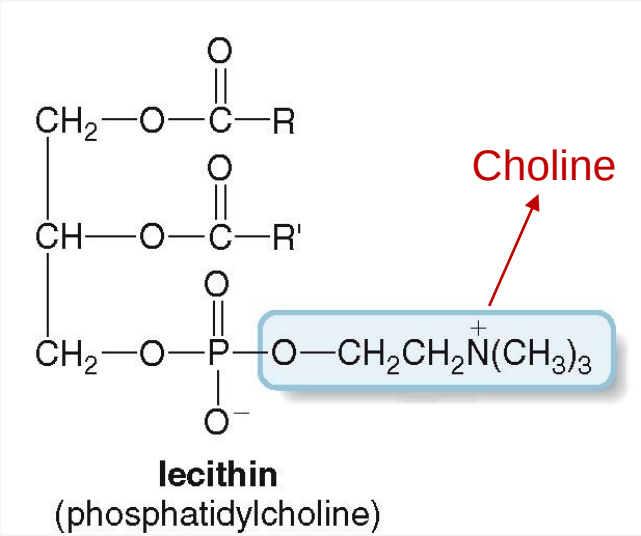
## Phosphoglycerols

- There are two types of phosphoglycerols;




**cephalin**
(phosphatidylethanolamine)

- **Cephalins** are found in most cell membranes,
- They are particularly abundant in brain tissue.
- They are also found in blood platelets, and play a role in blood clotting.




**lecithin**
(phosphatidylcholine)

**Lecithin** can act as an emulsifying agent:

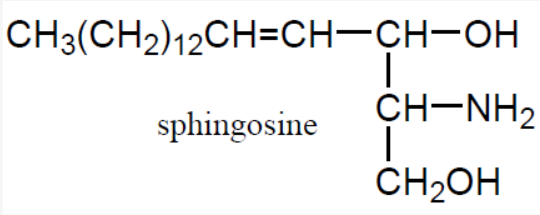
- important structural component of cell membranes.
- play a role in the transport of lipids in the blood stream.
- Commercially, lecithin extracted from soybeans is used as an emulsifying agent in margarine and candies to provide a smooth texture.

# Phospholipids

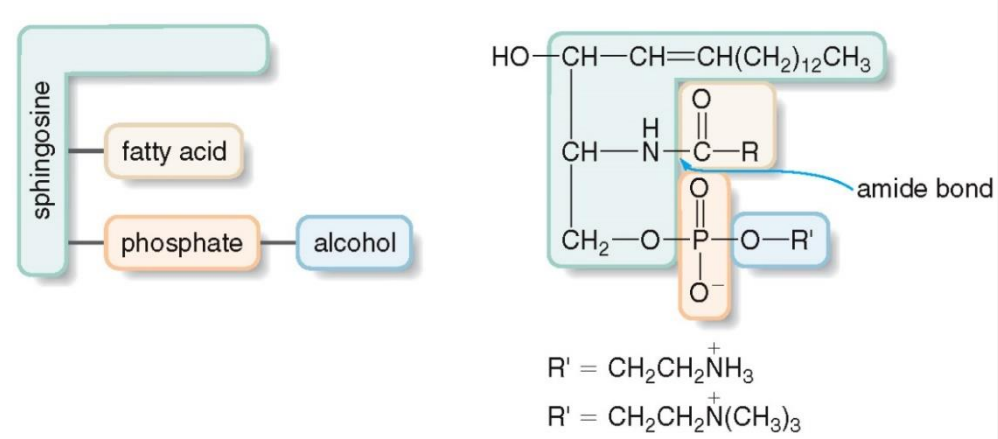
# Complex lipids

## Sphingomyelins

They do not contain a glycerol backbone, they have a sphingosine backbone instead.




They do not contain an ester; their single fatty acid is bonded to the backbone by an amide bond.



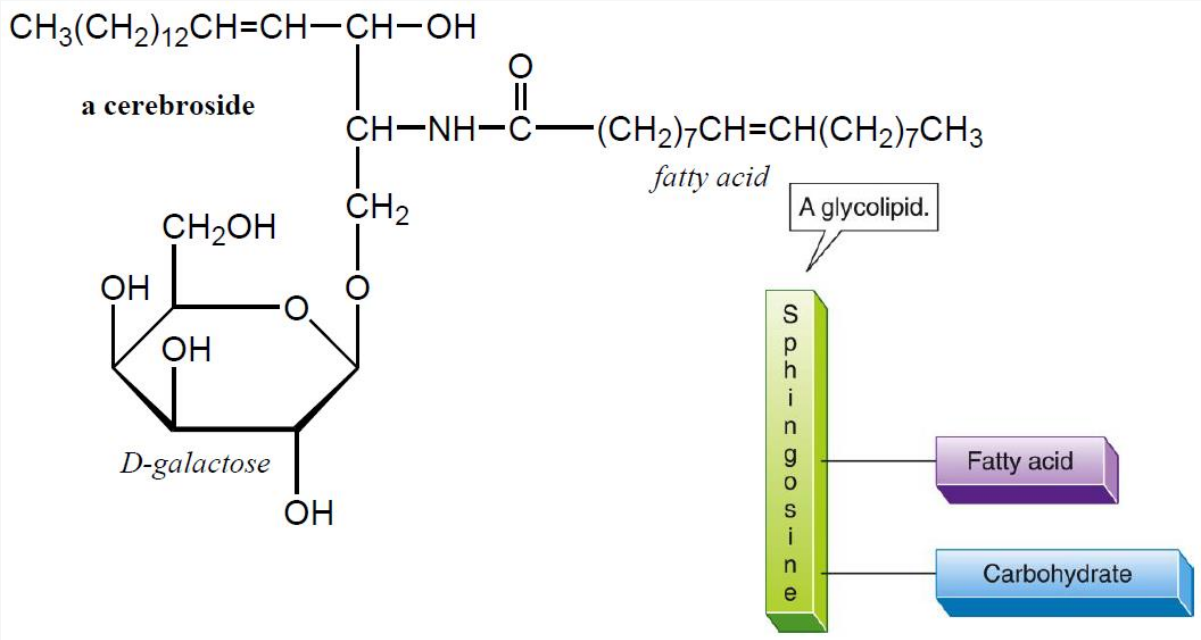

Sphingomyelins are found brain and nerve tissue, and in the myelin sheath that protects nerves.

# Phospholipids

# Complex lipids

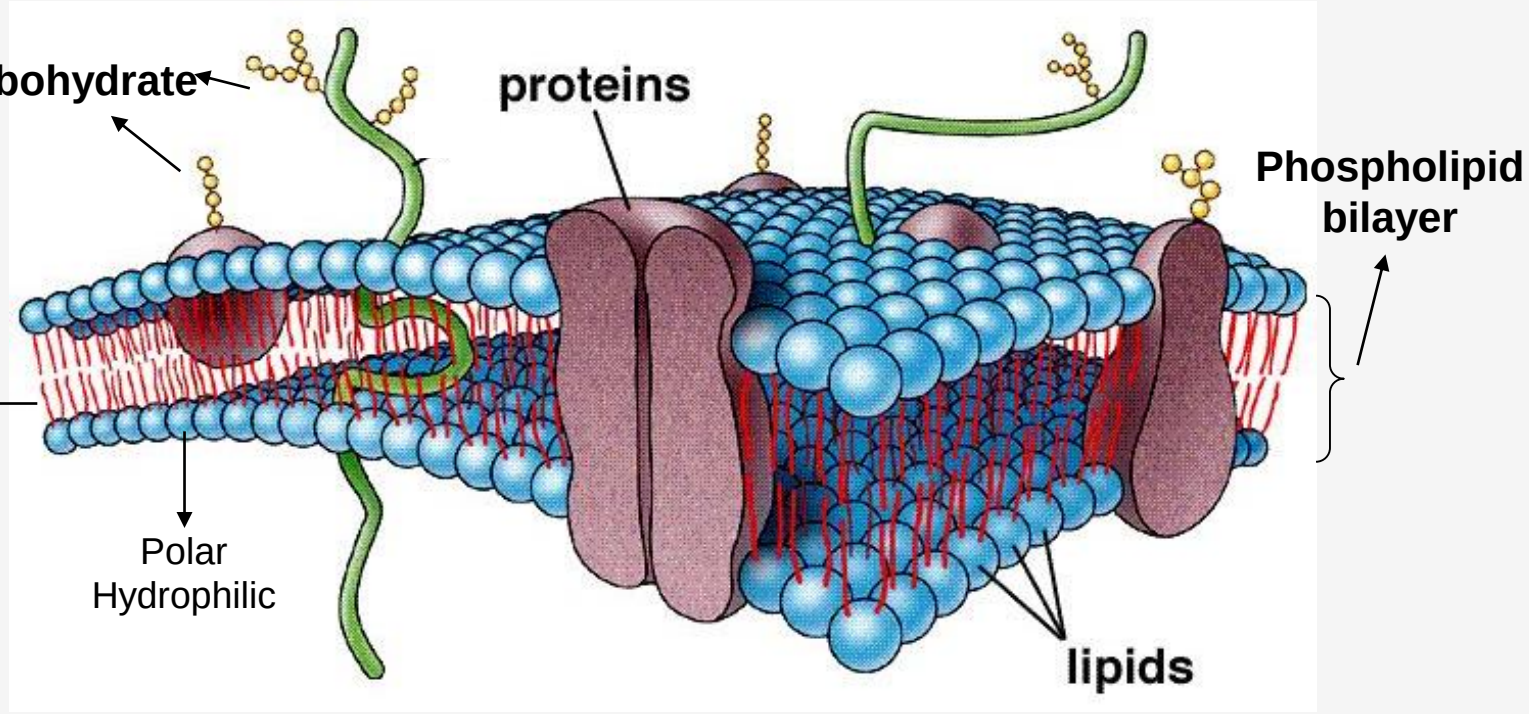
## Glycolipids

- **Glycolipids** are sphingolipids that contain carbohydrates (usually monosaccharides).
- They are also referred to as *cerebrosides* because of their abundance in brain tissue.



# Cell Membrane

## Fluid mosaic model



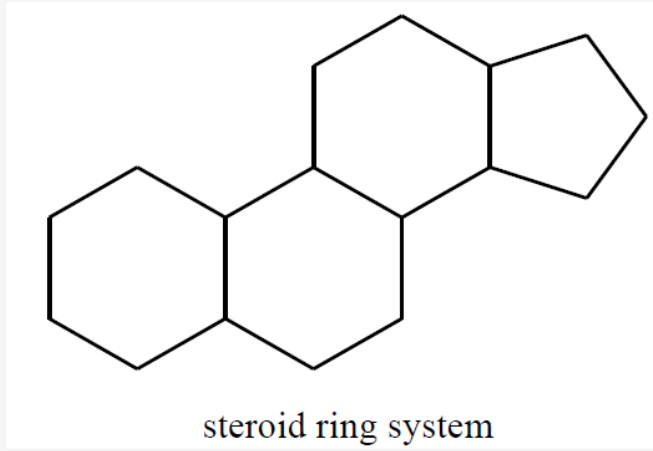

The cell membrane as being composed of a lipid bilayer, in which the nonpolar tails of lipids point towards the "interior" of the bilayer, leaving the polar, hydrophilic portions pointing outwards.

Semipermeable: selected nutrients can enter and waste products can leave.

# Steroids

## Nonsaponifiable (Nonhydrolyzable) lipids

- Steroids are classified as lipids because they are soluble in nonpolar solvents.
- They are nonsaponifiable because the components are not held together by ester linkages.
- The basic steroid structure contains four fused rings:



steroid ring system

- Steroids have

nucleus which is 4 carbon rings.

attached groups that make the different types of compounds.

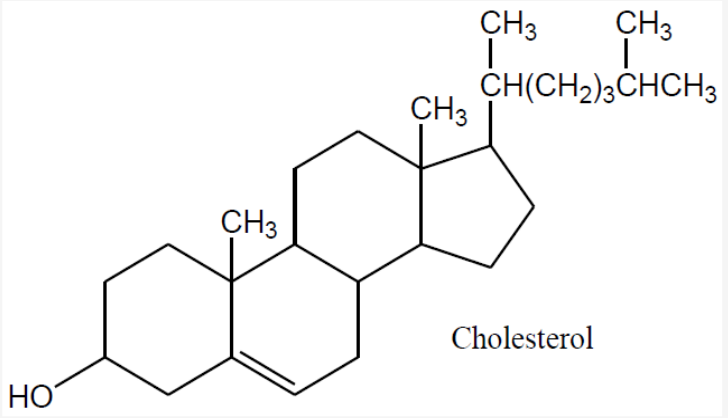
no fatty acids.

# Steroids

## Nonsaponifiable (Nonhydrolyzable) lipids

## Cholesterol

- Cholesterol is the most abundant steroid in the body.
- 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.
- There is apparently a correlation between high levels of cholesterol in the blood and atherosclerosis.




Cholesterol is obtained from meats, milk, and eggs.

Cholesterol is synthesized in the liver from fats, carbohydrates and proteins.

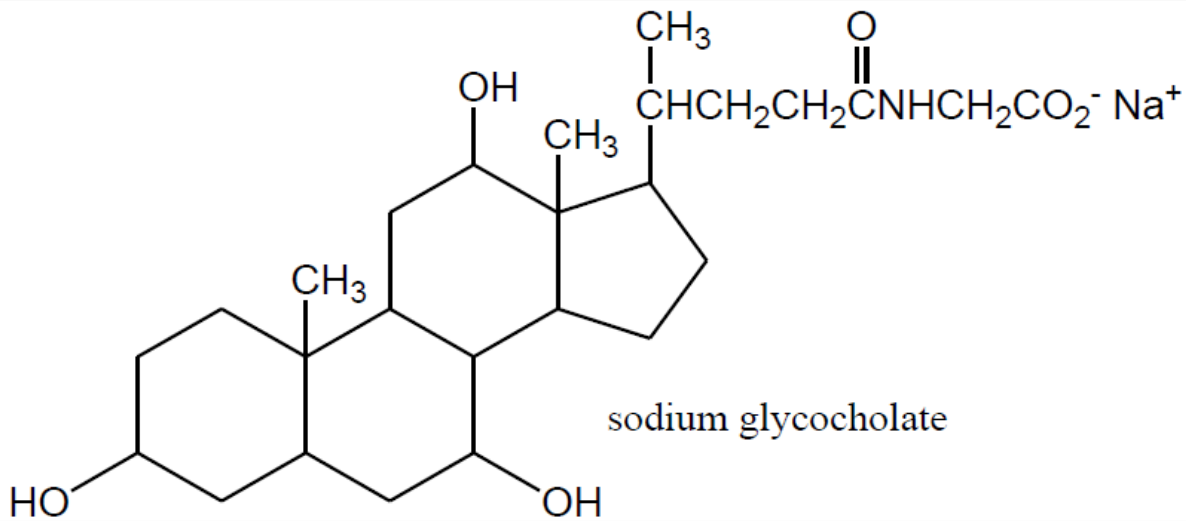
No cholesterol in vegetable and plants.

# Steroids

## Nonsaponifiable (Nonhydrolyzable) lipids

## Bile Salts

- Bile is a yellowish brown or green fluid produced in the liver and stored in the gall bladder.
- Bile salts act like soaps and other emulsifiers: they contain both polar and nonpolar regions, helping to break fats in foods into smaller pieces, allowing them to be hydrolyzed more easily.



sodium glycocholate

# Steroids

## Nonsaponifiable (Nonhydrolyzable) lipids

## Steroid Hormones

- **A hormone** is a molecule that is synthesized in one part of an organism, which then elicits a response at a different site.

- **Two types of steroids hormones:**

  **1. Sex hormones**

  Estrogens & progestins in females

  Androgens in males

  **2. Adrenal Cortical Steroids**

# Steroids

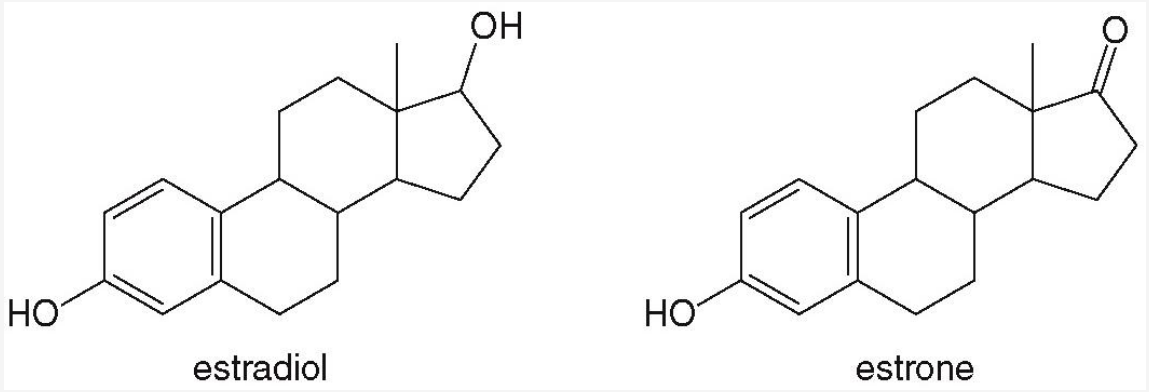
## Nonsaponifiable (Nonhydrolyzable) lipids

## Steroid Hormones

### Female Sex Hormones

### Estrogens

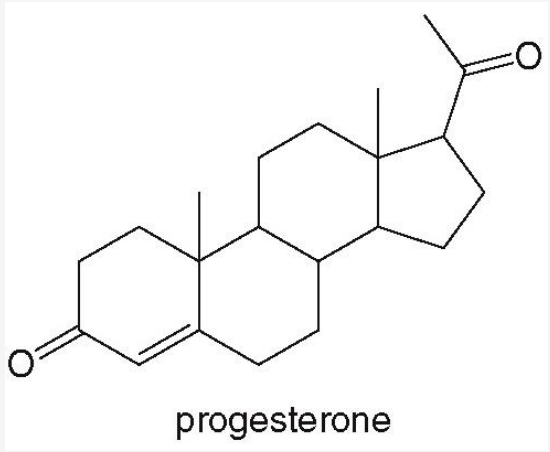
The estrogens estradiol and estrone control development of secondary sex characteristics, *regulate the menstrual cycle*, and are made in the ovaries.




estradiol estrone

### Progestins

The progestin progesterone is called the "pregnancy hormone"; it is responsible for the *preparation of the uterus for implantation of a fertilized egg*.




progesterone

# Steroids

## Nonsaponifiable (Nonhydrolyzable) lipids

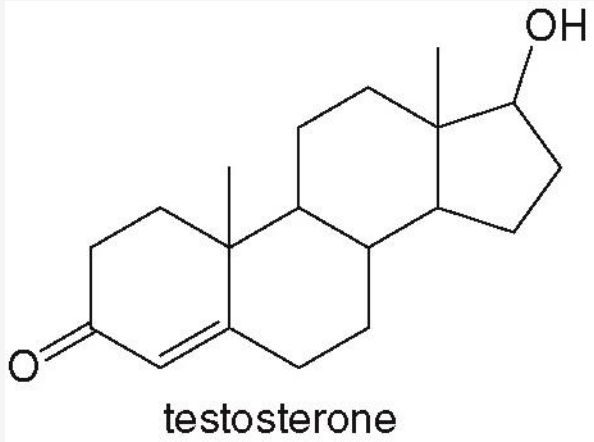
## Steroid Hormones

### Male Sex Hormones

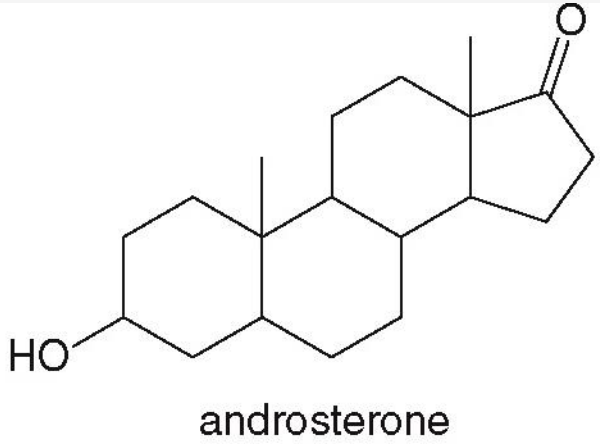
### Androgens

Testosterone and Androsterone are androgens made in the testes.

They control the development of secondary sex characteristics in males.



testosterone



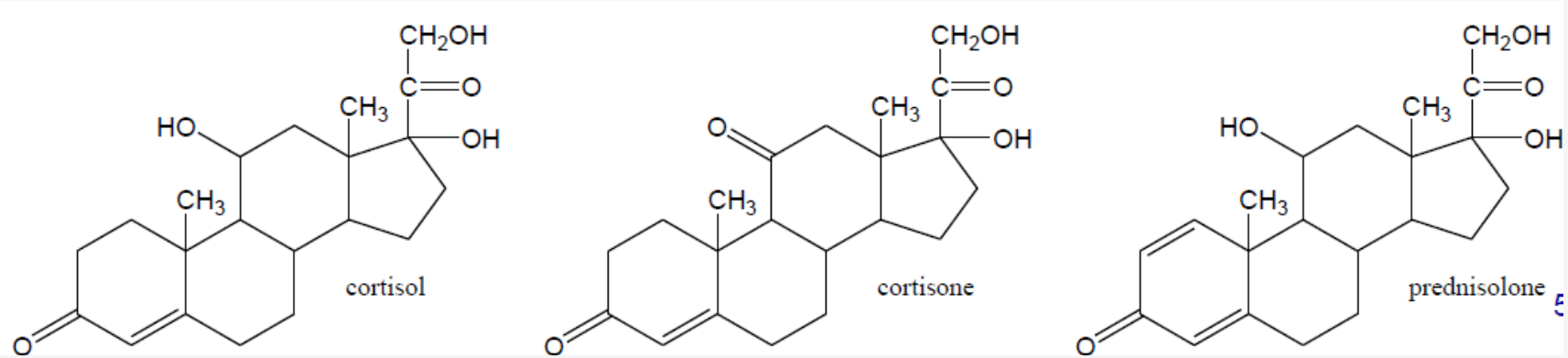
androsterone

## Steroid Hormones

### Adrenocorticoid Hormones

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

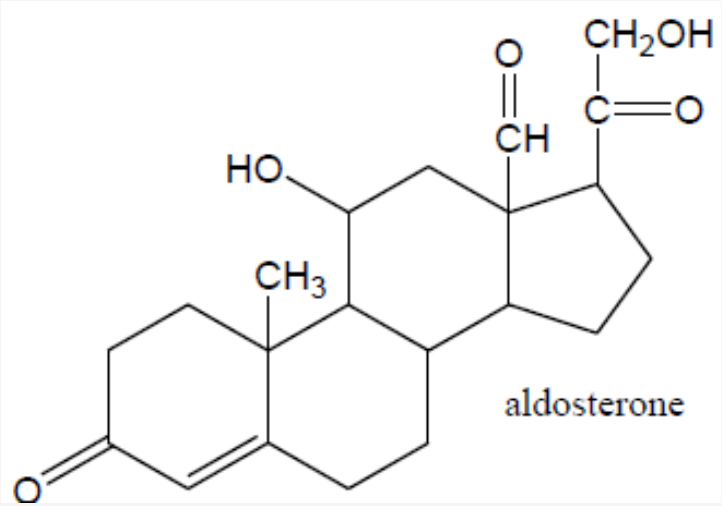
- **Glucocorticoids** such as cortisol affect the metabolism of carbohydrates.
- **Cortisol and its derivatives, cortisone and prednisolone** (synthetic) are powerful anti-inflammatory drugs used to treat arthritis and asthma.



## Steroid Hormones

### Adrenocorticoid Hormones

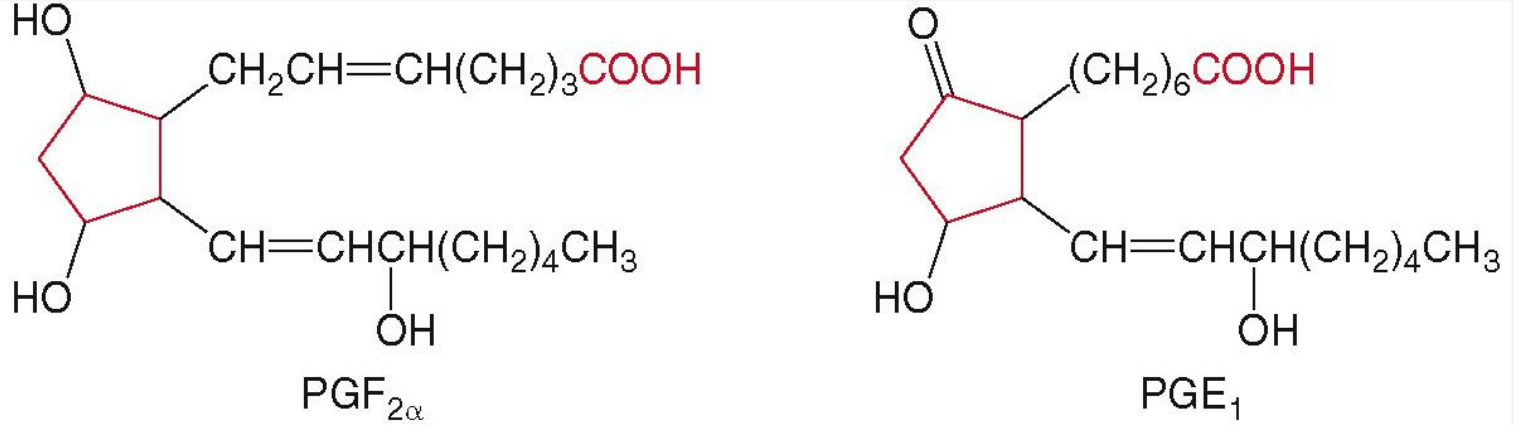
Mineralocorticoids regulate ion concentration (mainly $Na^+$).
**Aldosterone** influences the absorption of $Na^+$ and $Cl^-$ in kidney tubules, thus regulating the retention of water in the body.



# Prostaglandins

## Nonsaponifiable (Nonhydrolyzable) lipids

**Prostaglandins** are carboxylic acids that contain a five-membered ring and have a wide range of biological activities.



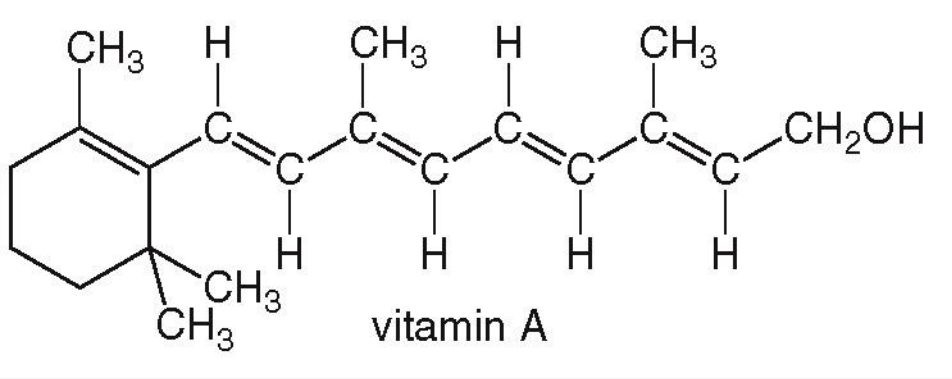

- **Prostaglandins** are responsible for inflammation.
- **Prostaglandins** also decrease gastric secretions, inhibit blood platelet aggregation, stimulate uterine contractions, and relax smooth muscles.
- Aspirin and ibuprofen relieve pain and inflammation by blocking the synthesis of these molecules.

# Vitamins

- They are organic compounds required in small quantities for normal metabolism.
- They must be obtained from the diet (our cells cannot synthesize them).
- Vitamins are either water soluble or fat soluble.
- The four fat-soluble vitamins (A, D, E, and K) are lipids and nonpolar.
- They are found in fruits, vegetables, fish, liver, and dairy products.
- Excess vitamins are stored in adipose cells to be used when needed.

# Vitamin A

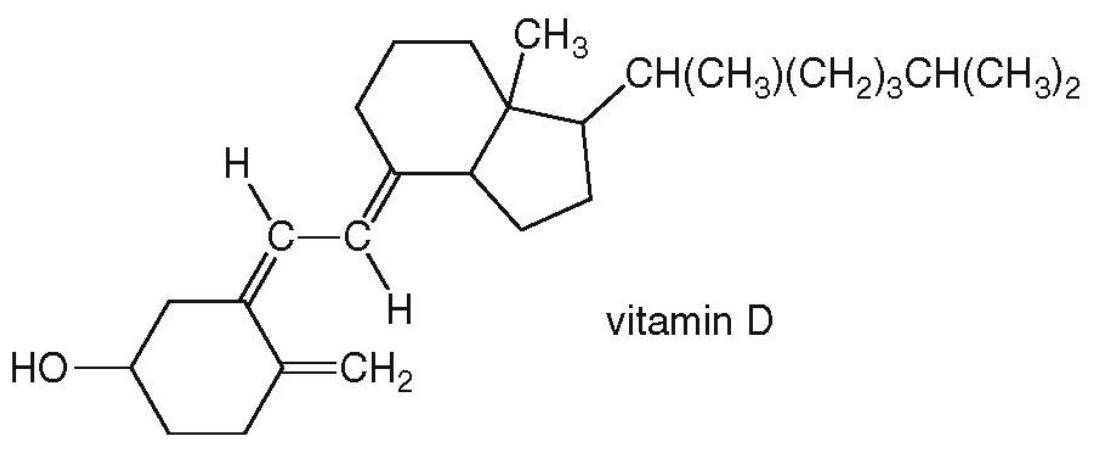
- It is found in *liver*, *fish*, and *dairy products*, and is made from β-carotene (the orange pigment in carrots).
- It is needed for vision and for healthy mucous membranes.
- Vitamin A deficiency causes night blindness and dry eyes and skin.



vitamin A

# Vitamin D

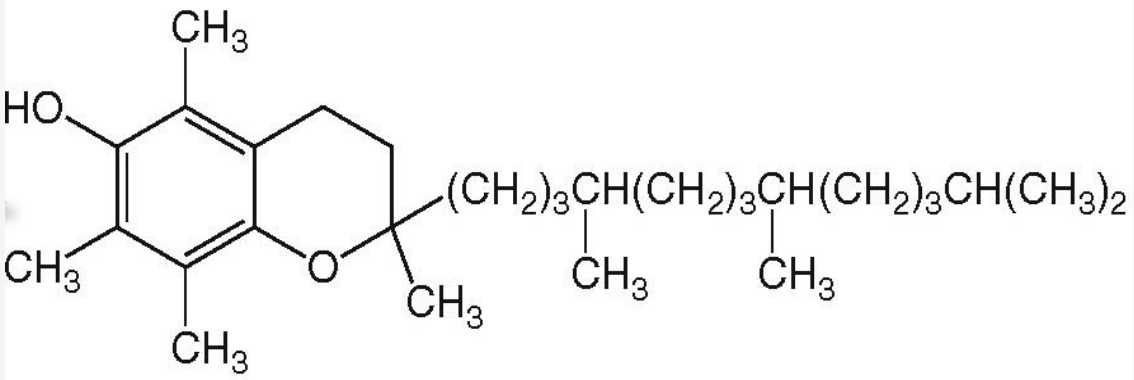
- Vitamin D can be synthesized from cholesterol.
- It can be obtained in the diet from many foods, especially milk, and helps regulate Ca and P metabolism.
- A deficiency of vitamin D causes rickets (bone malformation).



vitamin D

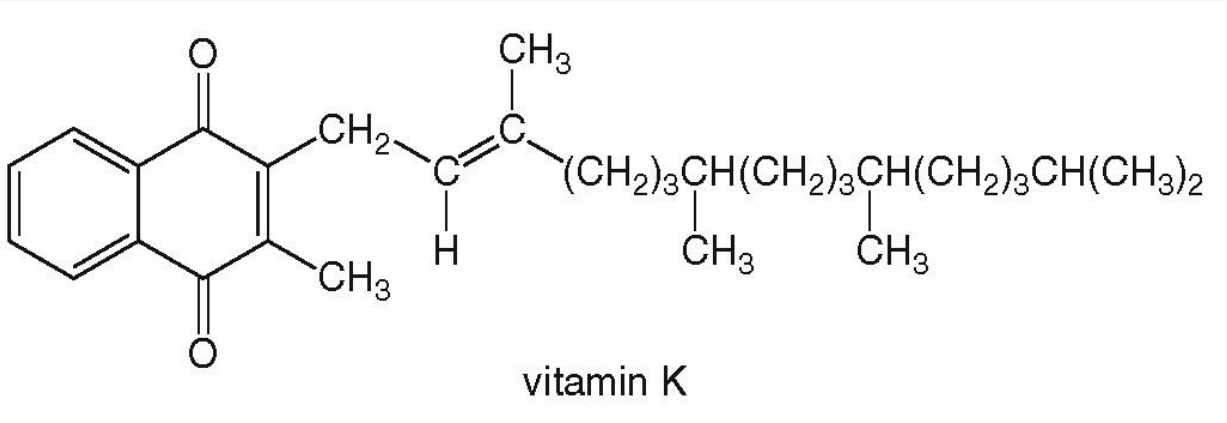
# Vitamin E

- Vitamin E is an antioxidant, protecting unsaturated side chains in fatty acids from unwanted oxidation.
- Deficiency of vitamin E causes numerous neurological problems, although it is rare.




# Vitamin K

- Vitamin K regulates the synthesis of clotting proteins (prothrombin), and deficiency of this leads to excessive or fatal bleeding.



vitamin K