108 Chem

Chapter 10

Fats, Lipids and Oils

Lipids

- Lipids are biological molecules (biomolecules) that are insoluble in water (nonpolar) but soluble in nonpolar organic solvents.
- They contain many nonpolar C—C and C—H bonds and few polar bonds resulting in their water insolubility
- They are not defined by a particular functional group, thus they have a variety of structures and functions.
- The word lipid comes from the Greek lipos, which means “fat.”
- Lipids are the waxy, greasy, or oily compounds found in plants and animals.

Classification of Lipids

Lipids are divided into:

1) Saponifiable (Hydrolyzable) lipids

They contain esters.

They can undergo saponification (hydrolysis under basic conditions)

A. Simple lipids:
contain two components
(fatty acid and an alcohol):
- Triglycerides (Fats & oils)
- Waxes

B. Complex lipids:
contain more than two components
(fatty acids, alcohol, and other components):
- phosphoglycerides
- Sphingolipids

2) Nonsaponifiable (Nonhydrolyzable) lipids

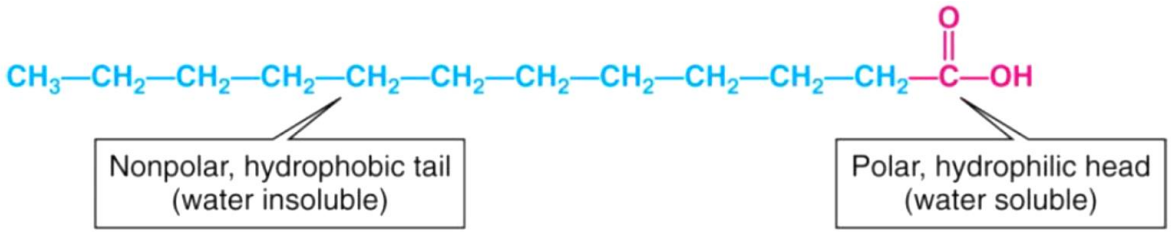
They do not contain ester groups.

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).



- 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).
- Functional groups are only the carboxyl group and the double bonds.
- The double bonds are usually in *cis* configurations.

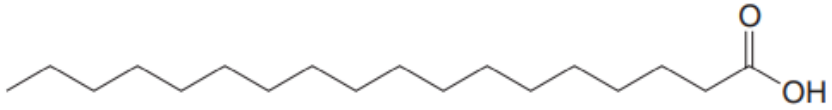
Saturated and Unsaturated Fatty Acids

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

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

(m.p. 71ºC)

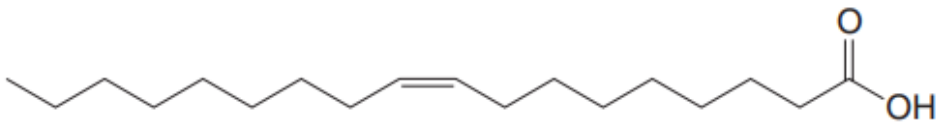
They are solids at room temperature. It is found in palm oil, which is frequently used in handmade soap



Stearic acid
(octadecanoic acid)

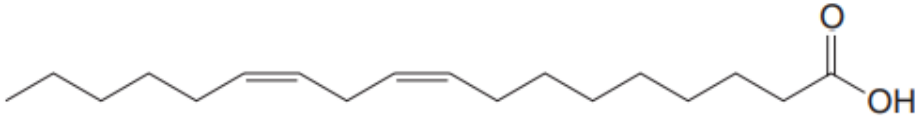
- Unsaturated fatty acids have one or more double bonds (generally *cis*) in their long hydrocarbon chains.

Oleic acid (18 carbons, one double bond)
(m.p. 13ºC)
It is derived mainly from "olive" oil. sesame oil, sunflower, shea butter, coconut oil, ... etc.



Oleic acid
(*cis*-9-octadecenoic acid)

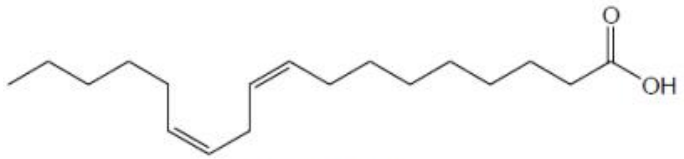
Linoleic acid (18 carbons, two double bonds)
(m.p. -5ºC)
It is found in soybean oil



Linoleic acid
(*cis,cis*-9,12-octadecadienoic acid)

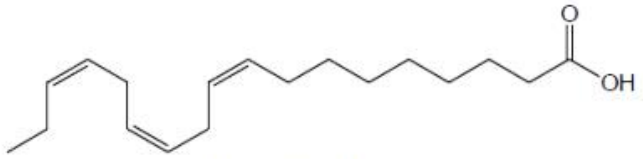
Essential Fatty Acids

- 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.
- 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

An omega-6 polyunsaturated fatty acid



Linolenic acid

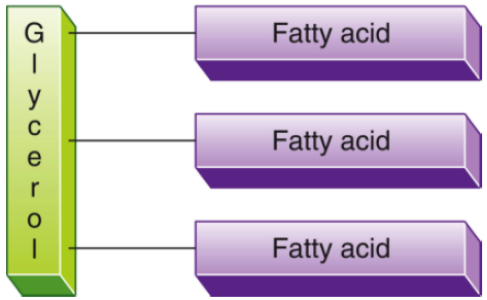
An omega-3 polyunsaturated fatty acid

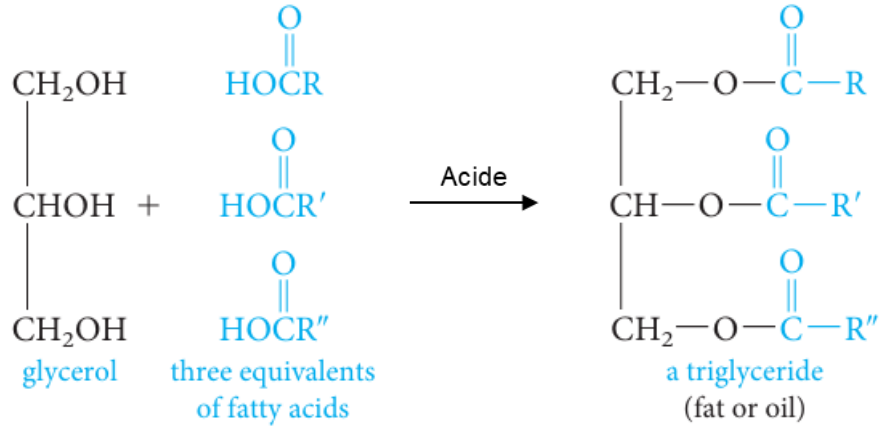
Some Important Fatty Acids

#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

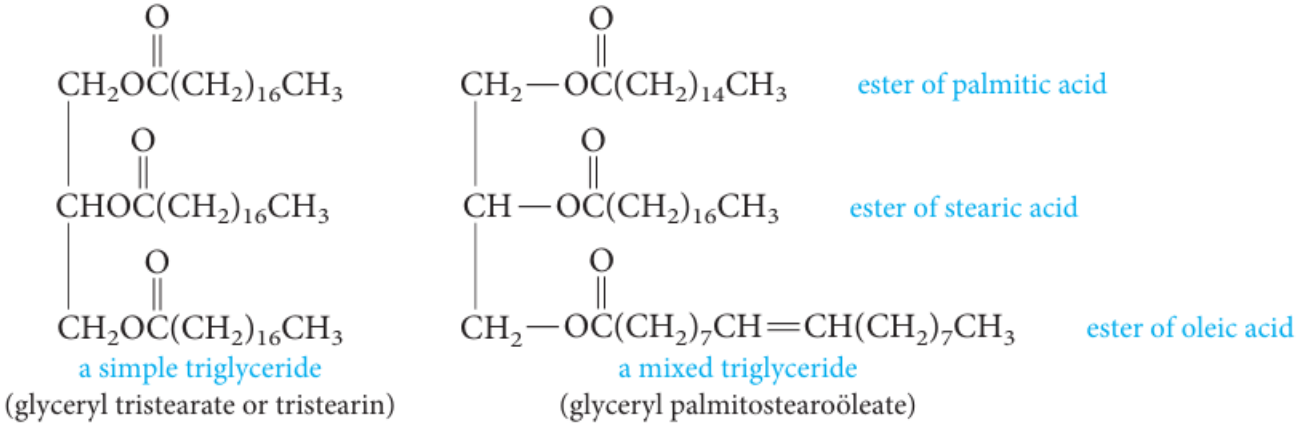
Simple lipids
Fats and oils: Triglycerides

- 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.





- There are two types of triglycerides: simple triglycerides, in which all three fatty acids are identical, and mixed triglycerides. Natural triglycerides are often mixtures of different triglyceride molecules.



Fats and oils: Triglycerides

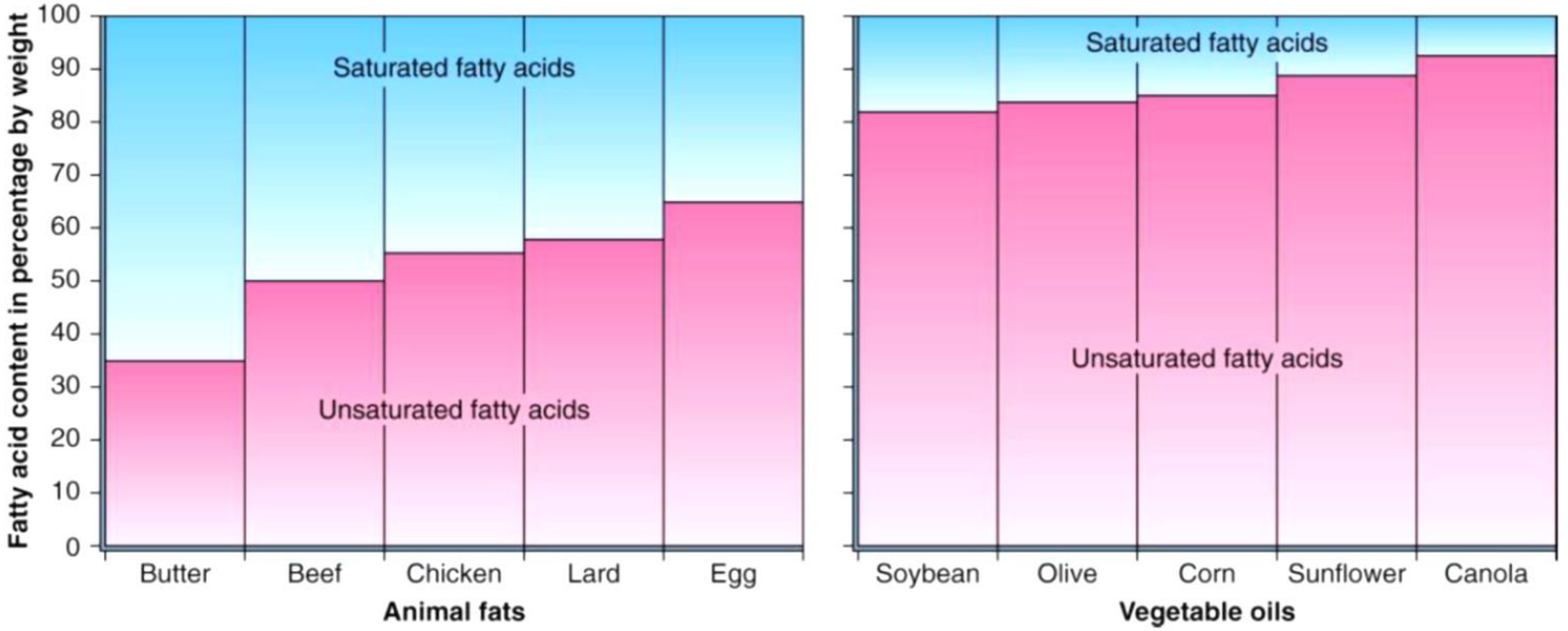
Fats are:

- 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.

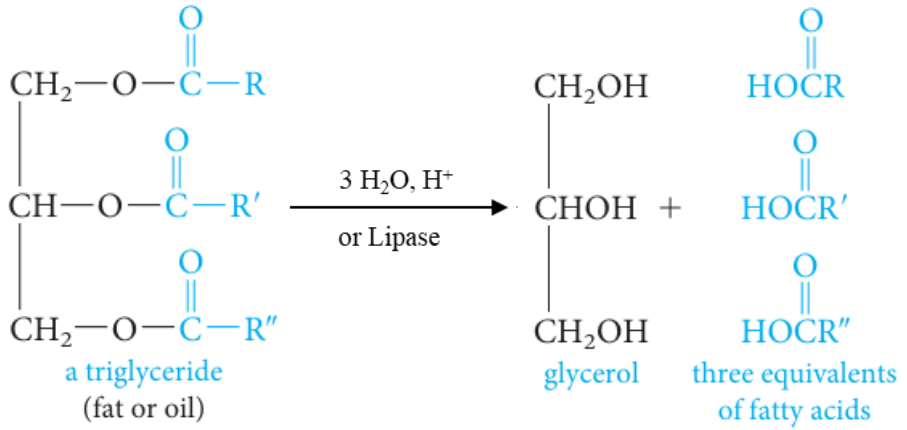
- A comparison of saturated and unsaturated fatty acids in some foods.



Chemical Properties of Fats and Oils

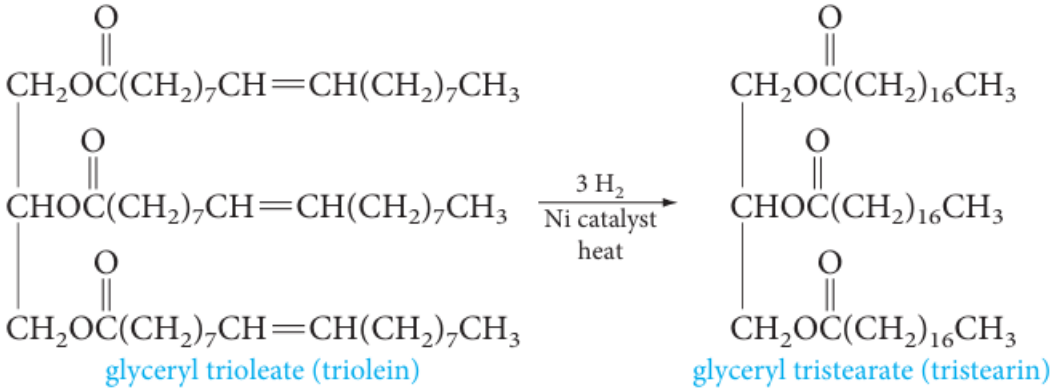
Hydrolysis of Triglycerides:

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



Hydrogenation:

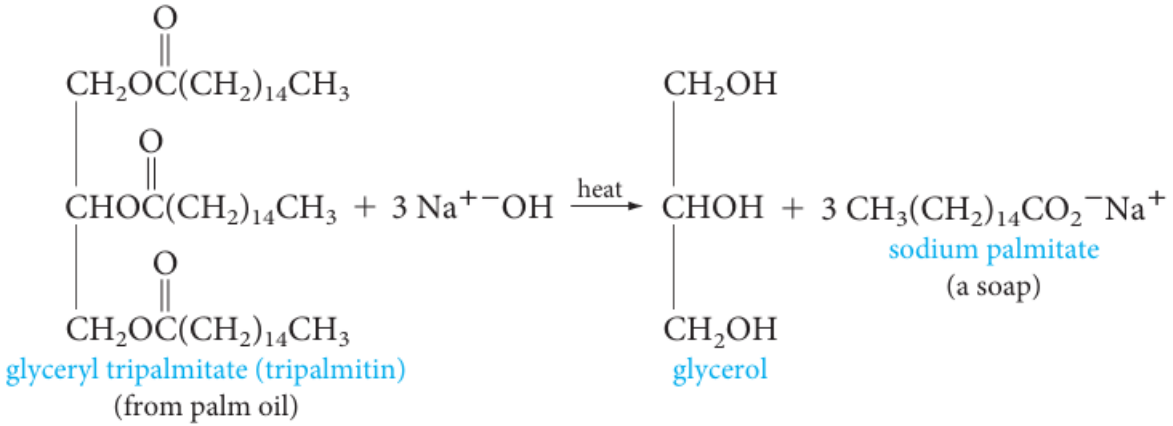
Vegetable oils, which are highly unsaturated, are converted into solid vegetable fats by catalytically hydrogenating some or all of the double bonds.



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.

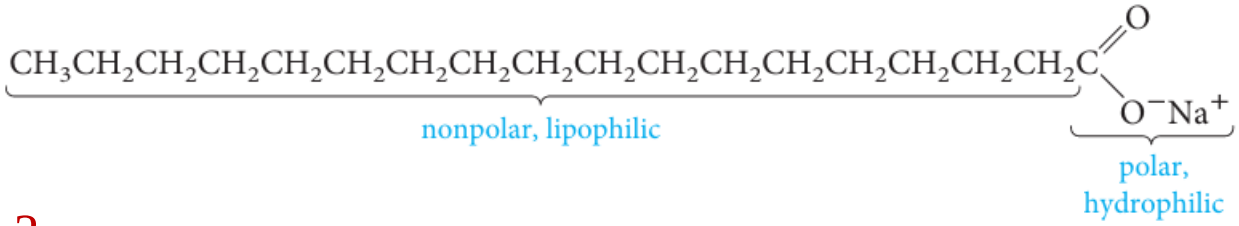


Soaps:

- 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.”

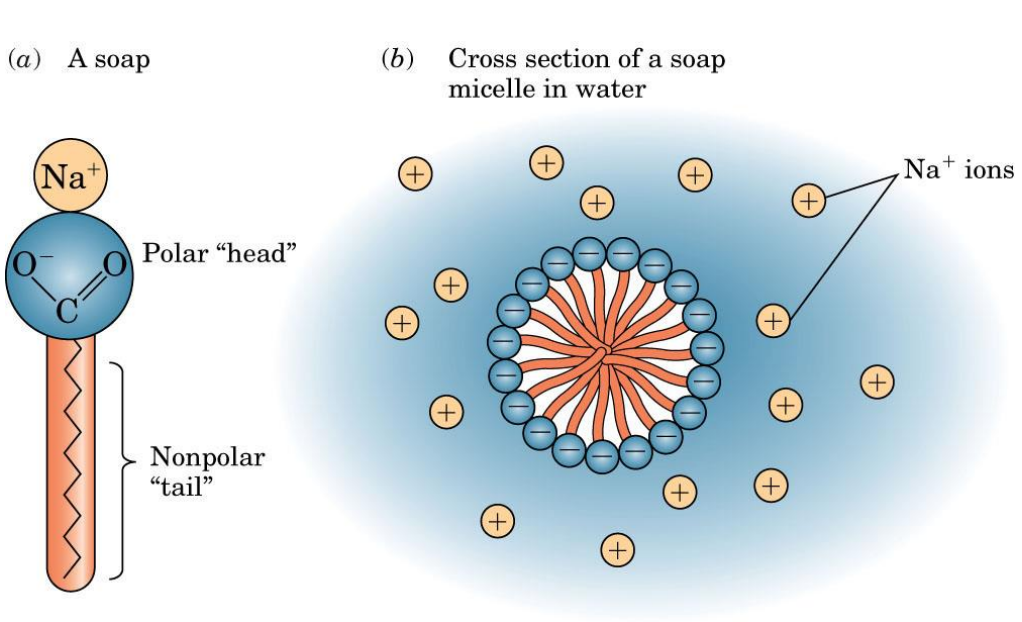
Chemical Properties of Fats and Oils

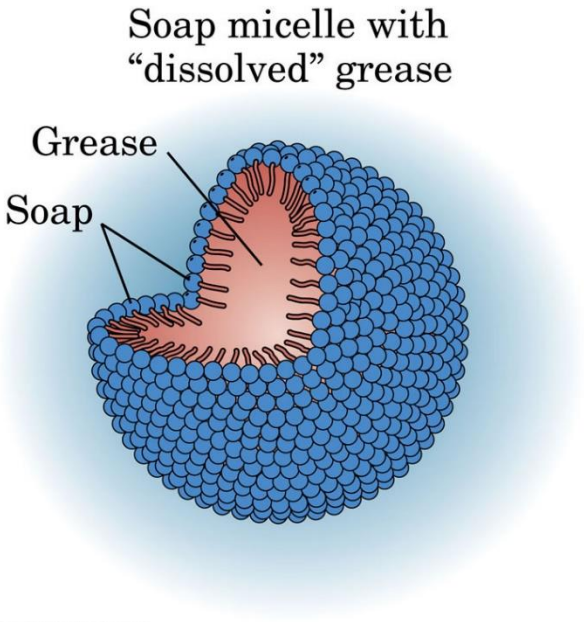
Soaps:



How Do Soaps Work?

Soap molecules form globular aggregates in water called micelles, with their polar hydrophilic heads facing the water and their nonpolar lipophilic tails in the center.

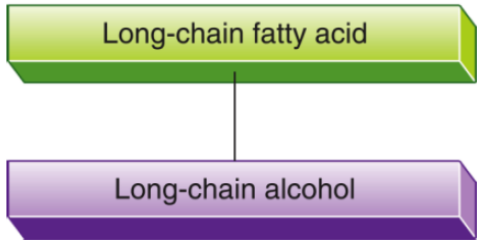




Simple lipids

Waxes

- Waxes differ from fats and oils in that they are simple monoesters of fatty acids.
- The acid and alcohol portions of a wax molecule both have long saturated carbon chains.



$CH_3(CH_2)_{13}CH_2C(=O)-O(CH_2)_{15}CH_3$

cetyl palmitate
(component of spermaceti,
a wax in sperm whale oil)

$C_{25\text{-}27}H_{51\text{-}55}C(=O)-OC_{30\text{-}32}H_{61\text{-}65}$

components of beeswax

- 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.

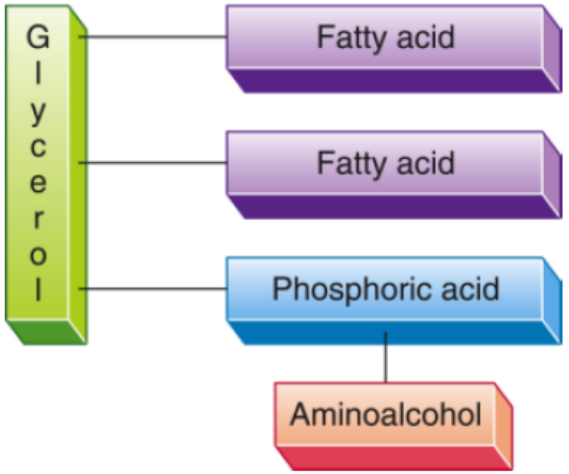
Complex lipids

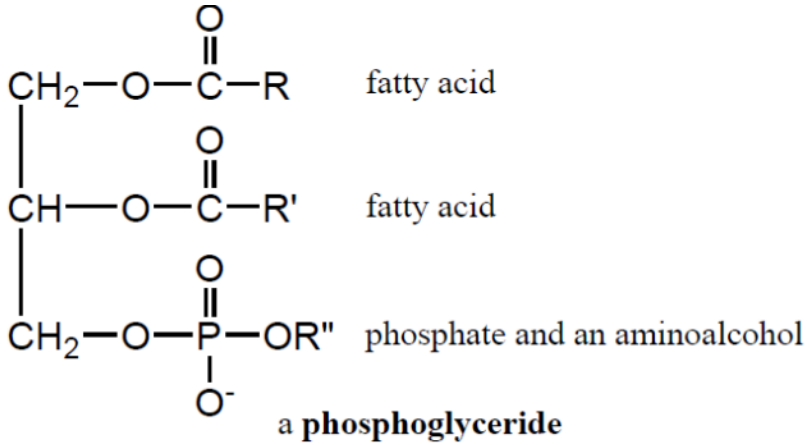
Phospholipids

- Phospholipids are related structurally to fats and oils, except that one of the three ester groups is replaced by a phosphatidylamine.
- There are two common types: Phosphoglycerol and Sphingolipids

1) Phosphoglycerol

- 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.

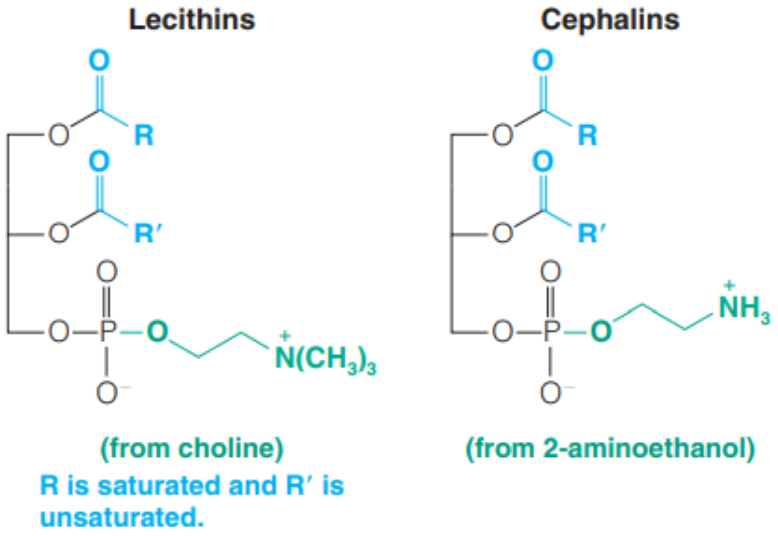




a **phosphoglyceride**

Phospholipids

- There are two types of phosphoglycerols:



1) Cephalins are found in most cell membranes, particularly abundant in brain tissue, found in blood platelets and play a role in blood clotting.

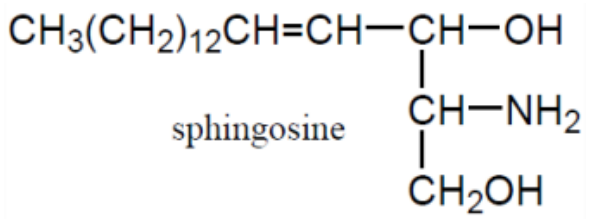
2) Lecithin can act as an emulsifying agent: important structural component of cell membranes, play a role in the transport of lipids in the blood stream.

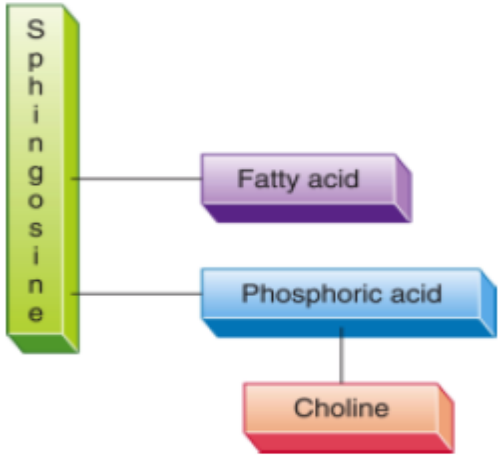
Commercially, lecithin extracted from soybeans is used as an emulsifying agent in margarine and candies to provide a smooth texture.

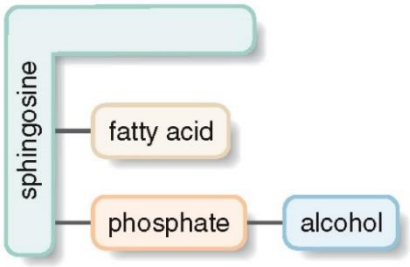
Phospholipids

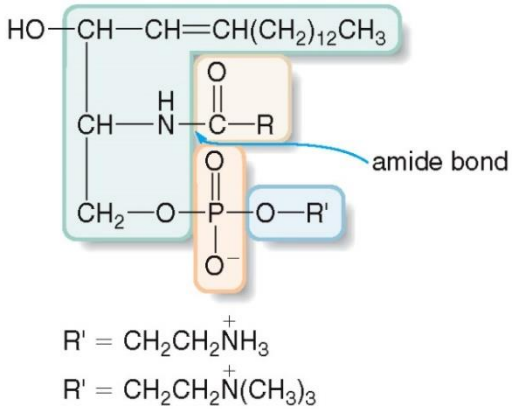
2) Sphingolipids

- Sphingolipids are complex lipids that contain sphingosine instead of glycerol.
- They do not contain an ester; their single fatty acid is bonded to the backbone by an amide bond.
- They are found brain and nerve tissue, and in the myelin sheath that protects nerves.





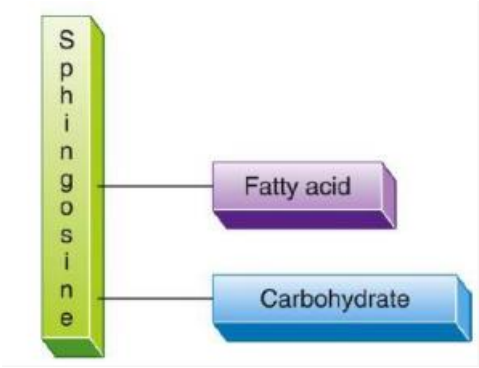


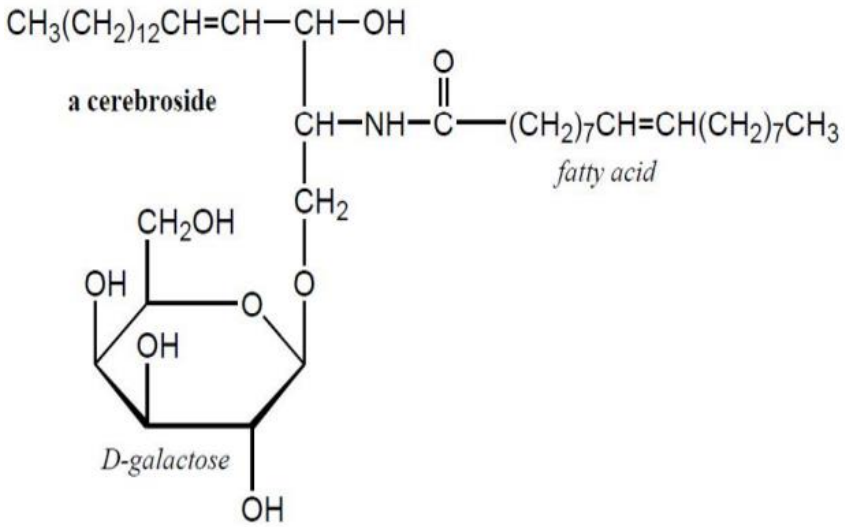


Phospholipids

3) Glycolipids

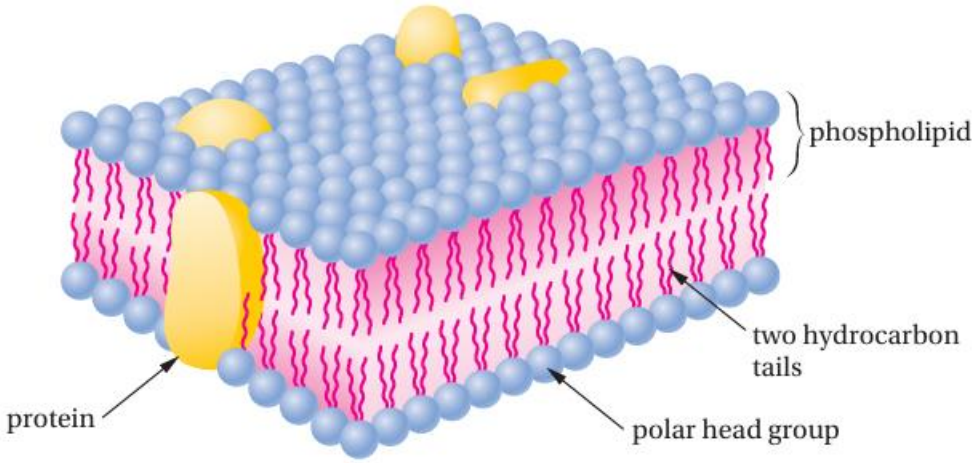
- Glycolipids are sphingolipids that contain carbohydrates (usually monosaccharides).
- They are also referred to as cerebrosides because of their abundance in brain tissue.





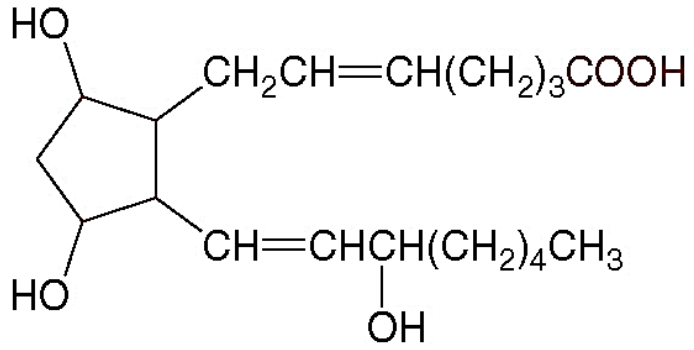
Phospholipids and cell membrane

- 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.

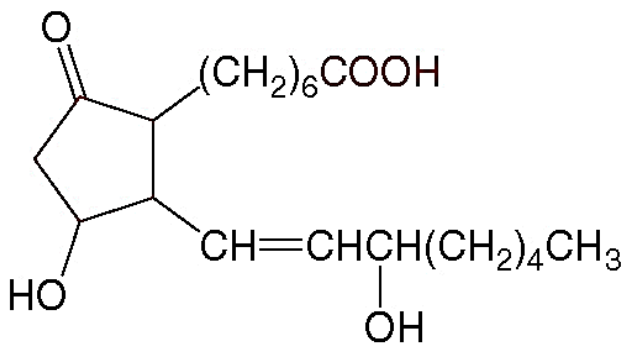


Nonsaponifiable (Nonhydrolyzable) lipids
Prostaglandins

- Prostaglandins are carboxylic acids that contain a five-membered ring and have a wide range of biological activities.
- Prostaglandins are responsible for inflammation.
- They 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.



$PGF_{2\alpha}$



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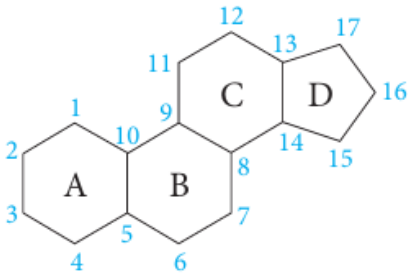
Nonsaponifiable (Nonhydrolyzable) lipids

Steroids

- 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:



the steroid ring system, showing the numbering

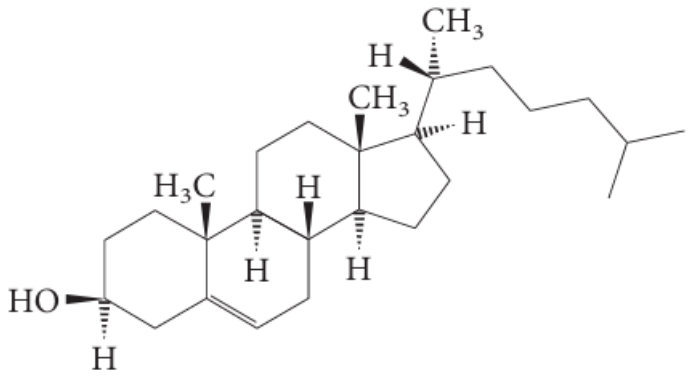
- Usually there are methyl substituents attached to C-10 and C-13 (called “angular” methyl groups) and some sort of side chain attached to C-17.

- The best known steroid is cholesterol, bile salts, sex hormones, Adrenocortical hormones and vitamin D.

Steroids

Cholesterol

- Cholesterol is the most abundant steroid in the body.
- It is an essential component of cell membranes.
- 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.

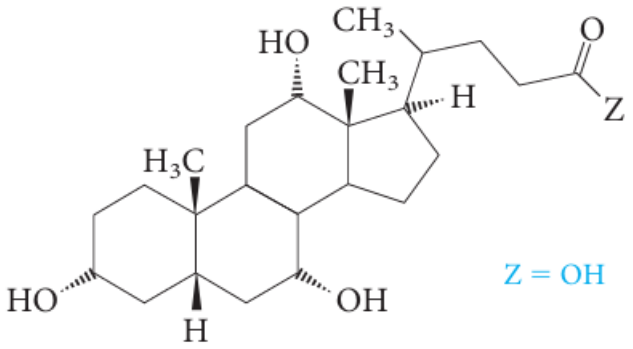


cholesterol

Steroids

Bile Salts

- Bile is a yellowish brown or green fluid produced in the liver and stored in the gallbladder.
- 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.



Z = OH cholic acid

Z = NHCH2CH2S(=O)(=O)−O⁻Na⁺ a bile salt

Steroids

Steroid Hormones

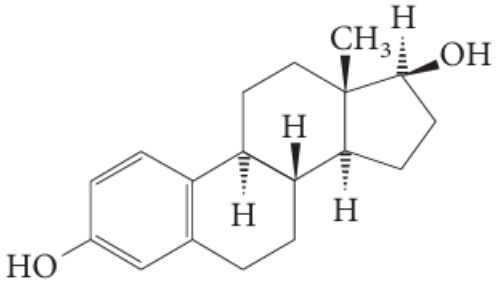
- A hormone is a molecule that is synthesized in one part of an organism, which then elicits a response at a different site.
- Two types of steroids hormones: 1. Sex hormones
  - Estrogens & progestins in females
  - Androgens in males

  2. Adrenocortical hormones

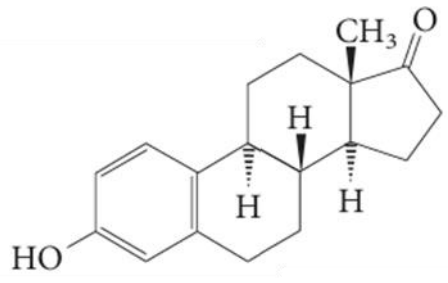
Steroid Hormones

Sex hormones

- Estrogens: Estradiol and Estrone control development of secondary sex characteristics.

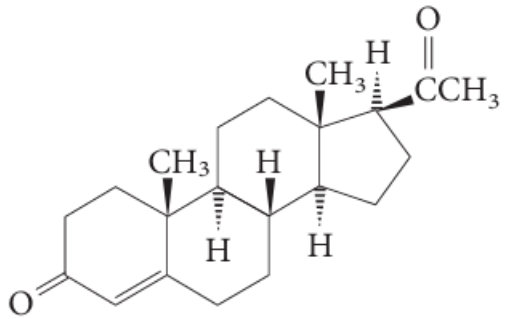


estradiol



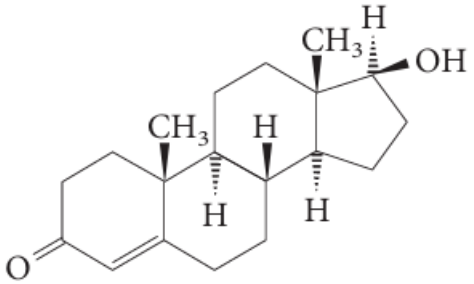
estrone

- Progestins : Progesterone is called the “pregnancy hormone”.

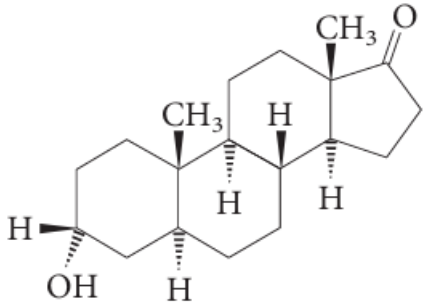


progesterone

- Androgens: Testosterone and Androsterone control the development of secondary sex characteristics in males.



testosterone

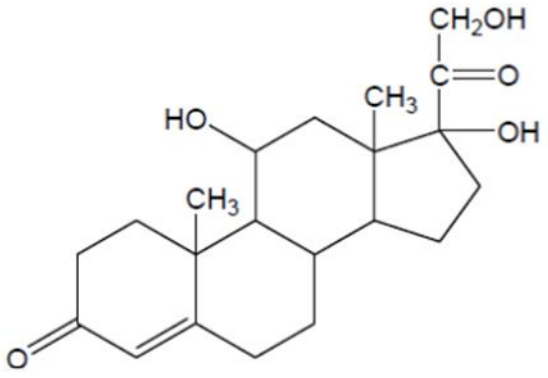


androsterone

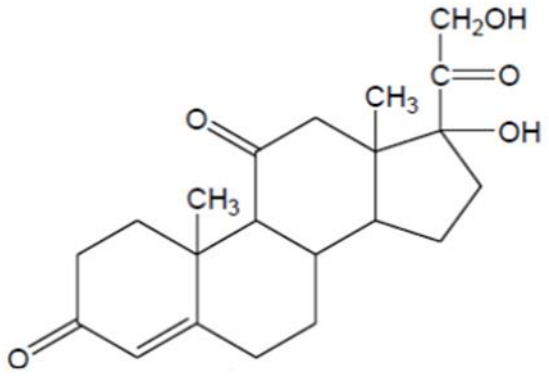
Steroid Hormones

Adrenocortical hormones

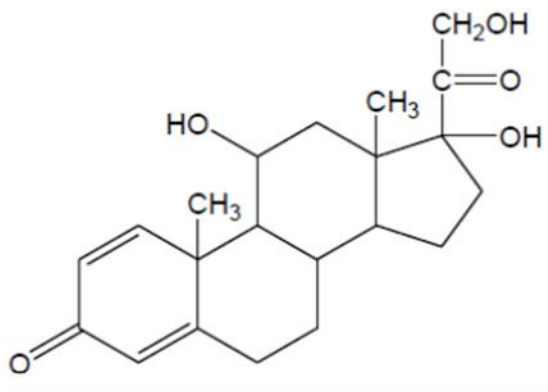
- They are produced in the adrenal glands (located on the top of the kidney).
- Glucocorticoids such as cortisol affect the metabolism of carbohydrates.
- Cortisol and its derivatives, cortisone and prednisolone (synthetic) are powerful anti-inflammatory drugs used to treat arthritis and asthma.



cortisol



cortisone



prednisolone

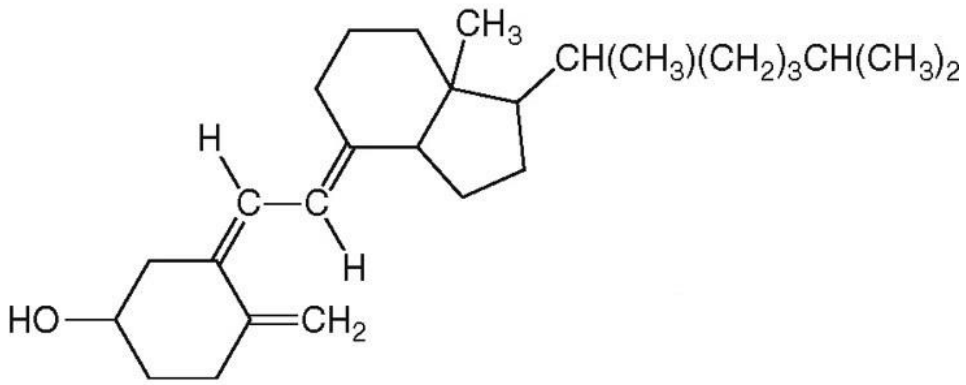
Vitamins

- 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.

Vitamins

Vitamin D

- It 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).

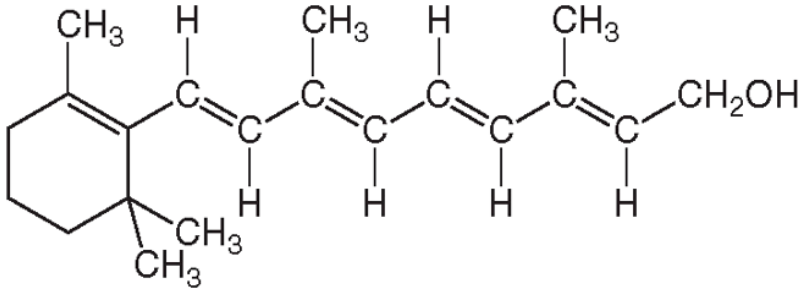


vitamin D

Vitamins

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.

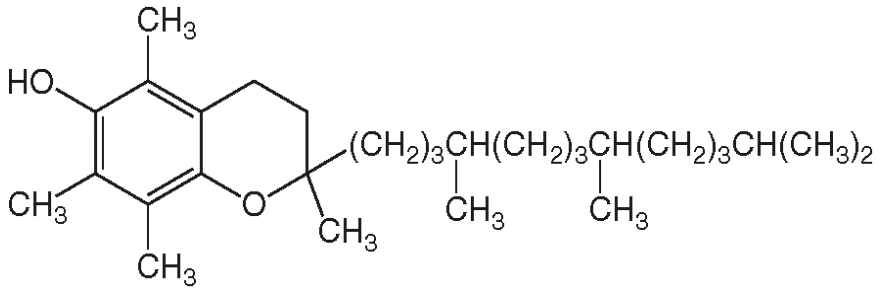


vitamin A

Vitamins

Vitamin E

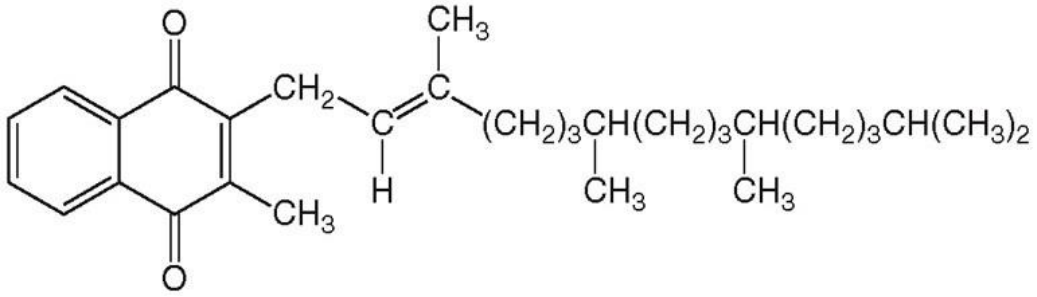
- It is an antioxidant, protecting unsaturated side chains in fatty acids from unwanted oxidation.
- Deficiency of vitamin E causes numerous neurological problems, although it is rare.



vitamin E

Vitamin K

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



vitamin K