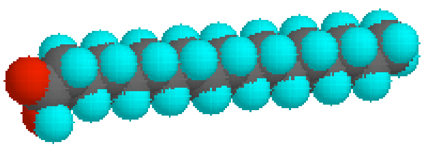
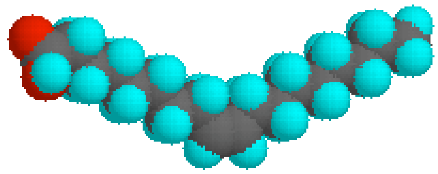
Lipids

Lipids are organic compounds that contain hydrocarbons which are the foundation for the structure and function of living cells. Lipids are non polar so they are soluble in nonpolar environments thus not being water soluble because water is polar.

Fatty Acids



Stearic acid
An 18-carbon fatty acid
with no double bonds



Oleic acid
An 18-carbon fatty acids
with one double bond

Fatty acids are "carboxylic acids (or organic acid), often with a long aliphatic tails (long chains), either saturated or unsaturated."[1] When a fatty acid is saturated it is an indication that there are no carbon-carbon double bonds and if the fatty acid is saturated it is an indication that it has at least one carbon-carbon double bond. As the following data indicate, the saturated acids have higher melting points than unsaturated acids of corresponding size. If a fatty acid has more than one double bond then this is an indication that it is a **polyunsaturated fatty acid**. The fatty acids most frequently found in nature are shown in the table below. "Most naturally occurring fatty acids contain an even number of carbon atoms and are unbranched."[2]

FATTY ACIDS

Saturated			Unsaturated		
Formula	Common Name	Melting Point	Formula	Common Name	Melting Point
$CH_3(CH_2)_{10}CO_2H$	lauric acid	45 ºC	$CH_3(CH_2)_5CH{=}CH(CH_2)_7CO_2H$	palmitoleic acid	0 ºC
$CH_3(CH_2)_{12}CO_2H$	myristic acid	55 ºC	$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H$	oleic acid	13 ºC
$CH_3(CH_2)_{14}CO_2H$	palmitic acid	63 ºC	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7CO_2H$	linoleic acid	-5 ºC
$CH_3(CH_2)_{16}CO_2H$	stearic acid	69 ºC	$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7CO_2H$	linolenic acid	-11 ºC
$CH_3(CH_2)_{18}CO_2H$	arachidic acid	76 ºC	$CH_3(CH_2)_4(CH{=}CHCH_2)_4(CH_2)_2CO_2H$	arachidonic acid	-49 ºC

Saturated fatty acids have higher melting points due to their ability to pack their molecules together thus leading to a straight rod-like shape. Unsaturated fatty acids on the other hand have cis-double bond(s) that create a kink in their structure which doesn't allow them to group their molecules in straight rod-like shape.

Question: Of the following pairs identify the one with the higher melting point?
a. palmitic acid and stearic acid
b. lauric acid and oleic acid
c. arachidic acid and arachidonic acid

1. http://en.wikipedia.org/wiki/Fatty_acid (09/06/2006)
2. http://www.cem.msu.edu/%7Ereusch/VirtualText/lipids.htm#fatacid (09/06/2006)

Waxes

Waxes are "esters formed from long-chain carboxylic acids and long-alcohols" (Bruice, Pg 1078). Three of the more common waxes seen are shown below.

spermaceti	beeswax	carnuba wax
$CH_3(CH_2)_{14}CO_2\text{-}(CH_2)_{15}CH_3$	$CH_3(CH_2)_{24}CO_2\text{-}(CH_2)_{29}CH_3$	$CH_3(CH_2)_{30}CO_2\text{-}(CH_2)_{33}CH_3$
From the head of sperm whales	Structural material of beehives	Coating on the leaves of Brazilian palm

Waxes are seen all over in nature. "The leaves and fruits of many plants have waxy coatings, which may protect them from dehydration and small predators. The feathers of birds and the fur of some animals have similar coatings which serve as a water repellent. Carnuba wax is valued for its toughness and water resistance"[3] (great for car wax).

Fats and Oils

Triacylglycerols are the products of a reaction in which three OH groups of glycerol are esterfied with fatty acids. "A **simple triacylglycerol** is a triacylglycerol with three of the same fatty acid components. A **mixed triacylglycerol** is a triacylglycerol that contains two or three different fatty acid components and are more common than simple triacylglycerols" (Bruice, Pg. 1078). **Fat** is the name given to a class of triglycerides that appear as solid or semisolid at room temperature, fats are mainly present in animals. **Oil** is the name given to class triglycerides that appear as a liquid at room temperature, oils are mainly present in plants and sometimes in fish.

- The fact that saturated fatty acid tails can bunch up closely together, its allows the triacylglycerols relatively high melting points, which in turn allows them to appear as solids at room temperature.
- The opposite goes for unsaturated fatty acids, their tails cannot pack as closely together so in turn they have relatively low melting points which causes them to appear as liquids at room temperature.
- Fats usually consist of *saturated* fatty acids while oils usually consist of *unsaturated* fatty acids.

By a process known as catalytic hydrogenation some or all of the double bonds of the polyunsaturated oils can be reduced which will allow them to be solids at room temperature. (Bruice, Pg. 1079)

$$RCH{=}CHCH_2CH{=}CHCH_2CH{=}CH\text{-} \xrightarrow[Pt]{H_2} RCH_2CH_2CH_2CH{=}CHCH_2CH_2CH_2\text{-}$$

Margarine and shortening originate from vegetable oils (i.e. soybean oil and safflower oil) that have been hydrogenated. This process is called "hardening of oils." When fats are consumed the body hydrolysis's the dietary fat in the intestine which regenerates the glycerol and fatty acids (Bruice, Pg. 1079). "**Soaps** are sodium or potassium salts of fatty acids. Thus, soaps are obtained when fats or oils are hydrolyzed under basic conditions" (Bruice, Pg. 700).

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[3]. http://www.cem.msu.edu/%7Ereusch/VirtualText/lipids.htm#wax (09/06/2006)

How does soap work?

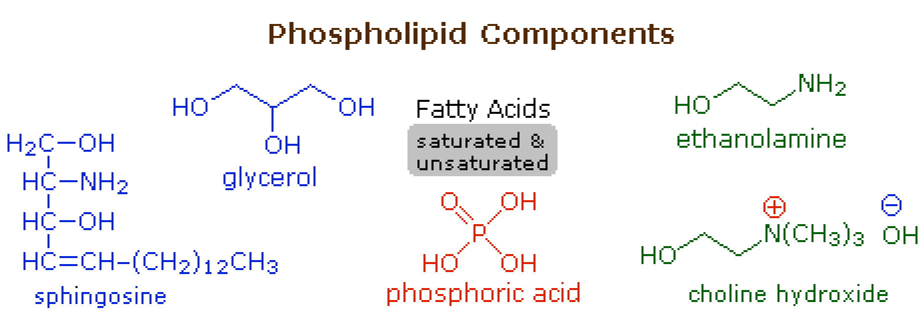
- "Carboxylic acids and salts having alkyl chains longer than eight carbons exhibit unusual behavior in water due to the presence of both hydrophilic (water loving) (CO_2) and hydrophobic (water fearing) (alkyl) regions in the same molecule."[4]
- "Nonpolar hydrocarbon chains attracted to nonpolar grease/oil or other stearate chains" (Pg. 92 of the summer 2006 Thinkbook by Dr. S. Hardinger).
- "The surfactant molecules reversibly assemble into polymolecular aggregates called **micelles.**"[4]
- The fact that soaps have hydrophobic and hydrophilic regions allows them to wet all of the areas of an object so it can be cleaned; the job of the micelles is removing the dirt in areas that are not water soluble.
- Problem- the contents of our supply of water includes calcium and magnesium, which allows for the derivation of the words "hard water." "These divalent cations cause aggregation of the micelles, which then deposit as a dirty scum."[4]
- Solution- the use of detergents because of their greater solubility.

Membranes

Membranes are lipid bilayers that act as a boundary to various cellular structures; however they also allow for careful transfer of ions and organic molecules into and out of the cell (Bruice, Pg. 1082).

Phospholipids

Membranes are chiefly made of phospholipids which are **Phosphoacylgycerols**. Triacylglycerols and phosphoaclyglycerols are similar however the terminal OH group of the phosphoaclyglycerol is esterfied with phosphoric acid instead of a fatty acid which leads to the formation of **phosphatidic acid**. The name **phospholipid** comes from fact that phosphoaclyglycerols are lipids that contain a phosphate group.



- **Hydrophobic effect**: "Hydrophobic lipid tails avoid water but associate with each other, resulting in phospholipid bilayer" (shown below) (Pg. 9. of the summer 2006 Thinkbook by Dr. S. Hardinger).

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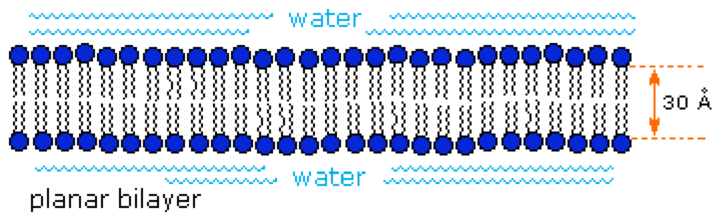
4. http://www.cem.msu.edu/%7Ereusch/VirtualText/lipids.htm#soap (09/06/2006)



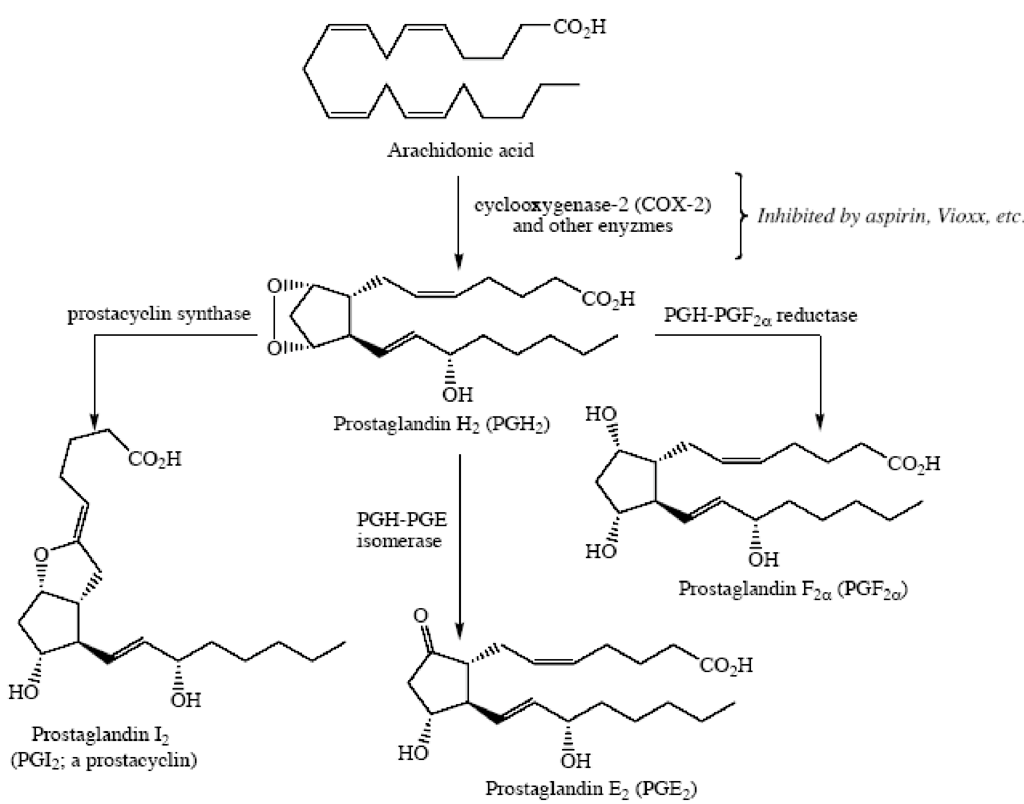
The blue circles are the hydrophilic heads and the black zig zag lines are the hydrophobic tails.

- Main biological function: Their role as a cell membrane

Prostaglandins

Prostaglandin is "any member of a group of lipid compounds that are derived enzymatically from fatty acids and have important functions in the animal body. Every prostaglandin contains 20 carbon atoms, including a 5-carbon ring."[5] Prostaglandins are responsible for an array of physiological effects, such as inflammation, blood pressure (PGE2, see below for structure), blood clotting (PGI2, see below for structure), fever, pain, the induction of labor (PGF2alpha, see below for structure), and sleep-wake cycle. (Bruice, Pg. 1085).

- Shown below is the wound response which is when arachidonic acid cascade leads to inflammation (Pg. 94 of the summer 2006 Thinkbook by Dr. S. Hardinger.)



(Source: Pg. 94 of the summer 2006 Thinkbook by Dr. S. Hardinger.)

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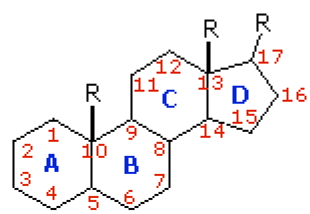
5. http://en.wikipedia.org/wiki/Prostaglandin (09/06/2006)

- Prostaglandins are named by following the PGX formula, where X designates the functional groups of the five-membered ring. PGAs, PGBs, and PGCs all contain a carbonyl group and a double bond in the five-membered ring. The location of the double bond determines whether a prostaglandin is PGA, PGB, OR PGC. PGDs and PGEs are beta-hydroxy ketones, PGFs are 1,3 diols. The subscript indicates the total number of double bonds in the side chains, and the "alpha" and "beta" indicates a cis diol and trans diol respectively. (Bruice, Pg. 1085)

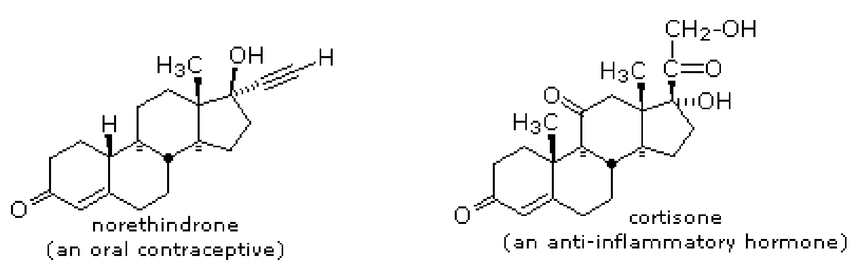
Steroids

The chemical messengers in our bodies are known as **Hormones** which are organic compounds synthesized in glands and delivered by the bloodstream to certain tissues in order to stimulate or inhibit a desired process. **Steroids** are a type of hormone which are usually recognized by their tetracyclic skeleton, consisting of three fused six-membered and one five-membered ring, as shown in the diagram below. The four rings are designated A, B, C & D as noted in blue, and the numbers in red represent the carbons.[6]

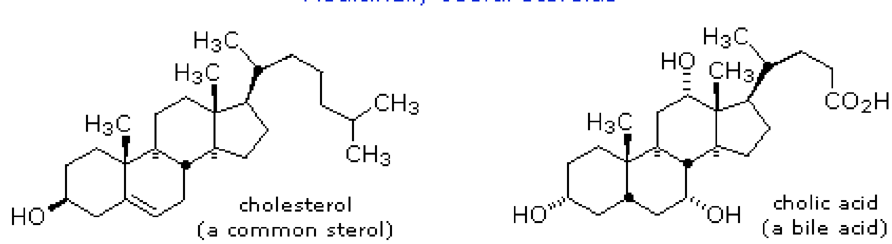


The Steroid
Carbon Skeleton

All steroids are products from the acetyl CoA biosynthetic pathway (see Pg. 95 of summer 2006 Thinkbook or Pg. 1101 in the Bruice 4th edition for the biosynthesis pathway diagram) which yields cholesterol.[7] Cholesterol is the most common steroid encountered by animals (Bruice, Pg. 1098). Some important steroids are shown below.



Medicinally Useful Steroids



Typical Animal Steroids

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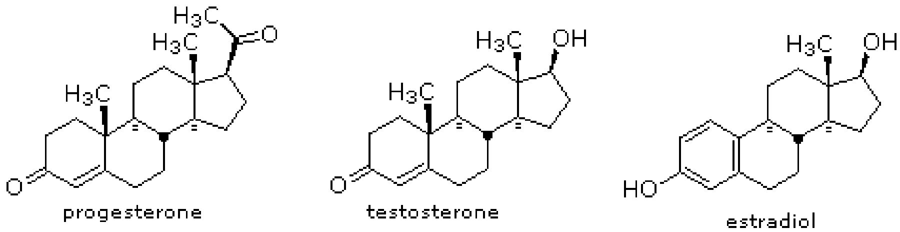
6. http://www.cem.msu.edu/%7Ereusch/VirtualText/lipids.htm#steroid (09/06/2006)
7. http://en.wikipedia.org/wiki/Steroid (09/06/2006)

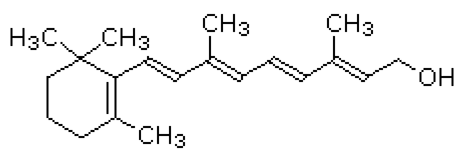


Steroid Sex Hormones

Lipophilic Vitamins

Vitamin: "An organic compound, other than fat, protein or carbohydrates, required for the normal growth maintenance of animals." (Pg. 97 of the summer 2006 Thinkbook by Dr. S. Hardinger). Vitamins A, D, E, and K are in the lipid family. (Bruice, pg. 1090)

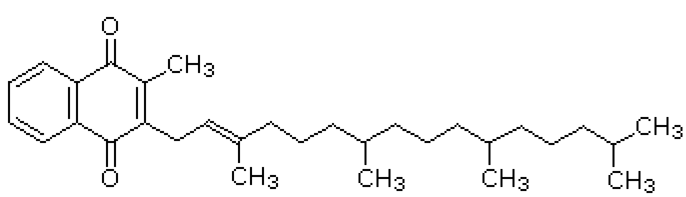
- Beta-Carotene is sliced to create two molecules of vitamin A. Vitamin A, which is also known as retinol, serves its main purpose in contributing to vision (Bruice, Pg. 1090). It works together with the light-harvesting portion of rhodopsin (vision protein) (Pg. 97 of the summer 2006 Thinkbook by Dr. S. Hardinger).



vitamin A

$C_{20}H_{30}O$ part of the visual pigment

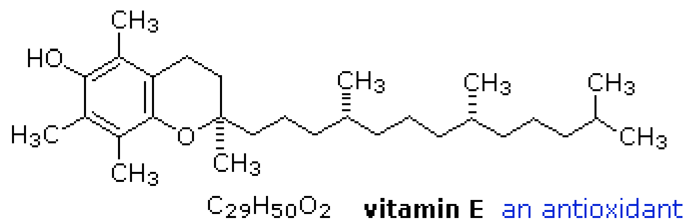
- Vitamin K plays a key role in allowing blood to clot properly. The letter K is derived from *koagulation,* which is German for "clotting." (Bruice, Pg. 1068).



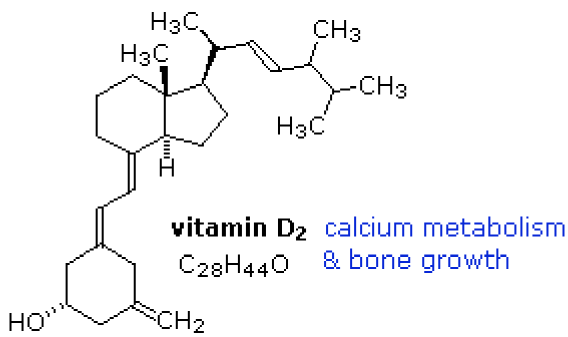
vitamin K_1 a blood clotting factor

$C_{31}H_{46}O_2$

- Vitamin E is a water-soluble compound that holds radicals in nonpolar membranes. Some of these are which we encounter everyday in our daily food consumption are known as *preservatives* or *antioxidants*. They are used to preserve food by preventing unwanted radical reactions (Bruice, Pgs. 352-353). "It also prevents oxidative cellular damage from radicals" (Pg. 97 of the summer 2006 Thinkbook by Dr. S. Hardinger).



- Vitamin D is a hormone foundation such that its main purpose is to help maintain normal levels of calcium and phosphorus in the blood. Vitamin D also contributes in keeping a strong and sturdy skeleton.[8]



Other Sources

1. P.Y. Bruice *Organic Chemistry (4th)*
2. All colored pictures, diagrams and tables were copied from, http://www.cem.msu.edu/%7Ereusch/VirtualText/lipids.htm last accessed on September 6, 2006.

[8]. http://en.wikipedia.org/wiki/Vitamin_D (09/06/2006)