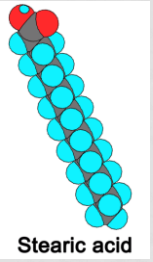
Chapter 8
Lipids



Chapter Objectives:

- Learn how to classify lipids.
- Learn the properties of the saturated and unsaturated fatty acids, and how they are linked to form triglycerides (fats and oils).
- Learn how to draw the products of hydrolysis, saponification, and hydrogenation reactions of triglycerides.
- Learn the basic structures of other lipids, including waxes, phosphoglycerides, lecithin, cephalins, sphingolipids, and glycolipids.
- Learn how lipids are important in cell membrane structure.
- Learn about the steroids and steroid hormones, and the prostaglandins.

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CHEM 2353 Fundamentals of Organic Chemistry
Organic and Biochemistry for Today (Seager & Slabaugh)
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Lipids

- **Lipids** are biological molecules that are insoluble in water but soluble in nonpolar solvents.
  - Lipids have a wider spectrum of compositions and structures because they are defined in terms of their physical properties (water solubility).
- Lipids are the waxy, greasy, or oily compounds found in plants and animals.
  - wax coating that protects plants
  - used as energy storage
  - structural components (cell membranes)
  - insulation against cold

Classification of Lipids

- Lipids are divided into:
  - **Saponifiable lipids** — contain esters, which can undergo saponification (hydrolysis under basic conditions) (waxes, triglycerides, phospho-glycerides, sphingolipids)
  - **Nonsaponifiable lipids** — do not contain ester groups, and cannot be saponified (steroids, prostaglandins)
- Saponifiable lipids can also be divided into groups:
  - **Simple lipids** — contain two types of components (a fatty acid and an alcohol)
  - **Complex lipids** — contain more than two components (fatty acids, an alcohol, and other components)

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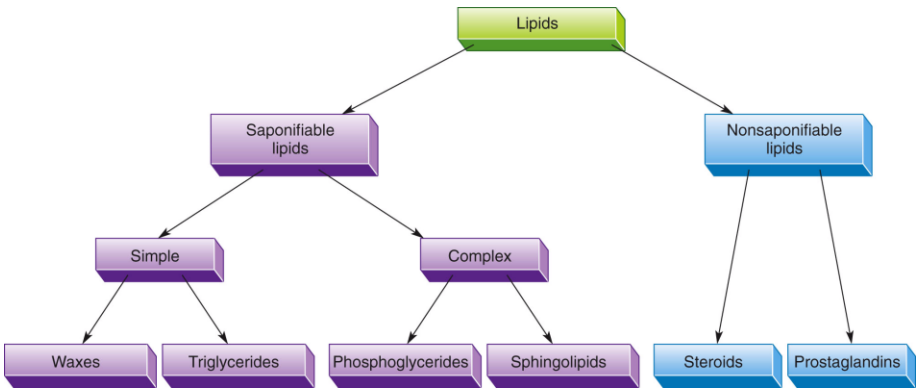
Classification of Lipids



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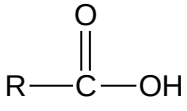
Fatty Acids

Fatty Acids

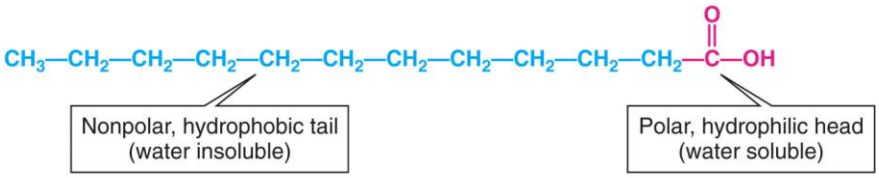
- **Fatty acids** are long-chain carboxylic acids:



a **carboxylic acid**

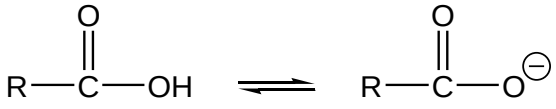
RCOOH RCO_2H

condensed ways of writing the carboxyl group



Properties of Fatty Acids

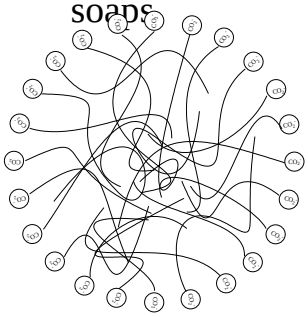
- The long, nonpolar hydrocarbon tails of fatty acids are responsible for most of the fatty or oily characteristics of lipids.
- The carboxyl (COOH) group is hydrophilic under basic conditions, such as physiological pH (7.4):

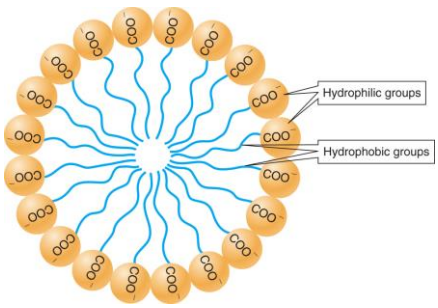


carboxylic acid ⇌ **carboxylate ion**

Fatty Acid Micelles

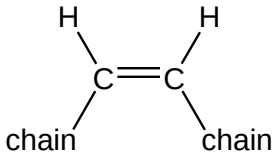
- In aqueous solutions, fatty acids associate with each other in spherical clusters called **micelles**, in which the hydrocarbon tails tangle each other up through dispersion forces, leaving a "shell" of polar carboxylate ions facing outwards, in contact with the water.
  - Micelles are important in the transport of insoluble lipids in the blood, and in the actions of soaps.





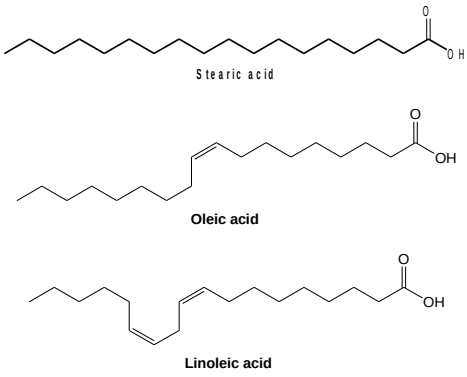
Characteristics of Fatty Acids

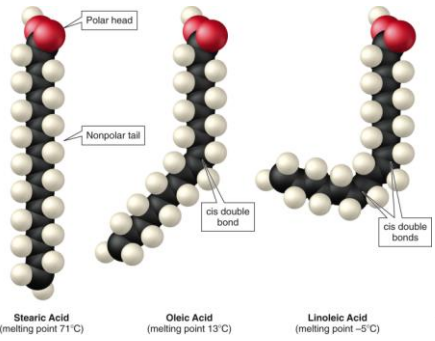
- They are usually have straight chains (no branches) that are about 10 to 20 carbon atoms in length.
- They usually have an even number of carbon atoms (counting the carboxyl carbon).
- The carbon chains may be saturated (all single bonds) or unsaturated (containing double bonds). Other than the carboxyl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



Saturated and Unsaturated Fatty Acids

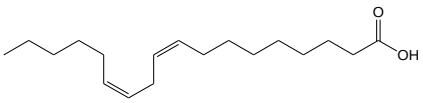
- The *cis*-double bonds in unsaturated fatty acids put an inflexible "kink" in the carbon chain, preventing the molecules from packing together as tightly as saturated fatty acids do.
  - For example, stearic acid (saturated), oleic acid (one double-bond), and linoleic acid (two double bonds) all have 18 carbons in the chain, but their melting points are drastically different:





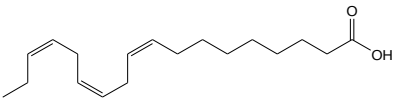
Essential Fatty Acids

- 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 hormonelike substances that regulate blood pressure, blood clotting, blood lipid levels, the immune response, and inflammatory reactions.



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	$CH_3(CH_2)_{12}COOH$	54ºC	Butterfat, coconut oil, nutmeg oil
16	Palmitic acid	$CH_3(CH_2)_{14}COOH$	63ºC	Lard, beef fat, butterfat, cottonseed oil
18	Stearic acid	$CH_3(CH_2)_{16}COOH$	70ºC	Lard, beef fat, butterfat, cottonseed oil
20	Arachidic acid	$CH_3(CH_2)_{18}COOH$	76ºC	Peanut oil
Monounsaturated				
16	Palmitoleic acid	$CH_3(CH_2)_5CH{=}CH(CH_2)_7COOH$	-1ºC	Cod liver oil, butterfat
18	Oleic acid	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	13ºC	Lard, beef fat, olive oil, peanut oil
Polyunsaturated				
18	Linoleic acid	$CH_3(CH_2)_4(CH{=}CHCH_2)_2(CH_2)_6COOH$	-5ºC	Cottonseed oil, soybean oil, corn oil, linseed oil
18	Linolenic acid	$CH_3CH_2(CH{=}CHCH_2)_3(CH_2)_6COOH$	-11ºC	Linseed oil, corn oil
20	Arachidonic acid	$CH_3(CH_2)_4(CH{=}CHCH_2)_4(CH_2)_2COOH$	-50ºC	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

Examples: Saturated and Unsaturated Fatty Acids

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

$CH_3(CH_2)_{14}COOH$

$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$

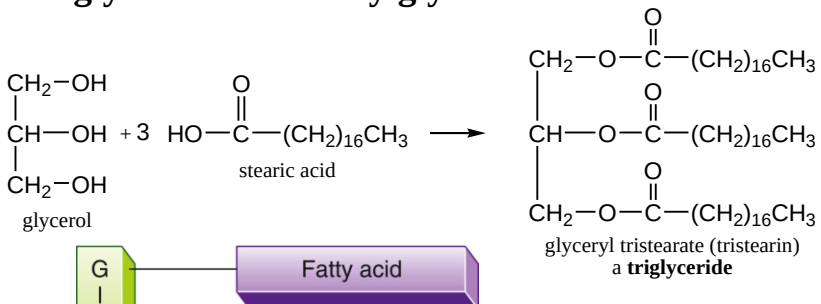
$CH_3(C_{14}H_{24})COOH$

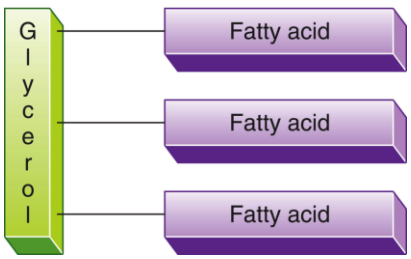
$CH_3(C_{10}H_{20})COOH$

The Structure of Fats and Oils

Triglycerides

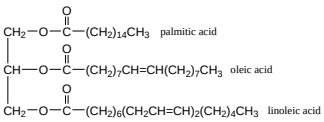
- Animal fats and vegetable oils are esters composed of three molecules of a fatty acid connected to a glycerol molecule, producing a structure called a **triglyceride** or a **triacylglycerol**:





Fats and Oils

- The fatty acids in a triglyceride molecule are usually not all the same; natural triglycerides are often mixtures of many 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 and Oils

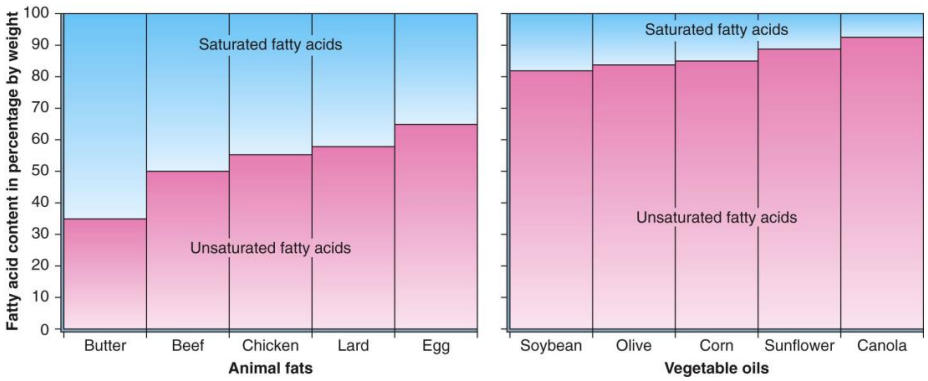
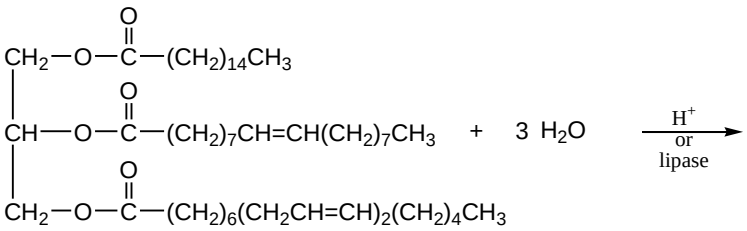


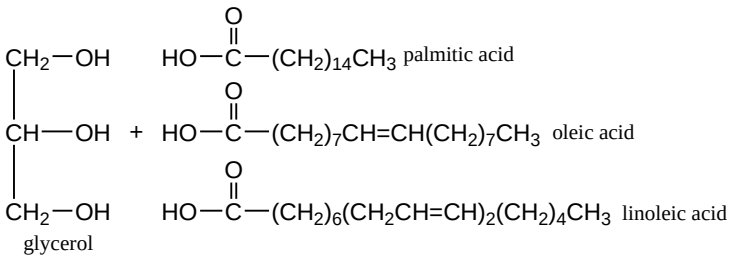
Figure 8.7 A comparison of saturated and unsaturated fatty acids in some foods.

Chemical Properties of Fats and Oils

Hydrolysis of Triglycerides

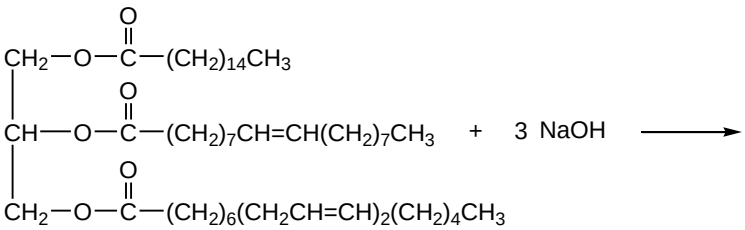
- Triglycerides can be broken apart with water and an acid catalyst (**hydrolysis**), or by digestive enzymes called **lipases**:

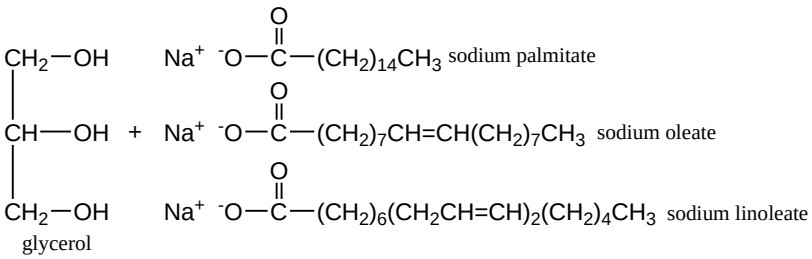




Saponification of Triglycerides

- In **saponification** reactions, triglycerides react with strong bases (NaOH or KOH) to form the carboxylate salts of the fatty acids, called **soaps**:





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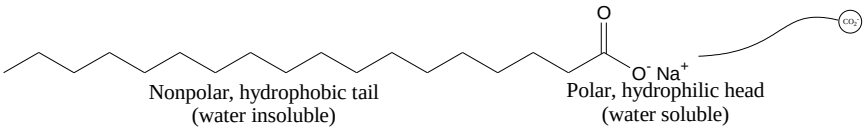
Soaps

- 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."



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

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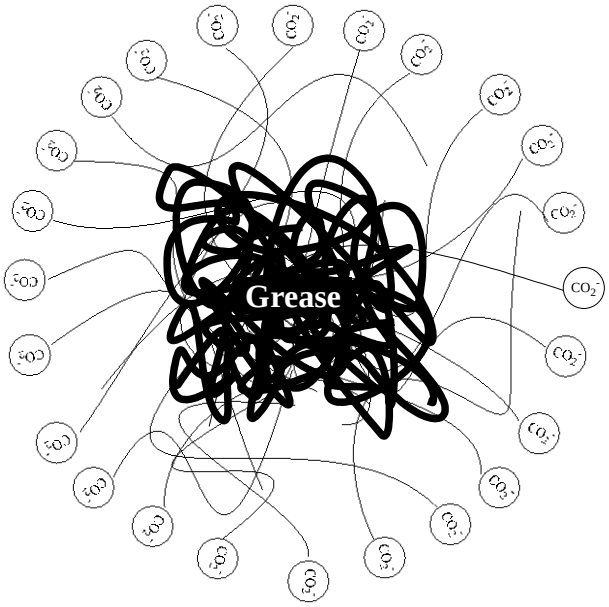
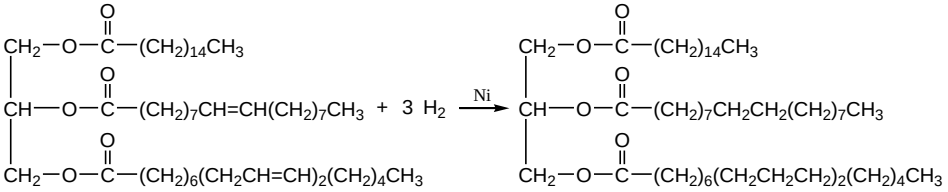
Soaps



a **soap micelle**

Hydrogenation

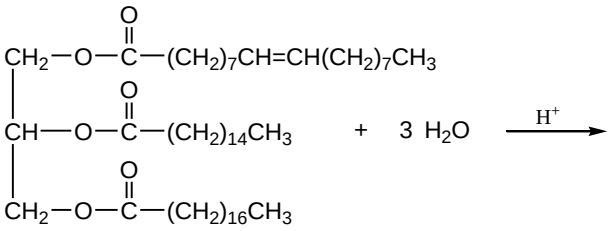
- In **hydrogenation** reactions, alkenes are converted into alkanes with hydrogen gas (H_2) and a catalyst (Pt, Ni, or some other metal). This process is used to convert unsaturated vegetable oils, which are liquids at room temp., to saturated fats, which are solids at room temp. (shortening, etc.).

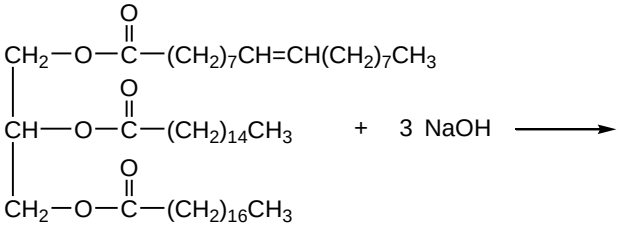


- In *partially hydrogenated vegetable oils*, not all of the double bonds are saturated, allowing the texture of the product to be controlled. In the process, this twists some of the naturally-occurring *cis* double bonds into *trans* isomers (*trans* fats).

Examples: Reactions of Triglycerides

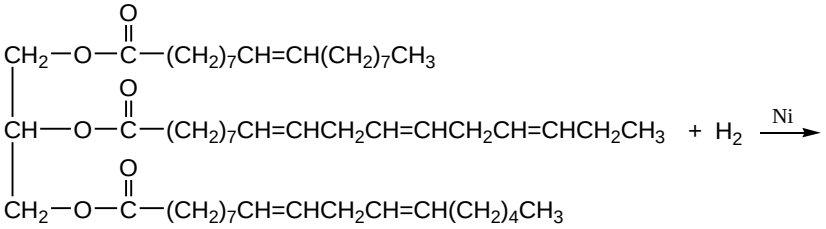
- Write the products of the following reactions:





Examples: Reactions of Triglycerides

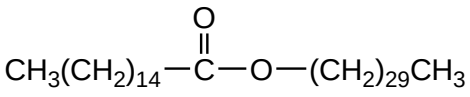
- Write the products of the following reactions:



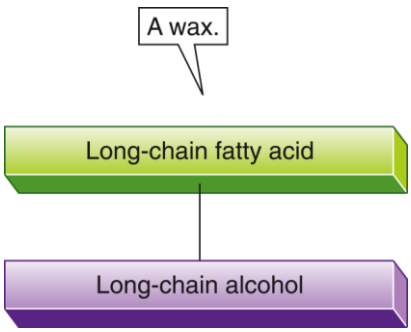
Waxes

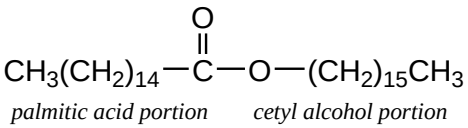
Waxes

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



myricyl palmitate — found in beeswax

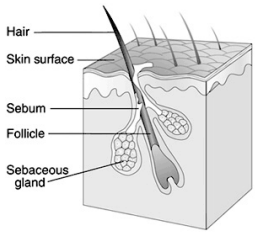




cetyl palmitate — found in spermaceti oil

Waxes

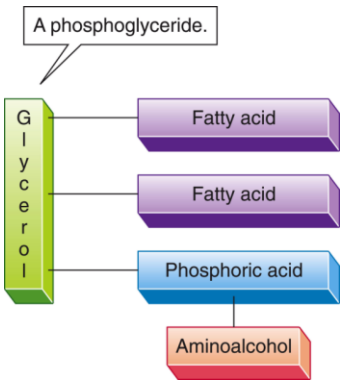
- Waxes are insoluble in water, and not as easily hydrolyzed as fats and oils. They often occur in nature as protective coatings on feathers, fur, skin, leaves, and fruits.
- Sebum, secreted by the sebaceous glands of the skin, contains waxes that help to keep skin soft and prevent dehydration.
- Waxes are used commercially to make cosmetics, candles, ointments, and protective polishes.

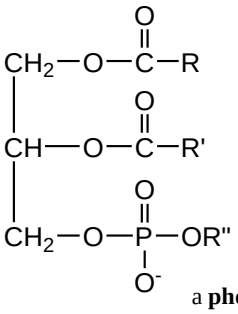


Phosphoglycerides

Phosphoglycerides

- **Phosphoglycerides** are complex lipids that are major components of cell membranes. Phosphoglycerides and related compounds are also called **phospholipids**.

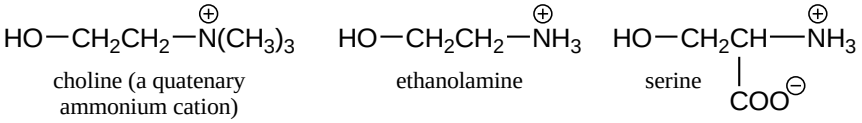




a **phosphoglyceride**

Aminoalcohols in Phosphoglycerides

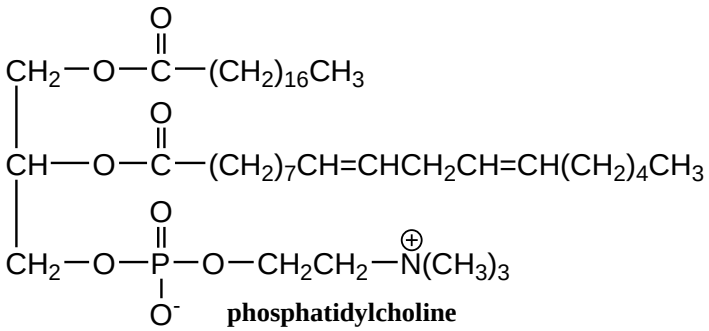
- The most abundant phosphoglycerides contain the alcohols *choline*, *ethanolamine*, or *serine* attached to the phosphate group:



choline (a quatenary ammonium cation) | ethanolamine | serine

Lecithin

- Phosphoglycerides that contains the aminoalcohol choline are called **lecithins**:



phosphatidylcholine

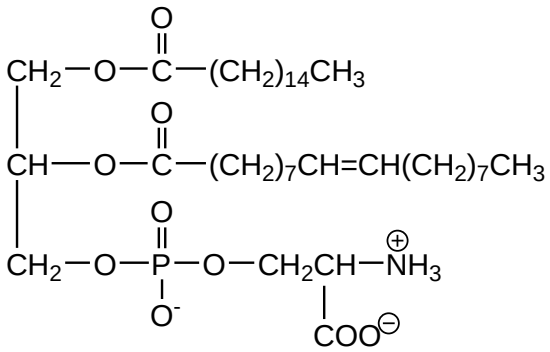
- The fatty acids at the first and second positions are variable, so there are a number of different possible lecithins.

Lecithin

- Because lecithins contain negatively charged oxygen atoms in the phosphate group and positively charged nitrogen atoms in the quaternary ammonium salt group, that end of the molecule is highly hydrophilic, while the rest of the molecule is hydrophobic.
- This allows lecithin to act as an emulsifying agent:
  - forms an important structural component of cell membranes.
  - forms micelles which play a role in the transport of lipids in the blood stream.
  - Commercially, lecithin extracted from soybeans is used as an emulsifying agent in margerine and candies to provide a smooth texture.

Cephalin

- Phosphoglycerides that contains the aminoalcohols ethanolamine or serine are called **cephalins**:

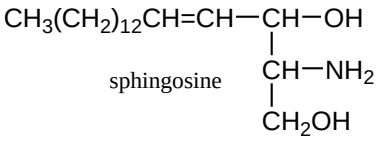


- Cephalins are found in most cell membranes, and are particularly abundant in brain tissue. They are also found in blood platelets, and play a role in blood-clotting.

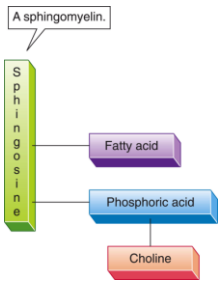
Sphingolipids

Sphingolipids

- **Sphingolipids** are complex lipids that contain sphingosine instead of glycerol.

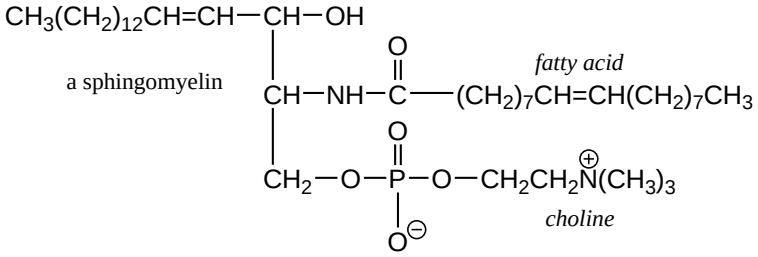


- One important type of sphingolipds are the *sphingomyelins*:



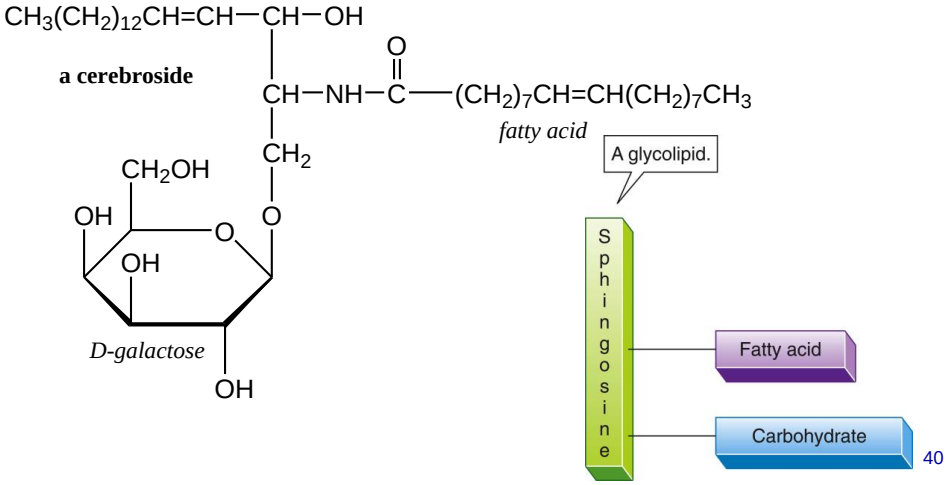
Sphingomyelin

- In the sphingomyelins, a choline is attached to sphingosine through a phosphate group, along with a single fatty acid attached to the sphingosine N via an amide linkage.
- Sphingomyelins are found brain and nerve tissue, and in the myelin sheath that protects nerves.



Glycolipids

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



Biological Membranes

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Cell Structure

- Cells are tiny membrane-enclosed units of fluid.
- **Prokaryotic cells** are found in bacteria and cyanobacteria. They lack a nucleus or organelles.
- **Eukaryotic cells** make up the tissues of other organisms. They are more complex cells, containing a nucleus and other organelles.
- The external cell membrane acts as a selective barrier between the cell and its environment, enclosing the cellular fluid (cytoplasm) and organelles.
- Internal membranes enclose the **organelles**, creating cellular compartments that have separate organization and functions.

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Cellular Organelles

Organelle	Function
Endoplasmic reticulum	Synthesis of proteins, lipids, and other substances
Lysosome	Digestion of substances taken into cells
Microfilaments and microtubules	Cellular movements
Mitochondrion	Cellular respiration and energy production
Nucleus	Contains hereditary material (DNA), which directs protein synthesis
Plastids	Contain plant pigments such as chlorophyll (photosynthesis)
Ribosome	Protein synthesis

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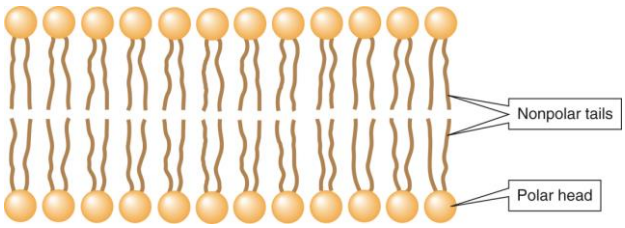
Membrane Structure

- Most cell membranes contain about 60% lipids and 40% proteins:
  - phosphoglycerides (e.g., lecithin and cephalin)
  - sphingomyelin
  - cholesterol
- The **fluid-mosaic model** of the cell pictures 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.



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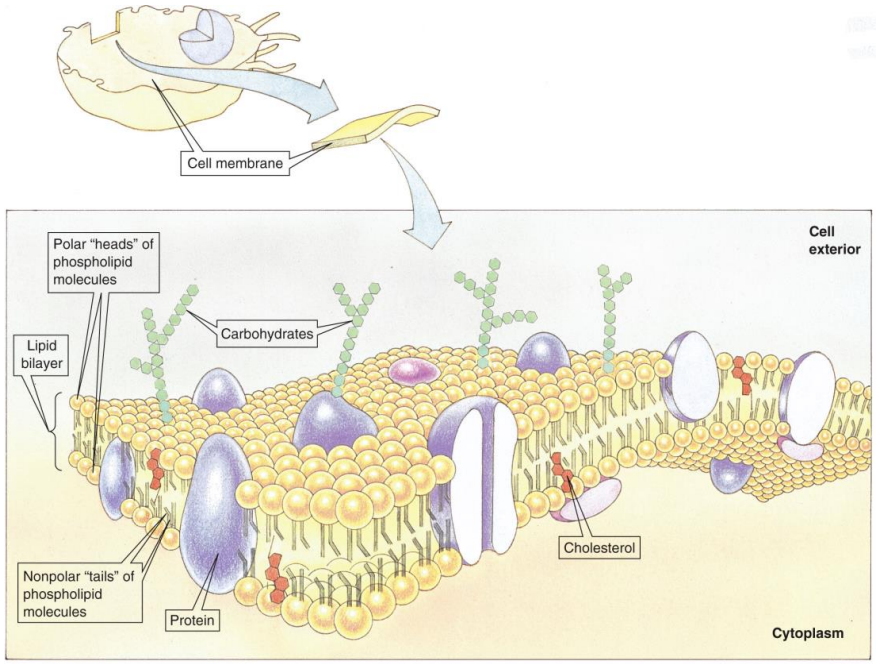
Membrane Structure

  - When the membrane is broken, the repulsion between the nonpolar portion and water causes the membrane to re-form.

- Cell membranes also contain unsaturated fatty acid chains that increase the flexibility or fluidity of the membrane.
- Some of the proteins in the membrane "float" in the lipid bilayer like icebergs, while others extend through the bilayer.
- The lipid molecules are free to move laterally within the bilayer like dancers on a crowded dance floor.

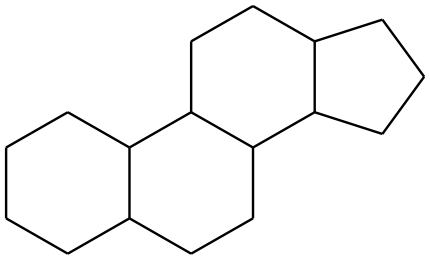
The Fluid-Mosaic Model



Steroids

Steroids

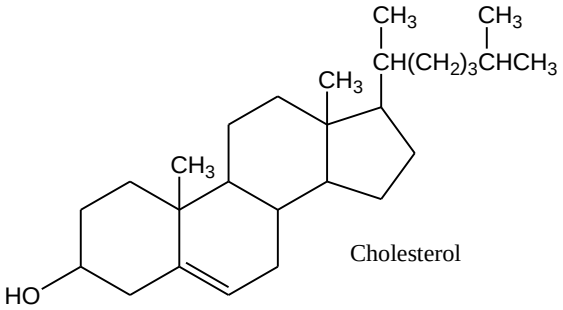
- **Steroids** are classified as lipids because they are soluble in nonpolar solvents, but they are non-saponifiable because the components are not held together by ester linkages.
- The basic steroid structure contains four fused rings:



steroid ring system

Cholesterol

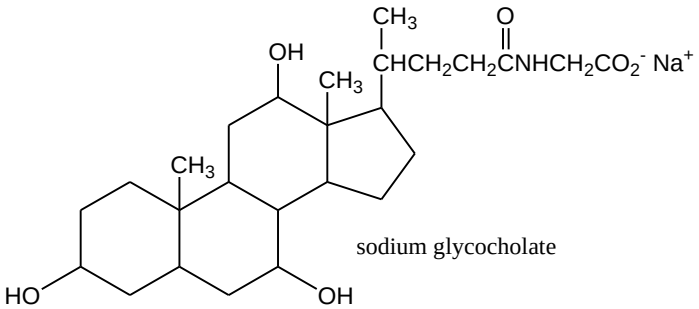
- **Cholesterol** is the most abundant steroid in the body. It is an essential component of cell membranes, and is a precursor for other steroids, such as the bile salts, sex hormones, vitamin D, and the adrenocorticoid hormones.
- There is apparently a correlation between high levels of cholesterol in the blood and atherosclerosis.



Cholesterol

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

Gallstones

- Bile salts also emulsify cholesterol in the bile, so it can be removed in the small intestine. If cholesterol levels are too high or the levels of bile salts is too low, the cholesterol precipitates and forms gallstones.
  - Gallstones can block the duct that allows bile to be secreted into the duodenum. Fats are no longer digested properly, and bile pigments absorbed into the blood causes the skin to become yellow and the stool to become gray.

Steroid Hormones and Prostaglandins

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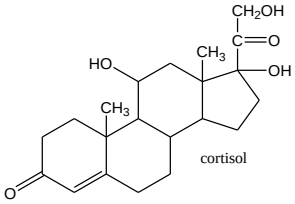
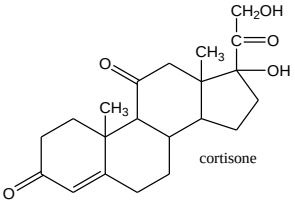
Adrenocorticoid Hormones

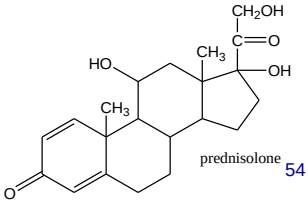
- **Hormones** are chemicals released by cells or glands in one part of the body that send out messages that affect cells in other parts of the body. Many hormones are based on steroids.
- The **adrenocorticoid hormones** are produced in the adrenal glands (located on the top of the kidney).
  - Glucocorticoids 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.



cortisol



cortisone



prednisolone

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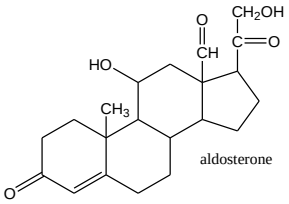
Adrenocorticoid Hormones

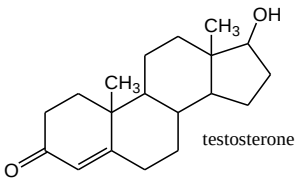
– **Mineralocorticoids** regulate ion concentration (mainly Na^+). Aldosterone influces the absorption of Na^+ and Cl^- in kidney tubules, thus regulating the retention of water in the body.



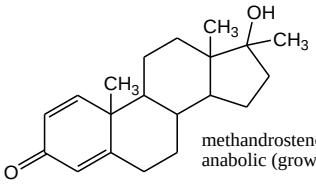
aldosterone

Sex Hormones

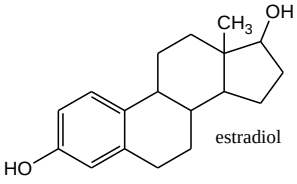
- **Sex hormones** produced in the testes and ovaries regulate the production of sperm and eggs and aid in the development of secondary sex characteristics.



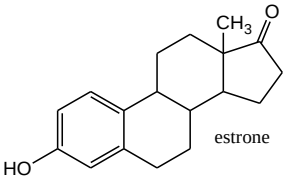
testosterone



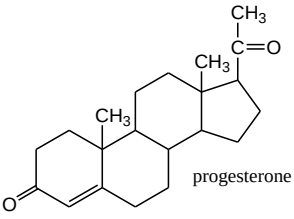
methandrostenolone — a synthetic anabolic (growth-promoting) steroid



estradiol



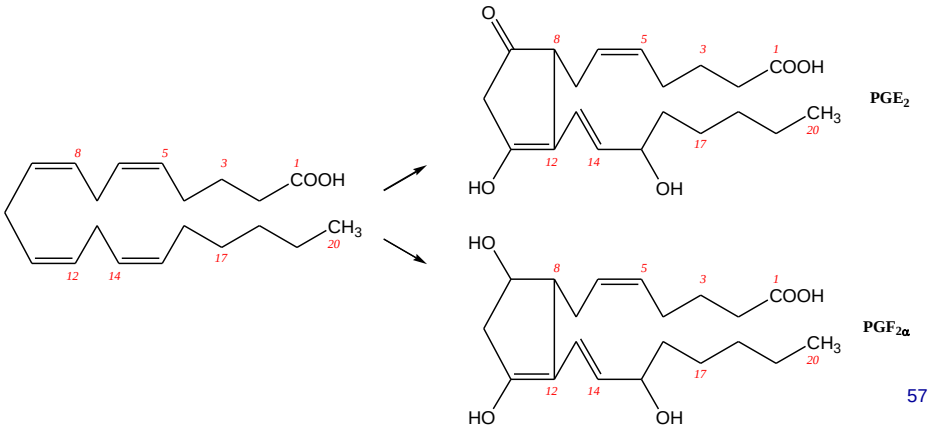
estrone



progesterone

Prostaglandins

- Prostaglandins are cyclic compounds synthesized from arachidonic acid. Like hormones, they are involved in a host of body processes, including reproduction, blood clotting, inflammation, and fever. (Aspirin works by inhibiting prostaglandin production, alleviating inflammation and fever.)



The End