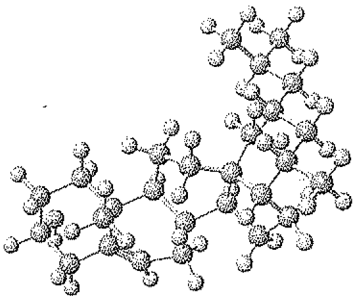


CHAPTER 15

Lipids

15.1 The Nature of Lipids

Although the human body, as well as other organisms, is composed primarily of water, about 70% by weight in animals, the organic biomolecules that constitute the remaining 30% are part of a complex mixture that supports, protects, regulates, directs, and defends the whole entity. Among these is the class known as **lipids.** The functions of lipids range from energy source to membrane formation. Even so, lipids have a very general chemical definition. They are organic molecules soluble to a great extent in nonpolar solvents such as diethyl ether, chloroform, carbon tetrachloride, or benzene. These solvents are used to extract lipids from their more polar neighbors: salts, proteins, carbohydrates, and nucleic acids. A key structural component of all lipids is a large proportion of carbon-carbon and carbon-hydrogen bonds. This makes these compounds hydrophobic (literally "water-fearing") rather than hydrophilic ("water-loving") as are most carbohydrates, proteins, and nucleic acids. Within this loose definition are subcategories such as polar and nonpolar lipids, saponifiable and nonsaponifiable lipids, simple and complex lipids.

lipid
organic biomolecules soluble to a great extent in nonpolar solvents

- *Nonpolar lipids* are those with few or no polar bonds. Examples include fats and oils, waxes, and some steroids.
- *Polar lipids* have both polar and nonpolar bonds allowing for limited solubility both in polar and nonpolar solvents. Examples are the phospho- and sphingolipids.
- *Saponifiable lipids* are those that can undergo hydrolysis in the presence of a base such as NaOH or KOH. Fats, oils, and waxes, as well as phospho- and sphingolipids, are saponifiable.
- *Nonsaponifiable lipids* will not be hydrolyzed in the presence of base. Most steroids are nonsaponifiable.
- *Simple lipids* have relatively uncomplex structures and either will not be broken down by chemical processes or can be broken down into a limited number of simple compounds. Examples are the steroids and fats and oils.
- *Complex lipids* are those with variations in their structures; they can be broken down into several simpler compounds. Sphingolipids are complex.

nonpolar lipid
lipid with few or no polar bonds

polar lipid
lipid with both polar and nonpolar bonds allowing for limited solubility in polar and nonpolar solvents

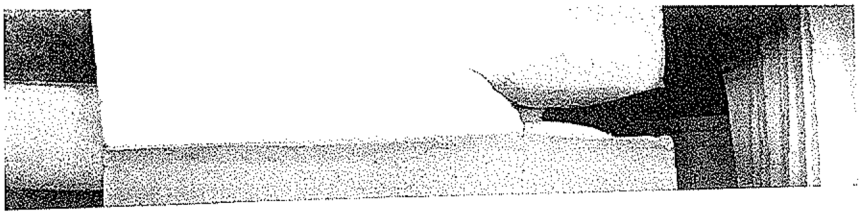
saponifiable lipid
lipid that can undergo hydrolysis to simpler compounds in the presence of a base such as NaOH or KOH

nonsaponifiable lipid
lipid that cannot be hydrolyzed in the presence of base

simple lipid
lipid with relatively uncomplex structure; it either will not be broken down by ordinary chemical processes or can be broken down into a limited number of simple compounds

complex lipid
lipid that can have variations in its structure and can be broken down into several types of simpler compounds

This chapter will cover most of the major structural variations possible for lipids and their functions.



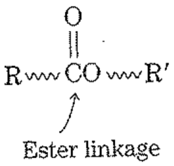
GETTING INVOLVED

- ✓ What is a good, generic definition of lipids that includes their chemical properties and structures?
- ✓ How does a lipid differ in fundamental structure from a carbohydrate or protein?
- ✓ Differentiate between the members of each pair of lipid types:
  - polar and nonpolar lipids
  - simple and complex lipids
  - saponifiable and nonsaponifiable lipids

15.2 Waxes—Simple Esters of Long-Chain Alcohols and Acids

wax
ester of a long-chain carboxylic acid and a long-chain alcohol

Structurally, **waxes** are defined as esters of long-chain carboxylic acids and long-chain alcohols. They are simple, nonpolar, and saponifiable.

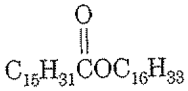


$$R\sim\overset{O}{\overset{\|}{C}}O\sim R'$$

Ski waxing

Natural waxes differ from paraffin wax in that they are high-molecular-weight esters produced directly by living organisms, whereas paraffin wax is a mixture of high-molecular-weight hydrocarbons separated during the fractionation of petroleum. Following are some representative natural waxes and the structures of their principal components.

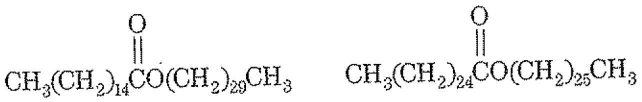
1. *Spermaceti.*



$$C_{15}H_{31}\overset{O}{\overset{\|}{C}}OC_{16}H_{33}$$

Spermaceti is a soft wax obtained from the head of the sperm whale; it has a melting range of 42–50°C. It consists largely of cetyl palmitate (above). Because of its softness, it can be used as a base emollient for ointment medications and cosmetics. Also, like paraffin wax, it is used in the production of candles.

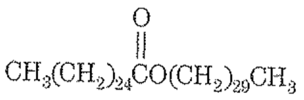
2. *Beeswax.* Beeswax is taken from the honeycomb and is a mixture of esters of alcohols and acids having up to 36 carbons and some high molecular weight hydrocarbons.



$$CH_3(CH_2)_{14}\overset{O}{\overset{\|}{C}}O(CH_2)_{29}CH_3 \qquad CH_3(CH_2)_{24}\overset{O}{\overset{\|}{C}}O(CH_2)_{25}CH_3$$

Beeswax has a melting range of 62–65°C and is used in shoe polishes, candles, wax paper, and the manufacture of artificial flowers.

3. *Carnauba wax.* Carnauba wax is a very hard wax capable of producing a high polish; it has a melting range of 82–86°C. It is obtained from the leaves of the Brazilian palm tree and is used in automobile and floor waxes and in deodorant sticks. When carnauba wax is hydrolyzed, some hydroxy acids are produced, indicating the presence of large polyesters in the wax; these could contribute to its hardness and durability.



$$CH_3(CH_2)_{24}\overset{\overset{\displaystyle O}{\|}}{C}O(CH_2)_{29}CH_3$$

GETTING INVOLVED

- ✓ What is the principal organic functional group in waxes?
- ✓ Why are waxes classified as lipids?

Problem 15.1

Write chemical reactions for the hydrolysis (saponification) of the lipids in beeswax (see sections 13.6(a–b)).

15.3 Fats and Oils—Triesters of Glycerol

Fats and **oils** of either animal or vegetable origin are triesters of the trihydroxy alcohol, glycerol. Consequently they are called **triacylglycerols, glycerides,** or **triglycerides.** The acids making up the triester are known as **fatty acids** because of their length, usually 10–24 carbons in higher organisms.

fat
triester of glycerol wherein the acids are long-chain and highly saturated

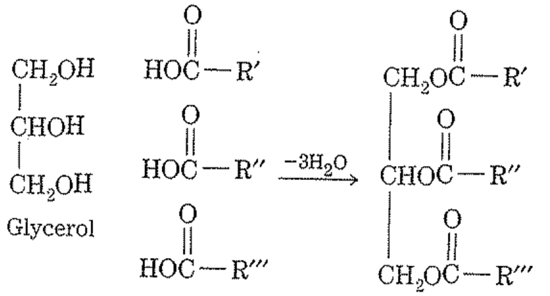
oil
triester of glycerol wherein the acids are long-chain and highly unsaturated

triacylglycerol
see **fat** and **oil**

glyceride
see **fat** and **oil**

triglyceride
see **fat** and **oil**

fatty acid
long-chain (10–24) carboxylic acid



Fatty acids A fat or oil (triester of glycerol)

The biosynthesis of fatty acids starts with the two-carbon acetate unit, so the final product has an even number of carbons linked in an unbranched chain. Bacteria are known to produce not only fatty acids with an odd number of carbons, but also ones with branched and cyclic chains. The fatty acids in a triglyceride may be the same or may differ.

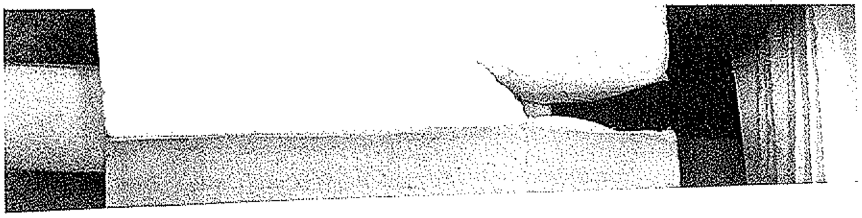
Fats and oils are structurally alike with one exception; most of the fatty acids in fats are saturated chains, whereas those in oils are unsaturated. A shorthand designation for the various common fatty acids uses a subscript indicating the number of carbons in the chain followed by a colon (:) and the number of double bonds. For example, stearic acid is $C_{18:0}$ and linoleic acid is $C_{18:2}$. See Table 15.1 for other examples.

The position of the double bond can be shown by the symbol delta, Δ, as a superscript with the position of the double bonds. The numbering of the chain begins with the carboxyl group. When more than one double bond is present, the relationship will be allylic; that is, the double bonds will be separated by a methylene group, $-CH_2-$. For example, linoleic acid is $C_{18:2}{}^{\Delta 9,12}$ and arachidonic acid is $C_{20:4}{}^{\Delta 5,8,11,14}$.

Another type of designation that is sometimes used refers to the position of the first double bond starting from the hydrocarbon end or $-CH_3$, called the omega (ω) carbon of the chain. In this case linoleic acid would be an **ω6 fatty acid.** There is currently much study as to the correlation of the amounts of **ω6** and **ω3** triacylglycerols in the diet and decreased risk of heart disease.

omega (ω) 6 fatty acid
an unsaturated fatty acid with its last double bond six carbons in from the methyl end of the chain

omega (ω) 3 fatty acid
an unsaturated fatty acid with its last double bond three carbons in from the methyl end of the chain



Connections 15.1 www.prenhall.com/bailey

Errors in the Metabolism of Fatty Acids—Lorenzo's Oil

In 1992 the movie *Lorenzo's Oil* detailed the real-life struggle of the Odone family, whose young son suffered from an inborn metabolic disorder known as adrenoleukodystrophy (ALD). ALD is an extremely rare condition passed as a recessive X-linked gene through the women in the family. Although carriers may show some mild symptoms of the condition, the actual occurrence is about 1 in 45,000 in the populations of the United States and Europe. At the age of six years, Lorenzo Odone began to show symptoms that could be mistaken for a variety of illnesses: personality disorder and loss of coordination and speech. The film chronicles the efforts of the parents to have their child properly diagnosed and treated for the fatal condition.

The genetic defect is correlated to the accumulation of very-long-chain fatty acids (22–26 carbon range) in the brain and adrenal cortex. One hypothesis is that these fatty acids destroy the myelin sheath of brain nerve fibers, leading to mental and physical deterioration, blindness, seizures, paralysis, and death. The Odones became self-taught experts in the field of lipids and their metabolism, eventually finding that a dietary supplement of a 4:1 mixture of olive oil, which contains oleic acid ($C_{18:1}$) as a major component, and triglycerides of erucic acid ($C_{22:1}^{\Delta 13}$) seemed to help slow the progress of ALD in their son. Erucic acid constitutes 40%–50% of the seeds of rapeseed, mustard, and wallflower and up to 80% of nasturtium seeds.

Although controversial in its development and inconsistent in its effects, this mixture, called Lorenzo's Oil, seems to stabilize low blood concentrations of very-long-chain fatty acids and has impeded the development of ALD in some young patients. The normal course of this affliction is about two years from diagnosis to death. Lorenzo Odone has passed adolescence, although he is in an almost vegetative state. Some others who were treated did not have their condition allayed. Recent controlled studies have shown few if any effects on the progress of a milder form of ALD. However, the devotion and studies of Augusto and Michaela Odone have indicated some possible avenues of research. Augusto is the current director of the Myelin Project.

Table 15.1 Common Fatty Acids

$CH_3(CH_2)_{10}CO_2H$	lauric acid ($C_{12:0}$)
$CH_3(CH_2)_{12}CO_2H$	myristic acid ($C_{14:0}$)
$CH_3(CH_2)_{14}CO_2H$	palmitic acid ($C_{16:0}$)
$CH_3(CH_2)_{16}CO_2H$	stearic acid ($C_{18:0}$)
$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H$	oleic acid ($C_{18:1}^{\Delta 9}$)
$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7CO_2H$	linoleic acid ($C_{18:2}^{\Delta 9,12}$)
$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7CO_2H$	linolenic acid ($C_{18:3}^{\Delta 9,12,15}$)
$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_3CO_2H$	arachidonic acid ($C_{20:4}^{\Delta 5,8,11,14}$)

Table 15.2 lists the composition of familiar triacylglycerols. You can see that oils are usually of plant or marine origin, whereas fats can be commonly found in animal sources. Some triacylglycerols have the same fatty acid at all three positions of esterification. They can be named with that in mind, such as tripalmitin and tristearin. Most naturally occurring fats and oils, however, contain a distribution of fatty acids.

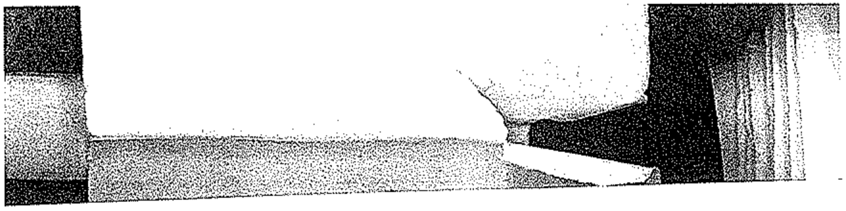
Unsaturation results in a noticeable lowering of the melting point, and hence the formation of an oil, a liquid, at room temperature. This physical difference is due to the structure of the chain. A saturated carbon chain has a staggered, relatively linear nature, which can lead to molecular packing in a semi-solid phase and a higher melting point. The double bonds in oils are geometrically in the *cis* configuration, which "kinks" the chain and makes it difficult to form an organized solid structure. As a result, the melting point is lowered significantly (See Figure 15.1).

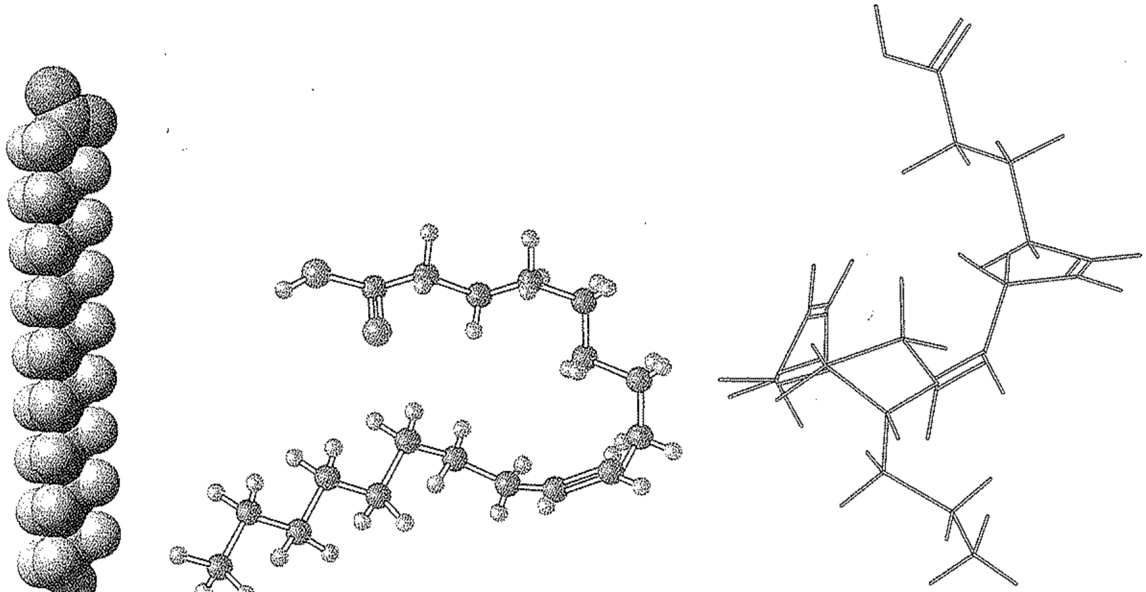
Margarines are produced by the partial catalytic hydrogenation of oils. The hydrogenation process used in the United States up to this time causes isomerization of many of the remaining double bonds from *cis* to *trans*. There may be some adverse health effects from these *trans* fatty acids. European methods of catalytic hydrogenation do not seem to cause such isomerization.

Table 15.2 Fats and Oils

				Percent Fatty Acid Composition[a]							
				Saturated Acids				Unsaturated Acids			
Fat or Oil	Iodine Number	Saponification Number	Melting Point, °C	$C_{12:0}$ Lauric Acid	$C_{14:0}$ Myristic Acid	$C_{16:0}$ Palmitic Acid	$C_{18:0}$ Stearic Acid	$C_{18:1}$ Oleic Acid	$C_{18:2}$ Linoleic Acid	$C_{18:3}$ Linolenic Acid	$C_{17:3}$ Eleostearic Acid
Animal Fats											
Beef tallow	31–47	190–200	40–46		3–6	24–32	20–25	37–43	2–3		
Lard	46–66	193–200	36–42		1	25–30	12–16	41–51	3–8		
Butter	36	227	32	1–4	8–13	25–32	8–13	22–29	0.2–1.5	3	
Marine Animals											
Cod liver oil	145–180	180–190			2–6	7–14	0–1	25–31	27–32		
Whale oil	120	195		0.2	9.3	15.6	2.8		35.8		
Vegetable Oils											
Coconut oil	10	255–258	25	44–51	13–18	7–10	1–4	5–8	0–1	1–3	
Corn oil	109–133	187–196	−20		0.1–1.7	8–12	2.5–4.5	19–49	34–62		
Cottonseed oil	105–114	190–198	−1		0–3	17–23	1–3	23–44	34–55		
Olive oil	79–90	187–196	−6			9.4	2.0	83.5	4.0		
Palm oil	54	199	35		1–6	32–47	1–6	40–52	2–11		
Peanut oil	84–102	188–195	−5			8.3	3.1	56	26		
Soybean oil	127–138	185–195	−16		0.3	7–11	2–5	22–34	50–60		
Linseed oil	179	190	−24		0.2	5–9	4–7	9–29	8–29	45–67	
Tung oil	168	193	−3					4–13		8–15	74–91

[a] These percentages do not include short-chain fatty acids or fatty acids present in minute amounts.





$C_{18:0}$
(a)

$C_{18:1}{}^{\Delta 9}$
(b)

$C_{20:4}{}^{\Delta 5,8,11,14}$
(c)

Figure 15.1 Space-filling, ball-and-stick, and wireframe models of (a) stearic acid, (b) oleic acid, and (c) arachidonic acid, respectively. The *cis* orientation of double bonds in naturally occurring unsaturated fatty acids produce a more rigid, curved molecule that interferes with tight packing for semi-solid structures, as occur in membranes.

GETTING INVOLVED

- ✓ What is the structure of a "fatty" acid?
- ✓ Draw the generic structure of a fat/oil.
- ✓ How are fats and oils the same? How are they different?
- ✓ Do naturally occurring fatty acids have a specific chain length?
- ✓ Why are fats and oils classified as lipids?
- ✓ Write and understand the shorthand designation for saturated and unsaturated fatty acids, that is, what are the meanings of the subscripts and superscripts in $C_n{}^{\Delta m}$, $C_{18:1}{}^{\Delta 9}$, for example?

Example 15.1

What is the shorthand designation for the following fatty acid? Is it an ω3 or ω6 fatty acid?

$$CH_3CH_2CH{=}CHCH_2CH{=}CH(CH_2)_6COOH$$

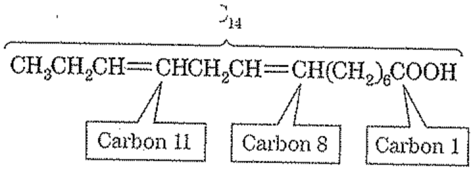
Solution

(a) Count the total number of carbons and the number of double bonds.

$$\overbrace{CH_3CH_2CH{=}CHCH_2CH{=}CH(CH_2)_6COOH}^{C_{14}}$$

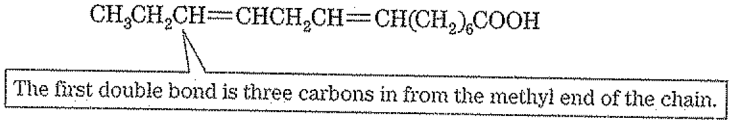
It is a $C_{14:2}$ fatty acid.

vith the carboxyl group. Number the double
ed organic compound.



$$\overbrace{CH_3CH_2CH{=}CHCH_2CH{=}CH(CH_2)_6COOH}^{C_{14}}$$

This is a $C_{14:2}{}^{\Delta 8,11}$ fatty acid.



$$CH_3CH_2CH{=}CHCH_2CH{=}CH(CH_2)_6COOH$$

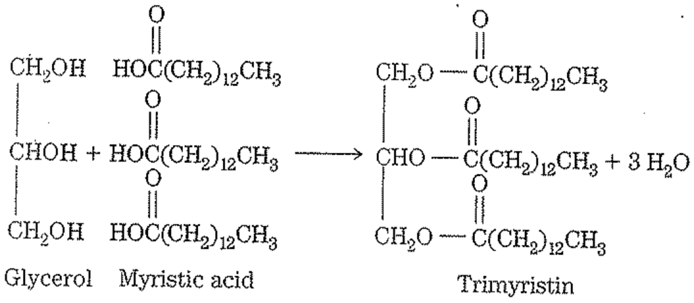
It is an ω3 fatty acid.

Example 15.2

Draw the structure of trimyristin, the fat found in nutmeg. Use Table 15.1 for the fatty acid, myristic acid.

Solution

Fats are triacylglycerols and trimyristin must therefore be composed of glycerol and three molecules of myristic acid—$C_{14:0}$. The components are joined by an esterification reaction.



Problem 15.2

Are fats and oils simple or complex, polar or nonpolar, saponifiable or nonsaponifiable?

Problem 15.3

Draw the structure for the following rare but real long-chain, unsaturated fatty acids:

(a) $C_{28:1}{}^{\Delta 9}$ (b) $C_{26:2}{}^{\Delta 5,9}$ (c) $C_{24:4}$—an ω6 fatty acid

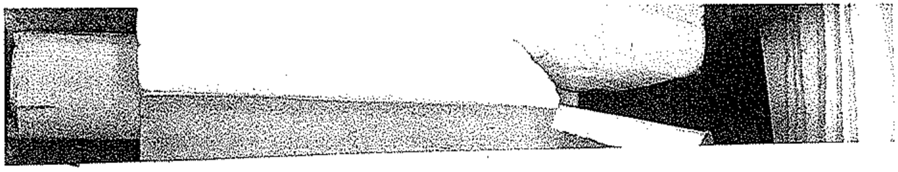
Problem 15.4

Draw the structure of a triglyceride consisting of $C_{16:0}$, $C_{18:2}{}^{\Delta 9,12}$, $C_{18:0}$.

Problem 15.5

Draw the structure of erucic acid, $C_{22:1}{}^{\Delta 13}$.

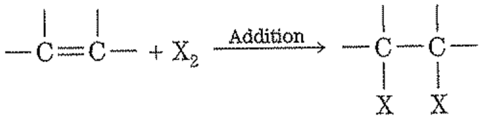
See related problems 15.13, 15.14, 15.16, 15.17.



15.4 Reactions of Fats and Oils

A. Addition Reactions

Most fats and oils are composed of unsaturated fatty acids as well as the saturated variety. Because of the presence of carbon-carbon double bonds, fats and oils undergo addition reactions characteristic of alkenes. We consider here the addition of halogens and hydrogen, where X_2 = hydrogen, halogen.



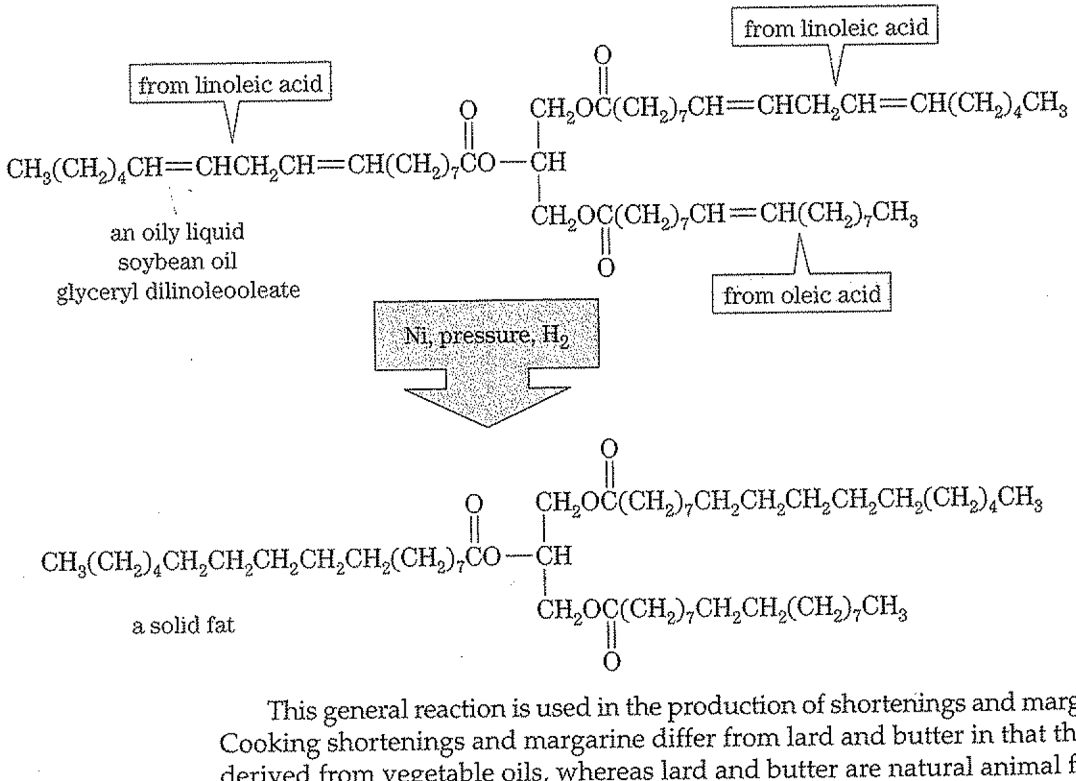
$$-\overset{|}{\underset{}{C}}{=}\overset{|}{C}- + X_2 \xrightarrow{\text{Addition}} -\overset{|}{\underset{X}{\underset{|}{C}}}-\overset{|}{\underset{X}{\underset{|}{C}}}-$$

iodine number
a measure of the extent of unsaturation in fats and oils; the number of equivalents of iodine that will add to 100 grams of a fat or oil

1. Addition of I_2 (*Iodine Number.*) The iodine number is a measure of the extent of unsaturation in fats and oils. It is expressed as the number of grams of iodine that will add to 100 grams of the fat or oil being tested. The greater the number of double bonds in a lipid, the greater the amount of iodine that adds to 100 grams of it. Thus, high iodine numbers indicate a high degree of unsaturation, and low iodine numbers indicate low unsaturation. In Table 15.2 note that the animal fats have low iodine numbers relative to the more highly unsaturated marine animal and vegetable oils.

hydrogenation of oils
the catalytic addition of hydrogen to unsaturated triacylglycerols (oils)

2. Addition of H_2 (*Hydrogenation.*) In the presence of a metal catalyst, such as nickel, hydrogen adds to the double bonds of fats and oils, producing more highly saturated glycerides. Consider, for example, the hydrogenation of the following oil, a possible component of soybean oil.

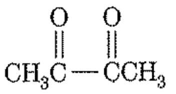


an oily liquid
soybean oil
glyceryl dilinoleooleate

a solid fat

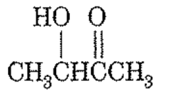
This general reaction is used in the production of shortenings and margarine. Cooking shortenings and margarine differ from lard and butter in that they are derived from vegetable oils, whereas lard and butter are natural animal fats. In the production of shortening or margarine, liquid vegetable oils are partially hydrogenated in the presence of a catalyst until the desired consistency is achieved. Enough unsaturation is left to create a low-melting, soft product. Complete hydrogenation (as in the example) would produce a hard, brittle fat.

In the manufacture of margarine, these partially hydrogenated vegetable oils (often soybean, corn, and safflower oils) are mixed with water, salt, and nonfat dry milk. Other oils are added to achieve the desired consistency and homogeneity. Vitamins, especially vitamin A, are added along with artificial flavoring and coloring. Diacetyl and methyl acetyl carbinol, which are responsible for the characteristic taste of butter, are common flavorings.



$CH_3C(=O)-C(=O)CH_3$

Diacetyl



$CH_3CH(OH)C(=O)CH_3$

Methyl acetyl carbinol

Finally, preservatives such as potassium sorbate and other salts of carboxylic acids, (Connections 12.1) and antioxidants such as butylated hydroxy toluene and other phenols, (section 9.3.D.2) are added.

B. Oxidation Reactions

1. ***Rancidification.*** Fats and oils, when exposed to air, tend to oxidize or hydrolyze to produce volatile carboxylic acids. These have a sour, unpleasant taste and aroma. The process, called rancidification, makes lard, shortenings, butter, margarine, cooking oils, and milk unpalatable and unusable.

rancidification
oxidation and hydrolysis of fats and oils to volatile organic acids, producing an unpalatable product

Oxidative rancidification involves the oxidation of carbon-carbon double bonds in the alkyl chains of fats and oils to produce carboxylic acids. In hydrolytic rancidification, one or more of the ester units of triacylglycerol are hydrolyzed back to the original acid. Antioxidants (section 9.3.D.2) are added to many edible fat and oil products to retard rancidification.

2. ***Drying Oils.*** When highly unsaturated oils are exposed to air, they undergo an alternative form of oxidation called *drying*, which causes them to harden. This process involves the attack of oxygen at allylic positions (carbons next to double bonds) in the oil to form intermolecular linkages. As oil molecules are drawn into close proximity, the double bonds polymerize, forming a gigantic, interlinking hard mass.

drying oil
an oil that can be hardened by the process of oxidation

This principle governs the drying action of an oil-based paint. Commercial oil-based paints consist of a pigment dispersed in a drying oil, such as linseed oil. When the paint is applied, a volatile thinner such as turpentine evaporates and the oil begins to polymerize, often under the influence of an added catalyst, eventually forming a hard, protective surface.

The drying process is spontaneous and highly exothermic. It can eventually provide enough heat to cause the combustion of cloth and paper. For this reason oily rags should not be stored in closed, unventilated areas.

Linoleum flooring is made from a thick suspension of cork and rosin in linseed oil. The suspension is pressed and allowed to "dry" (the linseed oil oxidizes). A similar process is used to make oilcloth. Tough, durable surface coatings result.

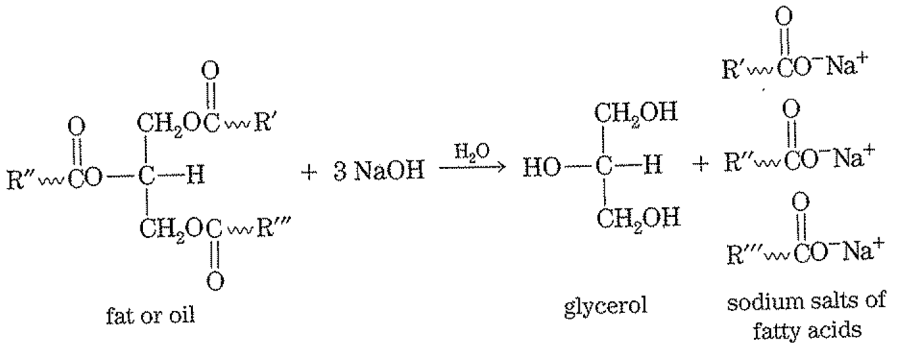
C. Saponification

Fats and oils are acid derivatives, triesters of glycerol. When any acid derivative reacts with water, the products are an acid and an alcohol. **Saponification** is the alkaline hydrolysis of esters, resulting in the production of glycerol (the alcohol) and the salts of the constituent fatty acids (since basic conditions are employed, acid salts are formed).

1. ***Production of Soap.*** The term *saponification* means "soap making." The salts of long-chain fatty acids produced by the saponification of fats and oils are **soaps.**

saponification
the alkaline hydrolysis of esters to produce soaps

soap
sodium and potassium salts of long-chain fatty acids; the hydrocarbon portion is hydrophobic (water-insoluble) but soluble in fats and oils and the ionic part is hydrophilic (water-soluble)



Soap has its origins in antiquity. It was prepared for over two thousand years by mixing fire ashes, which are quite alkaline, with tallow and water. Today, soap is made by two processes.

In the boiling, or kettle, process, up to 50 tons of rendered fat are melted in steel tanks three stories high and then injected with steam and sodium hydroxide solution. Following saponification, brine is added to salt out the soap; this forms an upper curdy layer. The soap is then separated, purified, and cut into bars or chips. Glycerol, for use in the plastics and explosives industries, is recovered from the lower layer, the aqueous salt solution.

The modern continuous soap-making process involves high-temperature water hydrolysis of fats and oils to fatty acids and glycerol. The fatty acids are vacuum-distilled, mixed in specific ratios, and neutralized with alkali to form the soap.

Tallow and coconut oil are frequently the initial glycerides used in the soap industry. Tallow is rendered by heating to produce a liquid. The unmelted protein material is filtered away; the melt is termed *lard*. Tallow or lard produces a good-cleansing but slow-lathering soap. Soaps from coconut oil form better lathers, so some coconut oil is often included in the lipid material to be saponified. Coloring, perfumes, disinfectants, and deodorants can also be added to body soaps. Heavy-duty hand soaps may contain scouring powders, sand, or volcanic pumice, for an abrasive effect. Glycerol confers transparency to bar soaps, while air beaten into the soap will allow it to float. Shaving cream is made by using the potassium salts of fatty acids colloidally dispersed into a foam.

saponification number
the number of milligrams of potassium hydroxide required to saponify 1 gram of a fat or an oil

2. ***Saponification Number.*** The **saponification number** is defined as the number of milligrams of potassium hydroxide required to saponify 1 gram of a fat or an oil. On a molecular basis, one mole of fat or oil requires three moles of KOH for complete saponification because there are three ester linkages in a fat or an oil molecule.

Because a gram of a high-molecular-weight fat has fewer molecules than a gram of a low-molecular-weight one, the weight of KOH needed for saponification will be lower for the high-molecular-weight fat. Thus, high-molecular-weight fats and oils have lower saponification numbers than fats and oils of lower molecular weight. Table 15.2 lists saponification numbers for some common fats and oils.

GETTING INVOLVED

- ✓ What types of chemical reactions are going on during the process of hydrogenation, rancidification, and saponification?
- ✓ Give a practical application of each of the preceding three processes.
- ✓ What is the chemical structure of a soap?

llowing groups in order of increasing iodine oleopalmitostearate; **(b)** stearic, oleic, linoleic, and linolenic acids.

Problem 15.7

Illustrate that you understand the processes of hydrogenation, rancidification, and saponification by reacting a diglyceride that has oleic and linolenic acids at the 1,3-positions of glycerol with the appropriate reagents.

Problem 15.8

Are margarines, the products of the hydrogenation of oils, naturally occurring? Are they "organic" (unprocessed)?

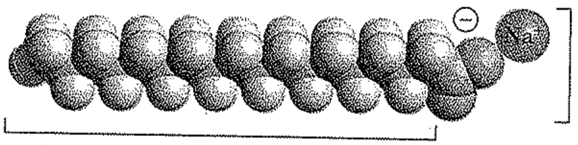
15.5 Soaps and Detergents

A. Structure of Soaps

Dirt adheres to our bodies and clothes by a thin film of fat, oil, or grease. For this dirt to be removed, the oily materials must first be dissolved. The most abundant liquid on earth, and the only one economically feasible for day-to-day washing, is water. But water is a polar liquid—and fats and oils, because of their long hydrocarbon chains, are nonpolar, that is, water-insoluble.

Soaps are structurally capable of solving this dilemma. Recall that soaps are salts of long-chain fatty acids. The long alkyl group has 12–18 carbons, is completely nonpolar, and consequently is soluble in fats and oils but insoluble in water. The other end of the molecule, a carboxylic acid salt, is very polar, in fact, ionic, and is water-soluble. A soap then has two diverse solubility properties—it has a **hydrophilic** end (water-loving), soluble in water, and a **hydrophobic** end (water-fearing), soluble in fats and oils.

hydrophilic	water-loving
hydrophobic	water-fearing



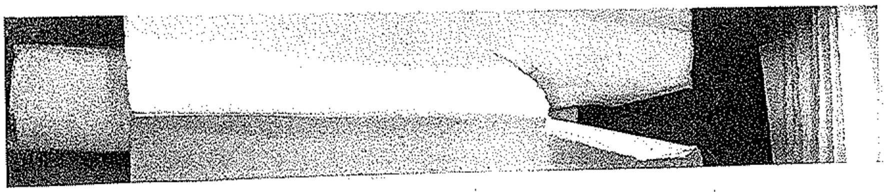
Soap, by simultaneously dissolving in oils and water, removes oil from dirty clothes and emulsifies the droplets in water.

GETTING INVOLVED

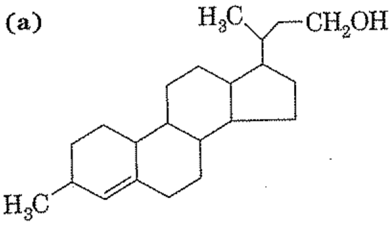
✓ What is meant by the terms "hydrophilic" and "hydrophobic"?

Problem 15.9

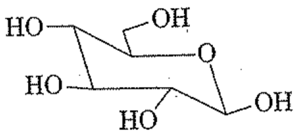
For each of the following compounds, find the portions that are hydrophilic and hydrophobic.



(a)



(b)



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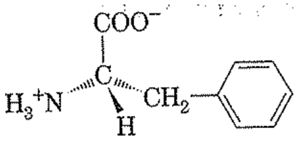
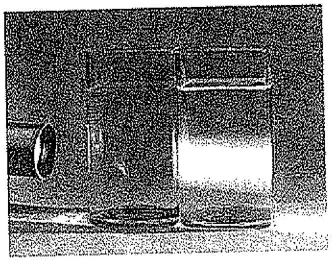




Tyndall light scattering using a soap solution

B. Mechanism of Soap Action

Let us take a closer look at what is happening in a soap solution, on a molecular basis (Figure 15.2). As a soap dissolves in water, the molecules orient themselves on the water's surface with the ionic end submerged and the nonpolar hydrocarbon chain bobbing above the surface like a buoy on the ocean. In this manner, the soap molecule satisfies its opposing solubility characteristics—the water-soluble, hydrophilic end is in the water and the nonpolar, hydrophobic end is not in contact with the water, but is surrounded by nonpolar N_2 and O_2 in air. This molecular orientation lowers the surface tension of water. The liquid surface is no longer made up of strongly associated, hydrogen-bonded water molecules, but of nonpolar, nonassociated hydrocarbon chains, somewhat like gasoline. This gives the water a better wetting capacity, allowing it to spread out

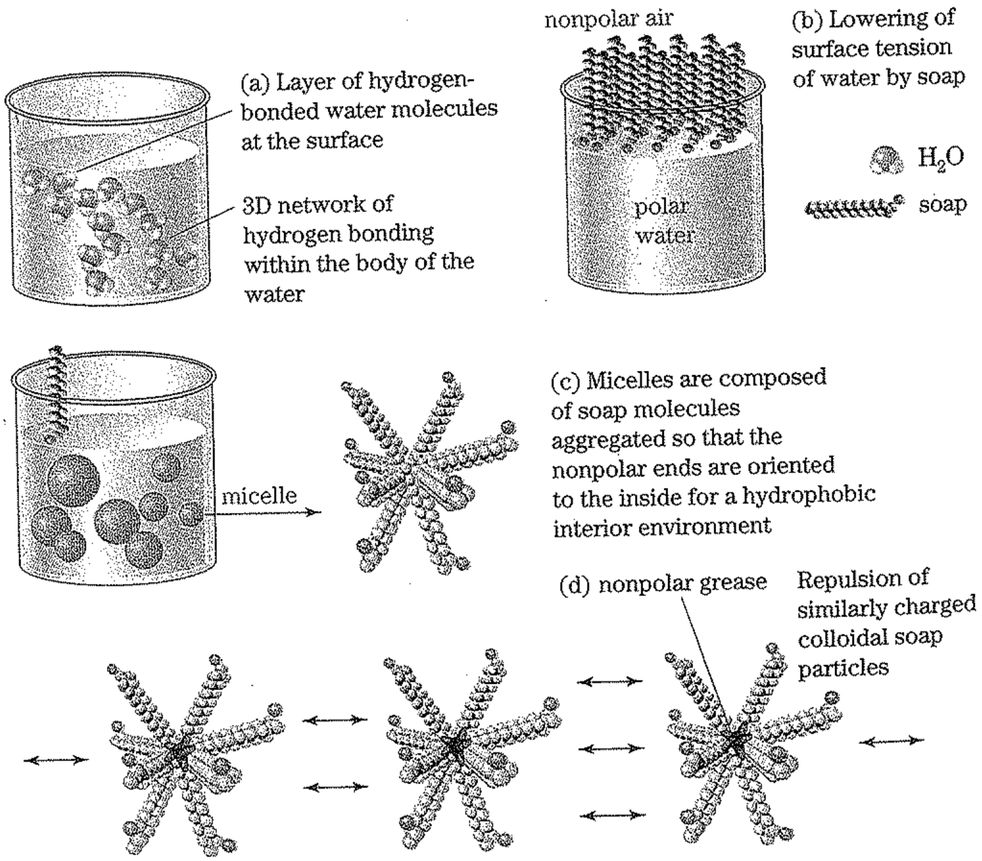


Figure 15.2
Mechanism of soap action.

and penetrate fabrics rather than bead up on the surface. Soaps or detergents are often added to herbicide and pesticide sprays to aid in the emulsification of the active ingredient in the water carrier and to promote better spreading of the solution over the leaves of the treated plants.

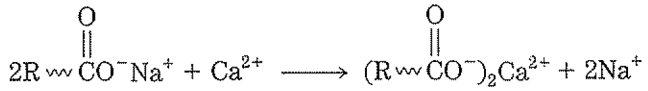
What happens to the soap molecules for which there is no room on the water's surface? They will have to orient themselves in such a way beneath the surface that the hydrophobic portions of the molecules have minimal contact with water. The soap molecules achieve this by grouping in three-dimensional clusters, with the nonpolar hydrocarbon chains filling the interior of the cluster and the water-soluble ionic ends composing the outer surface. The molecular conglomerations are called **micelles.** The solubility characteristics of the soap molecules are satisfied in that all the hydrocarbon chains are grouped together away from water (a hydrophobic core) and the ionic portions are in contact with water (Figure 15.2).

micelle
aggregation of polar/nonpolar molecules, like soap, in water such that the nonpolar portions of the molecules are arranged together inside, away from water and the polar portions protrude into the water

If some soiled clothing is submerged in the water, the nonpolar oil films are loosened, and they dissolve in the nonpolar hydrocarbon centers of the micelles. The micelles remain colloidally dispersed in the water, with no tendency to coagulate since there is an ionic repulsion between their charged outer surfaces. The oily films are thus washed away as finely dispersed oil droplets.

C. Detergents

Soaps, the sodium and potassium salts of long-chain fatty acids, have one serious disadvantage; they are insoluble in hard water. Hard water is water containing dissolved salts of calcium, magnesium, and iron picked up as water trickles over and filters through soil, rocks, and sand. Soaps react with these ions to form insoluble scums (the familiar bathtub ring).



$$2R\sim\overset{\overset{O}{\|}}{C}O^-Na^+ + Ca^{2+} \longrightarrow (R\sim\overset{\overset{O}{\|}}{C}O^-)_2Ca^{2+} + 2Na^+$$

Water-soluble Water-insoluble

Detergents, first introduced in 1933, are considerably more effective than soaps in hard water.

Detergents have the same two structural characteristics that soaps do:

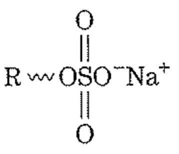
1. They possess a long, nonpolar, hydrophobic, hydrocarbon chain that is soluble in fats, oils, and greases.
2. They possess a polar, hydrophilic end that is soluble in water.

detergent
molecules that are not soaps but that have long non-polar, water-insoluble hydrocarbon chains that dissolve fats and oils, and a polar or ionic portion that is water-soluble

Furthermore, in the way they work, detergents are analogous to soaps (as described in section 15.5.B and Figure 15.2).

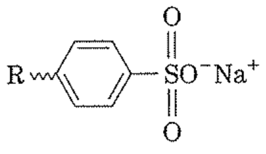
Synthetic detergents, syndets, fall into three main categories, determined by the structure of the water-soluble portion of the molecule. **Anionic detergents** have an ionic water-soluble end in which the portion attached to the hydrocarbon chain is negative. Alkyl sulfates and alkyl benzene sulfates (ABS) are the two most common anionic detergents.

anionic detergent
cleaning agent with a negatively (−) charged polar end, such as a sulfate or sulfonate

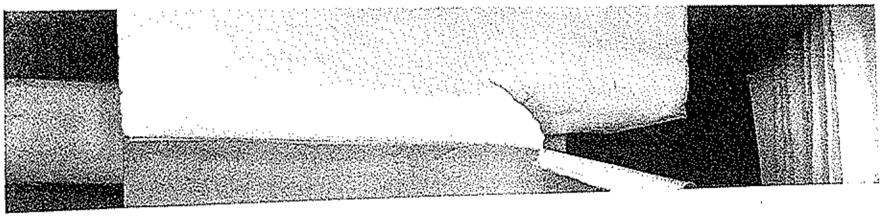


$$R\sim O\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}O^-Na^+$$

A sodium alkyl sulfate

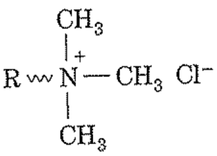


A sodium alkyl benzene sulfonate



cationic detergent
cleaning agent with a positively (+) charged polar end, such as an ammonium group

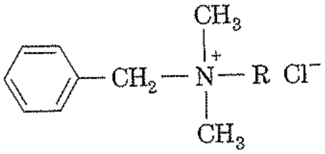
The water-soluble end of a **cationic detergent** is a positive quaternary ammonium salt.



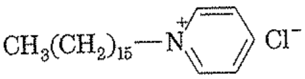
$$\mathrm{R{\sim}\overset{\overset{\displaystyle CH_3}{|+}}{\underset{\underset{\displaystyle CH_3}{|}}{N}}-CH_3\ \ Cl^-}$$

A quaternary ammonium salt

These detergents have significant germicidal properties, and similar compounds such as the ones shown are used in shampoos, mouthwashes, germicidal soaps, and disinfectant skin sprays.



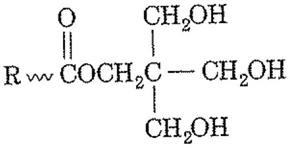
Benzalkonium chlorides
(R = 8–14 carbons)



Cetylpyridinium chloride

nonionic detergent
cleaning agent with an uncharged, polar end, such as an alcohol

In **nonionic detergents,** the water-soluble end is polar and can hydrogen-bond with water, but it is not ionic.

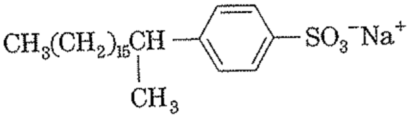


$$\mathrm{R{\sim}\overset{\overset{\displaystyle O}{\|}}{C}OCH_2\overset{\overset{\displaystyle CH_2OH}{|}}{\underset{\underset{\displaystyle CH_2OH}{|}}{C}}-CH_2OH}$$

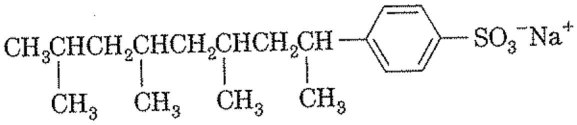
$$\mathrm{R{\sim}\overset{\overset{\displaystyle O}{\|}}{C}(OCH_2CH_2)_nOH}$$

biodegradable
materials that can be metabolized by soil and water bacteria

Most detergents today are **biodegradable.** This means that they can be metabolized by microorganisms in a sewage disposal plant before release into the environment. For a detergent to be biodegradable, the long alkyl chain must be unbranched. Detergents used in the 1950s and early 1960s had branched chains, were not readily biodegradable, and foamed when the water discharged from sewage plants was agitated.



A biodegradable detergent



A nonbiodegradable detergent

Chemically pure soaps are regulated by the federal Consumer Product Safety Commission and are considered generally safe for use by the public. Today's hand "soaps" are usually detergents with brighteners, abrasives, and perfumes added. Many are advertised as being germicidal or antibacterial. The detergent composition and advertising claims put them under regulation by the Food and Drug Administration.

GETTING INVOLVED

- ✓ Under what circumstances might it be better to use a detergent than a soap?
- ✓ In terms of chemical structure, how is a detergent similar to a soap and how is it different?
- ✓ Compare the cleaning actions of a soap and a detergent on a molecular level.
- ✓ Be able to identify the functional groups on detergents which classify them as cationic, anionic, and nonionic.
- ✓ Is a soap cationic, anionic, or nonionic?
- ✓ What type of structure might impede the biodegradability of a soap or detergent? **See related problems 15.15, 15.18, 15.19, 15.21.**

15.6 Biolipids—Structures and Functions

As we have seen so far in this chapter, the term *lipid* applies to more than one chemical structure. The common feature of all lipids is a relative insolubility in water of all or a large portion of the molecule. In a living organism, this property allows lipids to serve in many interesting capacities. They are found in cell membranes, as insulating tissue that protects organs from the external environment, as chemical fuel storage depots, and as regulators of metabolism.

We can consider the biolipids in seven general classes depending on both their structural and functional similarities: triacylglycerides (fats), phosphoglycerides, sphingolipids, steroids, prostaglandins (and derivatives), fat-soluble vitamins, and pigments.

A. Triacylglycerols

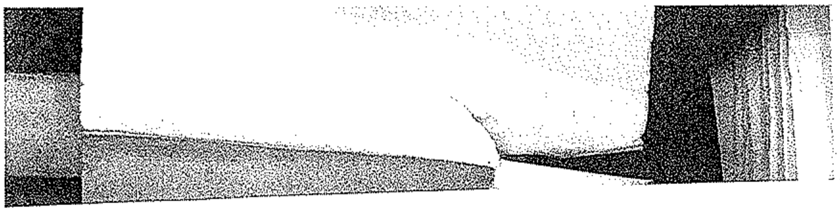
We need not review the structure of these lipids except to say that they are nonpolar, complex, and saponifiable. Let us continue with a discussion of their functions. Gram for gram, fats and oils deliver about 2.5 as much metabolic energy as do carbohydrates or proteins. Thus fat storage in adipose tissue is a concentrated energy reserve. In addition, we can store more fat than glucose (in the form of the polymer glycogen) because of the insolubility of fats in water. Since fats are hydrophobic, they will not attract water during storage. The hydrophilic nature of glycogen results in hydrogen bonding with water, which increases its weight. The insulating nature of fats keeps our vital organs warm, and their bulk acts as protection against trauma.

B. Phospholipids

Phospholipids contain one or more phosphate groups; they are complex, saponifiable, polar lipids. The most common phospholipids are a variation on the triacylglycerol structure with two long-chain fatty acids esterified to the first two positions of glycerol and a phosphate group in an ester linkage at the third position. Thus they are called *glycerophospholipids* (or **phosphoglycerides**). Since phosphate is a triprotic acid, it has three reactive acid groups and can form a second ester with an additional alcohol. This leaves an acid group that can ion-

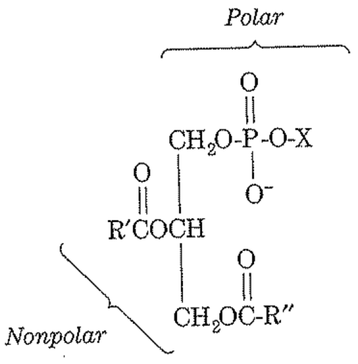
phospholipid
complex, saponifiable, polar lipid containing one or more phosphate groups

phosphoglyceride
complex, saponifiable, polar lipid; triester of glycerol in which two acids are saturated and unsaturated long-chain fatty acids and the third acid is phosphoric acid that is further esterified

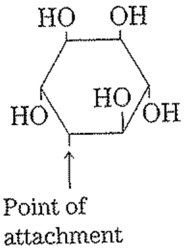


ize. The versatility of this structure produces a complex lipid with both hydrophilic and hydrophobic properties; this is called an **amphipathic** molecule.

amphipathic
molecule with a polar portion and a nonpolar portion



R′ is usually unsaturated
R″ is usually saturated

If X is	The name of the resulting phospholipid would be
$-H$	Phosphatidic acid
$-CH_2CH_2\overset{+}{N}H_3$	Phosphatidyl ethanolamine (cephalin)
$-CH_2CH_2\overset{+}{N}(CH_3)_3$	Phosphatidyl choline (lecithin)
$-CH_2\underset{COO^-}{CH}\overset{+}{N}H_3$	Phosphatidyl serine
	Phosphatidyl inositol

The amphipathic nature of both the phospholipids and sphingolipids (below) contributes to their function as membrane components in cells.

GETTING INVOLVED

- ✓ Which groups on phospholipids are responsible for their properties of being classified as complex, saponifiable, and polar lipids?
- ✓ Give an example of at least one other type of molecule in this chapter that is amphipathic.
- ✓ Are fats and oils or waxes amphipathic? Explain your answer in terms of their structures.

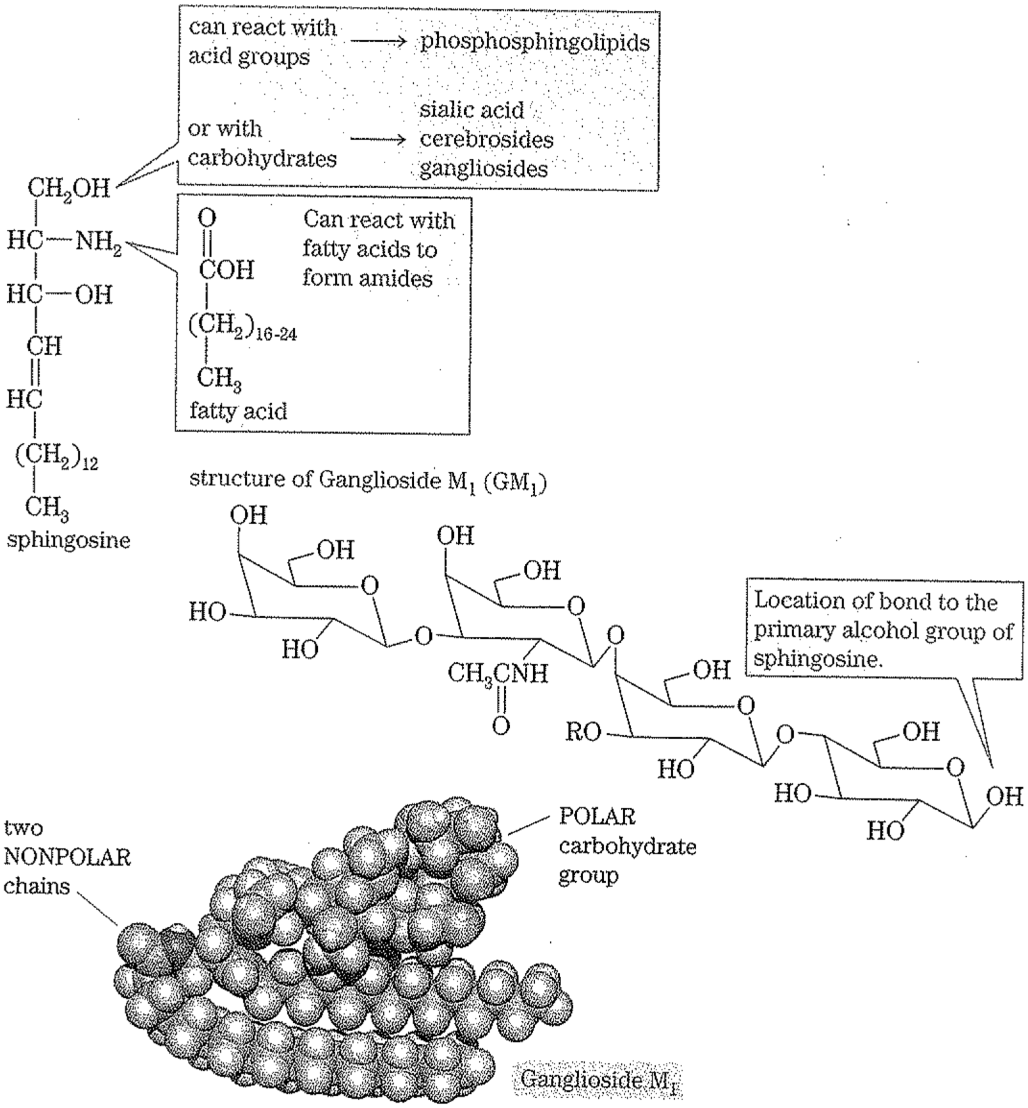
Problem 15.10
Draw out the structure of a lecithin containing linolenic acid as R′ and palmitic acid as R″.

Problem 15.11
What compounds would result from the complete hydrolysis of one mole of phosphatidylserine?

C. Sphingolipids

sphingolipid
complex, saponifiable, polar lipid; composed of sphingosine linked through an amide bond to a very-long-chain fatty acid and through an ester or acetal linkage to acids or carbohydrates

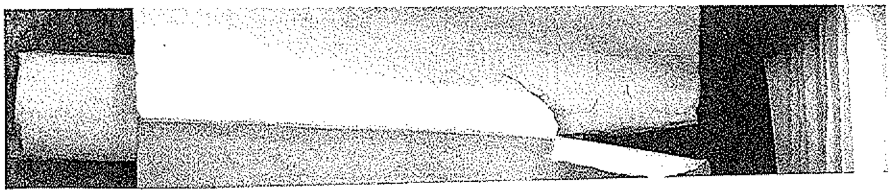
Sphingolipids are more complex than the phospholipids in that they are derivatives of the amino-alcohol sphingosine. The amine group forms an amide bond with an unsaturated fatty acid, resulting in a ceramide, and the alcohol either can be esterified with an acid, such as phosphoric acid, or can form an acetal or ketal with a carbohydrate molecule or polymer chain. If the phosphate is also esterified with ethanolamine or choline, the molecule is called a *sphingomyelin*. When one or more carbohydrate groups are attached to the ceramide hydroxyl, a glycolipid results. The most common glycolipids are cerebrosides, which contain a single monosaccharide and are important components of the myelin sheath of nerve cells, and gangliosides, which are believed to play a role in nerve signal transmission.



The amphipathic nature of these two types of biolipids causes them to interact with each other and water in a manner that goes one step further than that of the soaps. Rather than forming a monolayer of micelle, the molecules spontaneously arrange into a bilayer that, when extended, can fold back on itself to form a sphere, ellipsoid, or other encapsulated structure. In other words, they can form a cell **membrane,** the semipermeable barrier that allows some substances, but not others, to pass from one side to the other. This helps in the compartmentalization and efficiency of metabolic functions. The cell membrane has many other components, including cholesterol and proteins. Synthetic vesicles, called **liposomes,** can be formed from phospholipids and sphingolipids. Liposomes are used to study membranes and membrane transport and are being studied as

membrane
naturally occurring, semipermeable lipid bilayer composed of phospholipids, sphingolipids, cholesterol, and proteins

liposome
synthetic vesicle with a semipermeable barrier composed of phospholipids



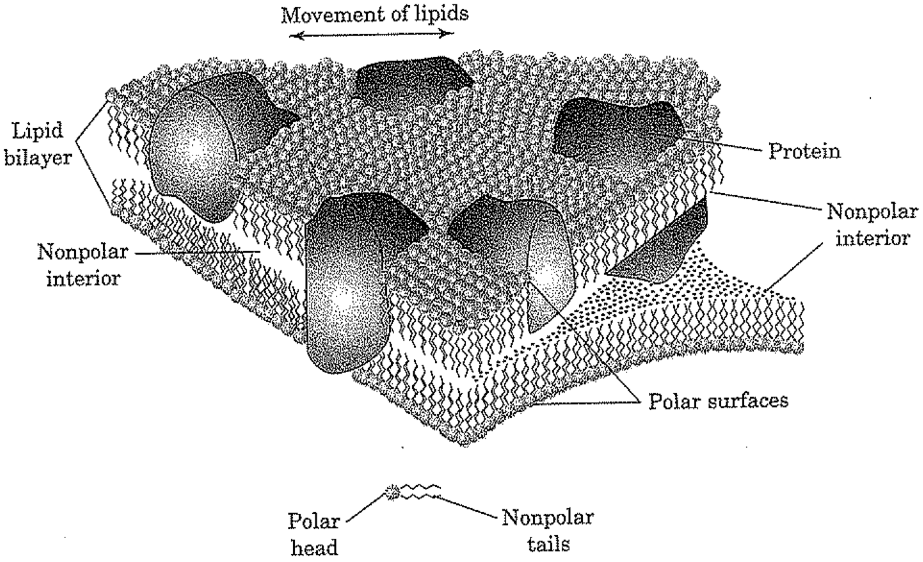


Figure 15.3 Cell membrane diagram showing structural arrangement of lipid bilayer.

a means to deliver drugs inside the body. Figure 15.3 illustrates the model proposed for membrane structure known as the "fluid mosaic" model.

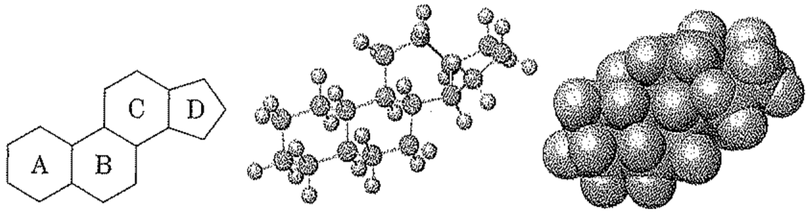
This model views the membrane as a mosaic of lipid and protein, in which the fluidity of the lipid permits both lipid and protein molecules to move laterally. The composition of a membrane varies both in the ratio of protein to lipid and in the percentages of various lipids. Protein content varies from about 20% in the myelin surrounding nerve cells to greater than 70% in the inner membrane of mitochondria. Cholesterol, a steroid, is another important component of the membrane. Having a more rigid structure than the other lipid portions of the membrane, it helps to maintain membrane structure. The concentration of cholesterol in a membrane usually varies directly in relation to the concentration of unsaturated fatty acids present in phospholipids. The carbohydrate portions of gangliosides and cerebrosides can act as cell recognition factors on the outer surface of the membrane and can be attached to proteins, which serve various functions, including that of cell recognition.

Disorders such as ALD, described in Connections 15.1, are frequently fatal, especially when they affect the membranes of nerve tissue. Tay-Sachs disease is a recessive trait that results in the accumulation of ganglioside G_{M2} in the brains of its victims due to the absence of an enzyme, hexoseamidase, to break down G_{M2}. Death occurs within four years after birth following a course of severe brain damage, paralysis, and blindness. Heterozygotes, people who carry only one gene for the disorder, number about 1 in 30 in the northern European population. They can be victims of a late-onset version of Tay-Sachs due to a decrease in hexoseamidase activity.

D. Steroids

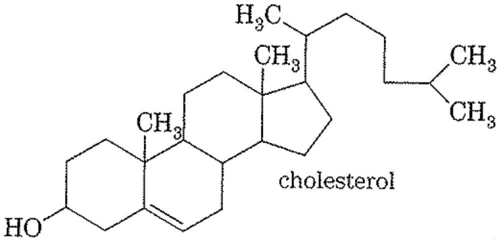
Steroids can be saponifiable or nonsaponifiable. All of the **steroids** have a system of four fused rings—three six-membered rings and one five-membered ring. Substituents on this large ring system contribute to functions that range from hormonal regulation to digestion to poison.

steroid
lipid with a four-fused-ring structure, three rings having six members and one ring with five members



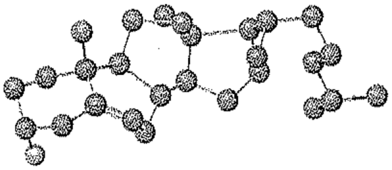
The steroid fused-ring nucleus is shown in three views: two-dimensional; three-dimensional ball-and-stick model; three-dimensional space-filling form. This fused ring system is common to all lipids in this class. Although the system itself is hydrophobic, the presence of hydrophilic side chains can modify the solubility properties of the molecule. The four rings are identified as A,B,C, and D as in the figure.

1. ***Cholesterol.*** The precursor to all steroid endocrine hormones is cholesterol, a simple, nonsaponifiable, nonpolar lipid. The liver is the primary source of its biosynthesis.

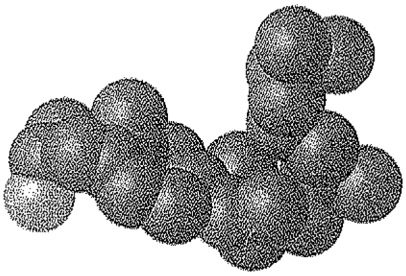


cholesterol

metabolic precursor to
- sex hormones
  - testosterone - male
  - estrogen, progesterone } female
- bile salts
  - important to digestion
- metabolic hormones
  - regulate metabolism of carbohydrates, proteins, salt, and water
- component of membrane structure

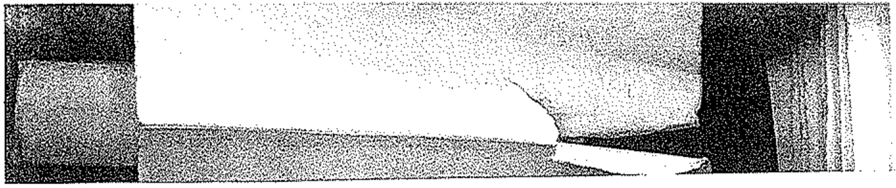


ball-and-stick model without hydrogens



space-filling model

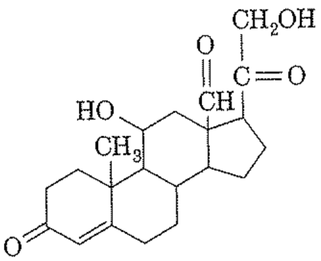
Being hydrophobic, cholesterol must be carried in water-soluble protein complexes through the bloodstream. These complexes contain varying amounts of triglyceride as well as cholesterol and are called *lipoproteins.* The more fat or triglyceride present in the lipoprotein complex, the less dense it will be. The complexes are divided into high-, low-, and very-low-density lipoproteins (as well as other fractions) or HDL, LDL, and VLDL, respectively. Complicated feedback mechanisms, many of which are in the liver, control the plasma concentrations of these complexes. High circulating concentrations of LDL increase the proba-



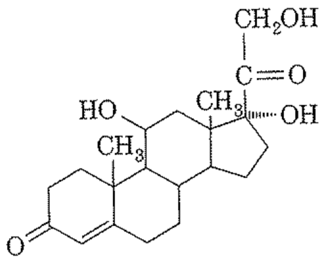
bility of atherosclerosis (fat and cholesterol deposits in blood vessels) and heart disease. Conversely, larger concentrations of HDL, which can result from engaging in regular exercise, are associated with a lower risk of cardiovascular disease. See Connections 5.4 for further discussion of cholesterol.

2. ***Steroid Hormones.*** The endocrine hormones are physiological regulators that are carried by the blood from the site of synthesis to the affected organs. The steroid hormones regulate the processes of metabolism, growth, sexual development, and reproduction. All are derived from cholesterol. The two main organs of secretion are the adrenal cortex and the gonads, that is, the ovaries and the testes.

The adrenal cortex, the outer portion of the adrenal glands which are located above the kidneys, is a primary organ of steroid hormone production. Adrenocortical hormones fall into two general categories: those regulating the metabolism of carbohydrates, proteins, lipids, and so on (glucocorticoids), and those influencing salt and water metabolism (mineralocorticoids). These compounds not only overlap in their functions but also have additional roles in the regulation of the cardiovascular and nervous systems, among others.



Aldosterone
(a mineralocorticoid)



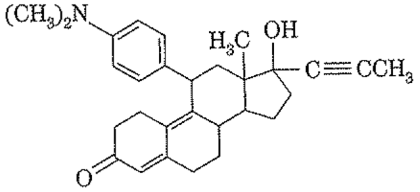
Cortisol
(a glucocorticoid)

Connections 15.2

www.prenhall.com/bailey

RU-486

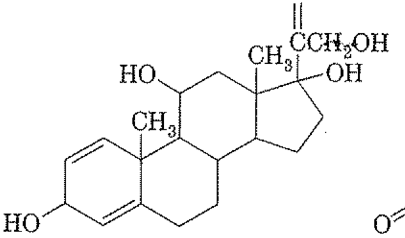
Very few chemicals in recent history have generated the political and social argument that RU-486 has in the area of reproductive rights and medical advancement. This compound is a steroid with the generic name of mifepristone. It blocks the action of progesterone and thereby interferes with the gestation of a fertilized egg; that is, it can terminate conception.



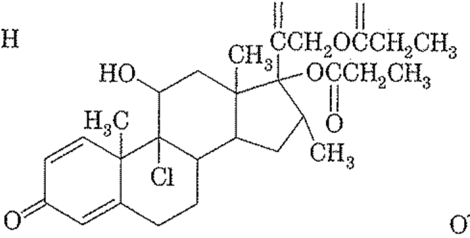
RU-486
mifepristone

Technically, RU-486 is not a contraceptive, because it does not have a chemical mechanism of action similar to that of norethindrone and mestranol, which mimic natural estrogens and progestins. Rather it is an antiprogestin or a contragestive in that it blocks the action of natural progesterone, which is responsible for maintaining the fetus during pregnancy. Without the proper hormonal environment, the fetus cannot survive. Given along with a prostaglandin within 49 days of the last menstrual period, RU-486 has caused a spontaneous abortion in about 95% of women tested. This testing and the current use of the drug have taken place primarily in Europe. Side effects are varied, and the treatment can take place in the privacy of a physician's examination room. There has been strong antiabortion group sentiment against the introduction of RU-486 into the United States for any purpose. In addition to its action as an abortifacient, mifepristone has also shown some promise for the treatment of breast cancer, glaucoma, and other conditions. It has been made available for limited use and research in the United States and will probably generate controversy for many years to come

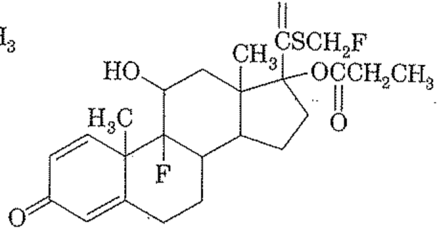
The glucocorticoids also have antiinflammatory activity, which makes substances like cortisol and the related compounds cortisone and prednisone valuable in the treatment of conditions such as severe allergic reactions and rheumatoid arthritis.



prednisolone
drug used for inflammatory
diseases and organ disorders



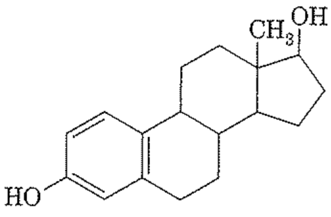
beclomethasone dipropionate
(Beconase®, Beclovent®)



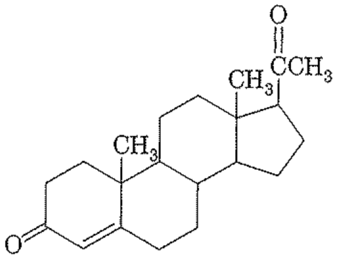
fluticasone propionate
(Flonase®)

aerosol inhalants used to reduce bronchial inflammation found in asthma

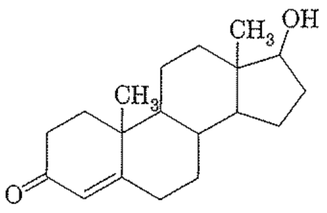
The sex hormones, androgens and estrogens, are responsible for the development of the secondary sex characteristics such as the distribution of body fat, protein, and hair, voice timbre, and development of the genital organs. There has been a deep concern over the use of testosterone and its derivatives by athletes to enhance muscle development. Although the use of androgenic (male) steroids does indeed increase muscle protein, their use can also promote the deposition of atherosclerotic plaque, can stimulate skin oil production, and can alter the psychological disposition of the user. Sex hormones and contraceptives were discussed in Connections 3.1.



estradiol
an estrogen



progesterone
a progestin

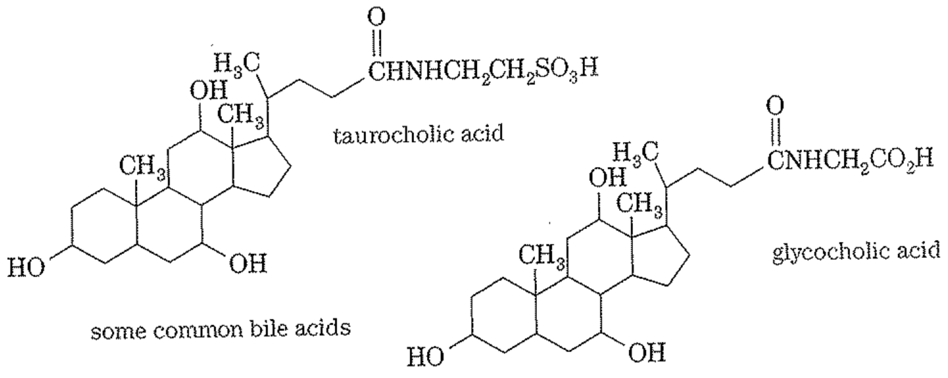


testosterone
an androgen

3. ***Bile Acids.*** The attachment of a polar group to the D-ring of the steroid nucleus leads to an amphipathic molecule called a **bile acid.** The salts of bile acids act in the digestive process as emulsifying agents. Since fats and oils are not water-soluble, the bile acids help to form micelles with them **(emulsification)** in the small intestine so that the triglycerides may be broken down by enzymes before absorption into the bloodstream.

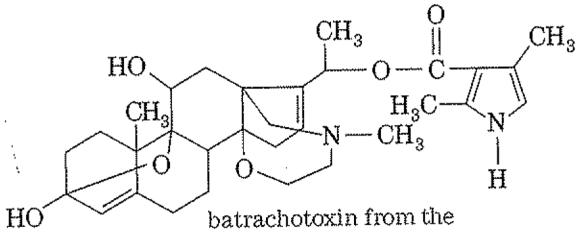
bile acid
amphipathic lipid, a steroid derivative produced in the liver and delivered to the intestines via the bile duct where it acts to emulsify ingested lipids

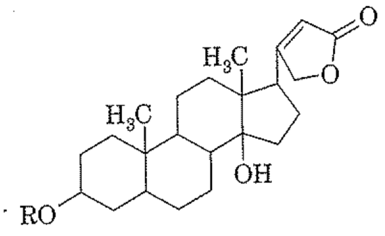
emulsification
the process of solubilizing polar and nonpolar compounds



some common bile acids

4. ***Toxins.*** Many steroids are toxic. The nonpolar nature of the molecules allows them to be easily absorbed. Once in the body, circulating in the bloodstream, they have access to any number of sites. Certain Colombian tree frogs produce a variety of toxic steroids that the indigenous population uses as arrow poisons. The foxglove plant produces the complex steroidal mixture known as digitalis. This material affects the strength of heart contractions, helping to relieve the condition known as congestive heart failure but acting as a deadly poison in larger than therapeutic amounts.


batrachotoxin from the skin of a Colombian tree frog; arrow poison


digitoxin
R can be a variety of carbohydrate attachments; cardiac stimulant

GETTING INVOLVED

- ✓ Draw a picture of a membrane lipid bilayer. Justify the arrangement of the phospholipids and sphingolipids in terms of their amphipathic parts: polar and nonpolar.
- ✓ How would cholesterol arrange itself in the bilayer?
- ✓ There are proteins embedded in the membrane and penetrating through the membrane. What would you automatically assume about the polarity of the outsides of these proteins?

See related problems 15.21, 15.23, 15.24, 15.25, 15.26.

E. Eicosanoids—Tissue Hormones

An **eicosanoid** is a compound formed from the $C_{20:4}$ fatty acid, arachidonic acid, or a fatty acid related to it. These unsaturated fatty acids result from the break-

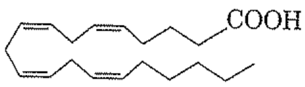
eicosanoid
compound formed from long-chain unsaturated fatty acids

down of the phospholipids in cell membranes during infection or as a reaction to toxic insult. Snake venoms contain enzymes called *phospholipases* that specialize in such breakdown as a means to gain access to blood and tissue cells.

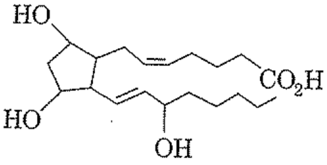
The eicosanoids consist of the prostaglandins, prostacyclins, thromboxanes, and leukotrienes. The first three types of compounds are related to each other both in structure and origin. In fact, the prostacyclins and thromboxanes are biosynthesized from prostaglandins. **Prostaglandins** can cause smooth muscle contraction or relaxation, vasodilation, stimulation of blood clotting, and a variety of other effects.

prostaglandin
lipid tissue hormone synthesized from long-chain fatty acids

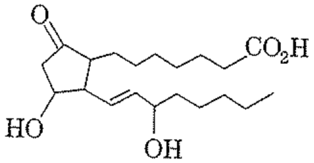
An enzyme called *cyclooxygenase* starts the process of arachidonate to prostanoid conversion. It is interesting to note that aspirin, acetyl salicylic acid, inhibits this enzyme, thereby decreasing the formation of prostaglandins. Aspirin also slows blood clotting time, another ramification of its anticyclooxygenase activity.



Arachidonic acid

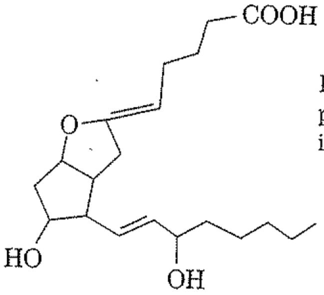


Prostaglandin $F_{2\alpha}$ ($PGF_{2\alpha}$)
Enzaprost® used to induce abortion

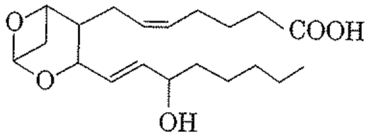


Prostaglandin E_1 (PGE_1)
a vasodilator

Prostacyclins are the PGI class of prostanoids. Thromboxanes are another product of prostaglandin metabolism. These two types of compounds are responsible for the prevention and stimulation of platelet cell aggregation, respectively, during the blood clotting process.

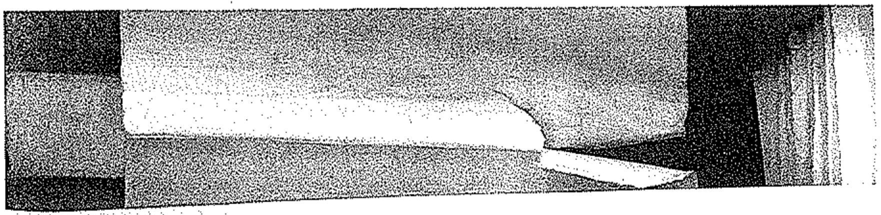


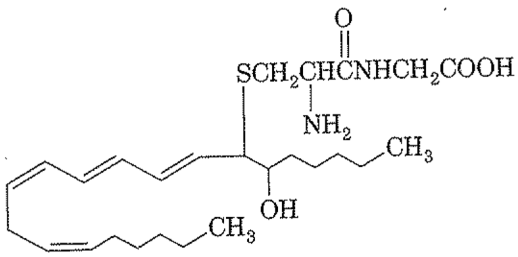
PGI_2 prostacyclin
platelet aggregation inhibitor



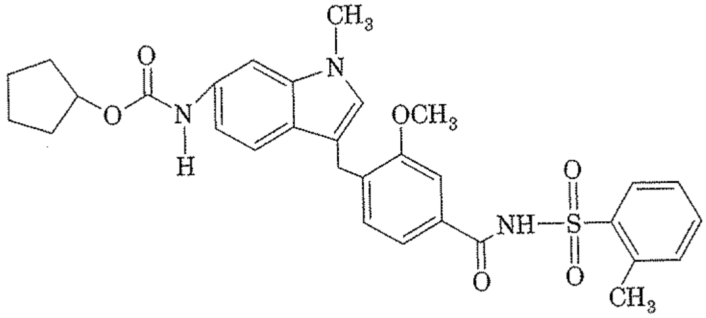
Thromboxane A_2 (TXA_2)
inducer of platelet aggregation; also causes contraction of the arteries

Leukotrienes follow a different pathway of biosynthesis catalyzed by the enzyme lipooxygenase. These compounds have potent bronchoconstricting effects and are primarily responsible for the difficulties in breathing experienced by asthmatics and those having a severe anaphylactic experience (shock) due to an insect sting or as a reaction to a drug to which they are allergic.





leukotriene D_4 (LTD_4)
along with LTE_4 causes bronchial
constriction during an asthma attack



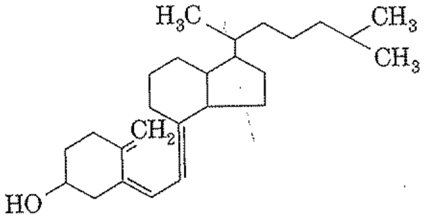
zifirlukast (a leukotriene antagonist)
Accolate®
drug used to prevent and
alleviate the brochoconstriction of asthma

F. Vitamins

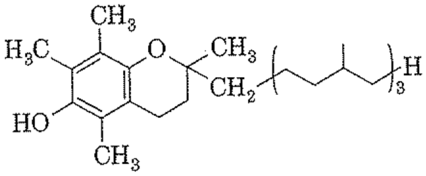
As the term *vitamin* suggests, vitamins are substances essential to life (*vita* is Latin for "life"). They cannot be produced by the normal metabolism of the body. Like hormones, vitamins can take many chemical forms, including those that are water-soluble (the B-complex vitamins and vitamin C) and others that are fat-soluble (A, D, E, and K). Although **water-soluble vitamins** must be supplied frequently, the fat-soluble ones are stored within the body until needed. As a result, it is possible to ingest an overdose of these vitamins.

fat-soluble vitamin
nonpolar, nonwater-soluble, essential dietary component; vitamins A, D, E, and K

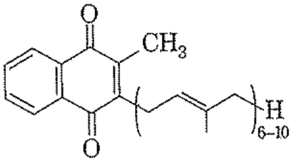
water-soluble vitamin
polar, water-soluble, essential dietary component such as the B complex vitamins and vitamin C



Vitamin D_3



Vitamin E



Vitamin K

Vitamin A and its role in the visual cycle and development have been discussed previously (Connections 3.3).

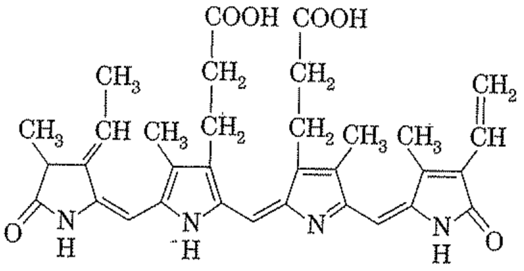
There are several forms of vitamin D, of which D_3 or cholecalciferol is one. It is formed from a precursor in the skin by the action of sunlight. Milk is supplemented with D_3 and D_2, activated ergosterol, obtained from yeast. Vitamin D facilitates the absorption of calcium and phosphorus from the small intestine and their incorporation into bone. A deficiency of vitamin D leads to a condition known as rickets and is evidenced by bone malformations such as bowlegs and extreme tooth decay. Overdoses result in hypercalcification and kidney problems.

Vitamin E, tocopherol, is rarely deficient in diets since it is found in most foods in sufficient quantities. Not much is known about its role in the human body except that it helps to maintain cell membranes by acting as an antioxidant.

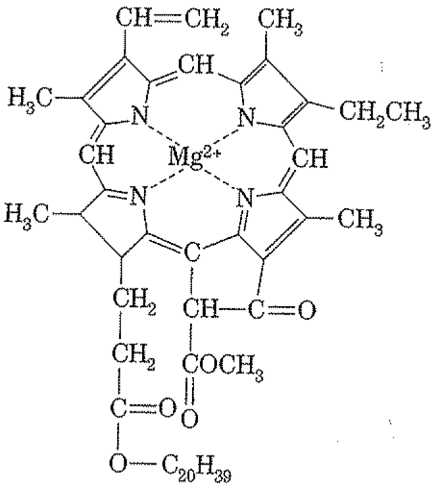
The K vitamins are produced by the bacteria inhabiting the intestinal tract. They aid in the complex mechanism of blood clotting; the rare deficiency results in a tendency to hemorrhage. Aspirin and related compounds are antagonistic to the K vitamins.

G. Pigments

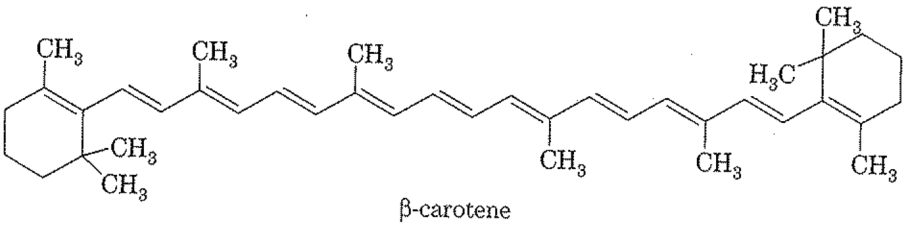
Plants and certain algae and bacteria can utilize solar energy for the biosynthesis of their important parts. This process is known as *photosynthesis*, and it requires membrane-bound compounds that can gather light efficiently. The most important of these pigments is chlorophyll. In addition, other compounds, such as the carotenoids and phycobilins, augment the amount of light energy absorbed by an organism. All of these materials are highly conjugated organic molecules and are themselves colored.



phycoerythrin
(red pigment)



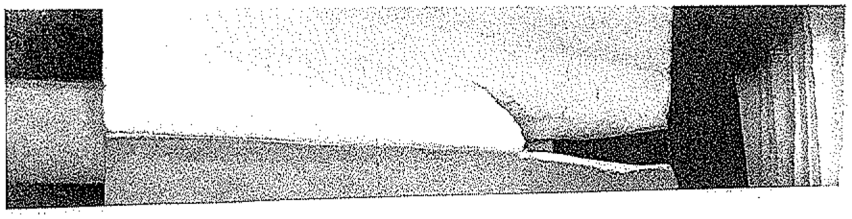
chlorophyll a

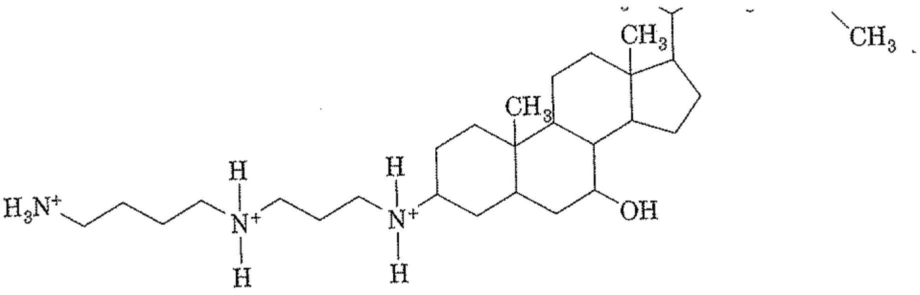


β-carotene
(vitamin A precursor)

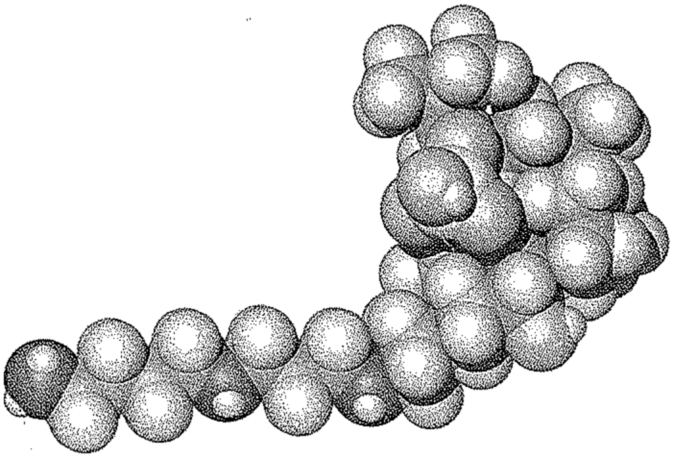
H. Other Functions

Various other lipids fulfill many biological functions. For example, squalamine, the first documented steroid antimicrobial to be found in animals, is endogenous (within the organism) to sharks.





squalamine
an antimicrobial steroid
isolated from sharks



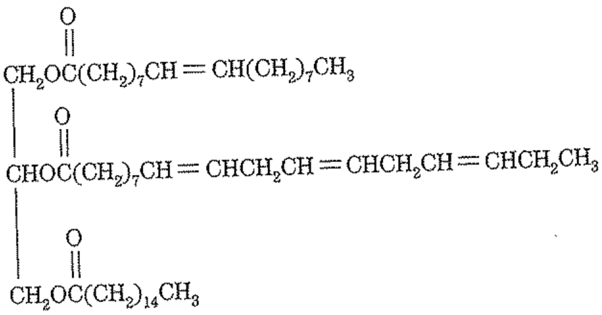
GETTING INVOLVED

Problem 15.12
Is squalamine a polar or nonpolar lipid? Explain your answer using various portions of the molecular structure.

Problems

15.13 **Structures of Fats and Oils:** Draw structures for the following fats and oils:
(a) a glyceride with three lauric acid units, trilaurin
(b) a glyceride with a myristic acid, a palmitic acid, and a stearic acid unit
(c) a glyceride with two myristic acid units and one oleic acid
(d) a glyceride likely to be found in corn oil
(e) a glyceride likely to be found in soybean oil

15.14 **Reactions of Fats and Oils:** Write chemical equations using the following glyceride to describe the reactions indicated:



$$\begin{array}{l} CH_2O\overset{\overset{O}{\|}}{C}(CH_2)_7CH=CH(CH_2)_7CH_3 \\ | \\ CHO\overset{\overset{O}{\|}}{C}(CH_2)_7CH=CHCH_2CH=CHCH_2CH=CHCH_2CH_3 \\ | \\ CH_2O\overset{\overset{O}{\|}}{C}(CH_2)_{14}CH_3 \end{array}$$

(a)
(b)
(c)
15.
sh
wi
(a)
(b)
(c)
15.
tur
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15.1
whi
terg
drop
15.2
drug
(a)
to p

(a) saponification with NaOH
(b) hydrogenation
(c) I_2/CCl_4

15.15 **Reactions of Soaps:** Write chemical equations showing the reaction of a soap such as sodium stearate with the following:

(a) hard water containing Mg^{2+}
(b) hard water containing Fe^{3+}
(c) an acid solution (HCl)

15.16 **Structure of Fatty Acids:** Draw out the structures of the following fatty acids:

(a) vaccenic acid$_{18:1}{}^{\Delta 11}$
(b) docosahexaenoic acid ($C_{22:6}{}^{\Delta 4,7,10,13,16,19}$)

Are these ω3 or ω6 fatty acids?

15.17 **Structure of Fatty Acids:** At which positions are the following ω6 fatty acids unsaturated?

(a) $C_{24:4}$ (b) $C_{30:5}$ (c) $C_{26:3}$

15.18 **Structures of Soaps and Detergents:** Which of the following would or would not be an effective soap or detergent in water? For each case, explain why.

(a) $CH_3(CH_2)_{14}CO_2{}^-Na^+$
(b) $(CH_3(CH_2)_{16}CO_2{}^-)_2Ca^{2+}$
(c) $CH_3CH_2CO_2{}^-Na^+$
(d) $CH_3(CH_2)_{14}CH_2N(CH_3)_3{}^+Cl^-$
(e) $CH_3(CH_2)_{16}CH_3$
(f) $CH_3(CH_2)_{14}CO_2H$
(g) $CH_3(CH_2)_{14}CH_2OSO_3{}^-Na^+$

15.19 **Properties of Soaps and Detergents:** For whichever compounds you identified as a soap or detergent in the previous question, indicate the hydrophobic and hydrophilic ends of the molecules.

15.20 **Consumer Chemistry:** In a grocery store or drugstore, examine the labels on the following products:

(a) Margarine. Make a list of the vegetable oils used to produce various brands of margarine.

(b) Shortenings. Make a list of the vegetable oils used to produce various brands.

(c) Oils. Make a list of the various types of oils (from different plant sources) available for sale in your local supermarket.

(d) Detergents. Determine if possible the type of detergent, and additives; if the selection is phosphate-based, record the percentage of phosphorus.

(e) Disinfectants. Find some products containing benzalkonium chlorides or cetylpyridinium chloride as antiseptics.

(f) Biolipids. Check various products as to biolipid content and consider the purpose of the compounds noted in that product. Your pharmacist should be able to help you with steroids.

15.21 **Properties of Fats and Oils:** What is the relationship between the melting point of a triacylglycerol and its iodine number?

15.22 **Structure:** How are detergents and phospholipids and sphingolipids alike in structure and function? How do they differ?

15.23 **Structure of Biolipids:** Using the compounds listed below, find the specified organic functional groups and indicate whether those functional groups are polar or nonpolar. If polar, will they donate or receive a hydrogen bond?

(a) testosterone—alcohol, aldehyde, ketone, unsaturation
(b) estradiol—aromatic ring, phenol, amine
(c) aldosterone—ketone, aldehyde
(d) glycocholic acid—amide, carboxylic acid, alcohol

15.24 **Functions of Biolipids:** How would the bile acids act as emulsifying agents for fats and oils in the intestines?

15.25 **Structure of Biolipids:** How many stereocenters are there in squalamine, the shark antimicrobial? How many stereoisomers are possible?

I_2CH_3