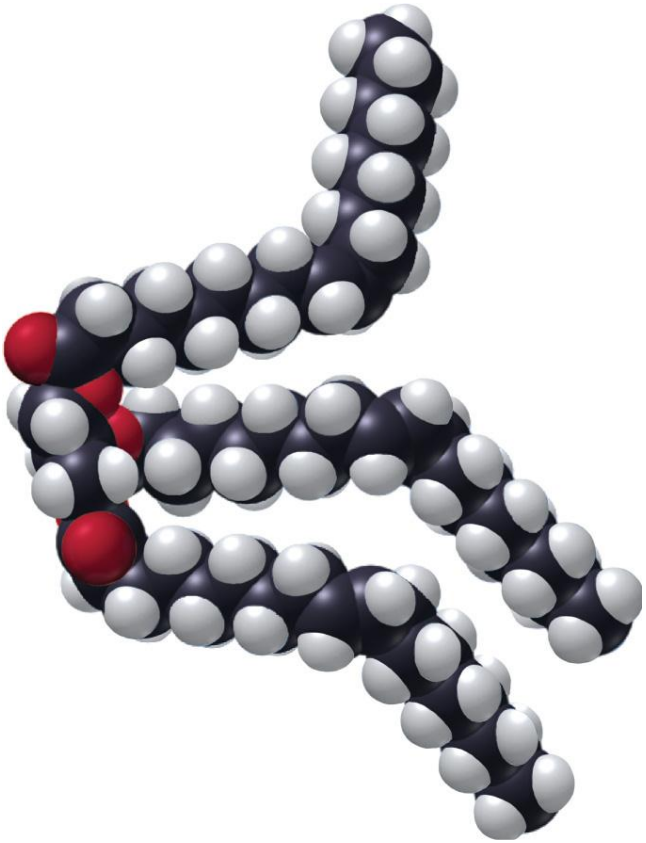
Chapter 15 Lipids



Lipids

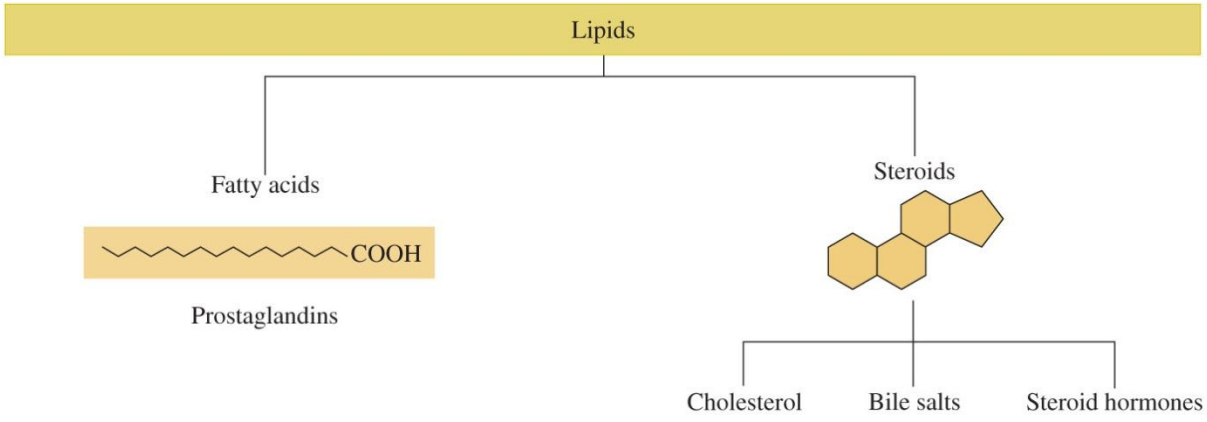
Lipids are

- biomolecules that contain fatty acids or a steroid nucleus
- soluble in organic solvents, but not in water
- named for the Greek word *lipos*, which means “fat”
- extracted from cells using organic solvents
- an important feature in cell membranes, fat-soluble vitamins, and steroid hormones

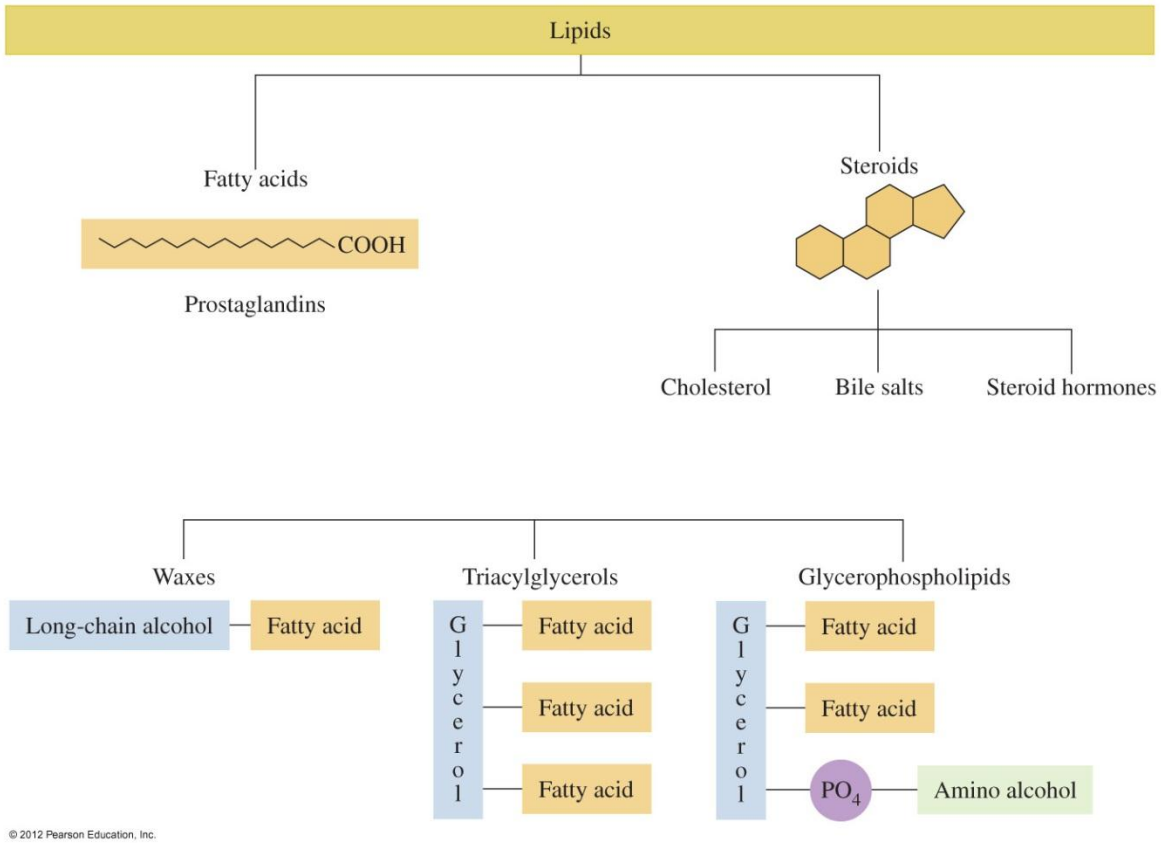
Types of Lipids

There are different types of lipids.

1. Lipids such as waxes, fats, oils, and glycerophospholipids are esters that can be hydrolyzed to give fatty acids and alcohols.
2. Steroids are also lipids; they do not contain fatty acids and cannot be hydrolyzed. They are characterized by the steroid nucleus of four fused carbon rings.



General Structure of Lipids



Lipids are naturally occurring compounds that are soluble in organic solvents but not in water.

Fatty Acids

Fatty acids are

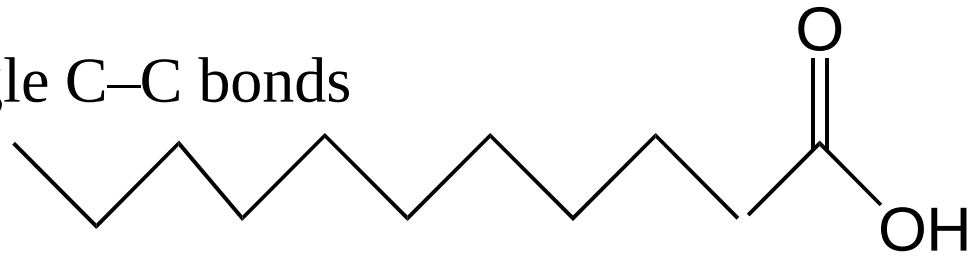
- long-chain carboxylic acids
- typically 12–18 carbon atoms
- insoluble in water
- saturated or unsaturated

Olive oil contains 84% unsaturated fatty acids and 16% saturated fatty acids.

Saturated and Unsaturated Fatty Acids

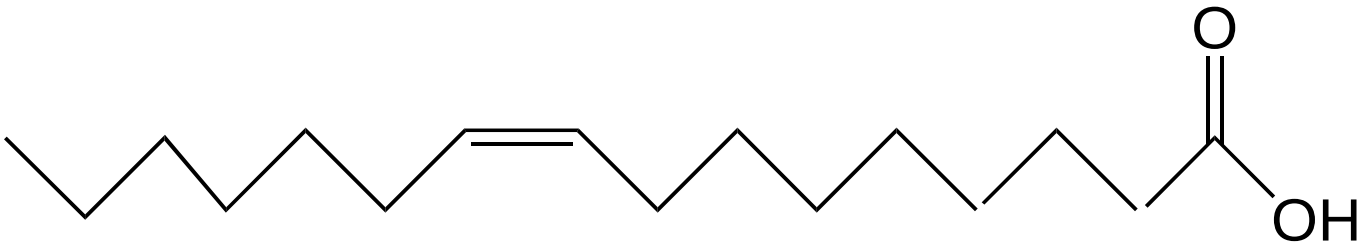
Fatty acids can be

- **saturated,** with all single C–C bonds



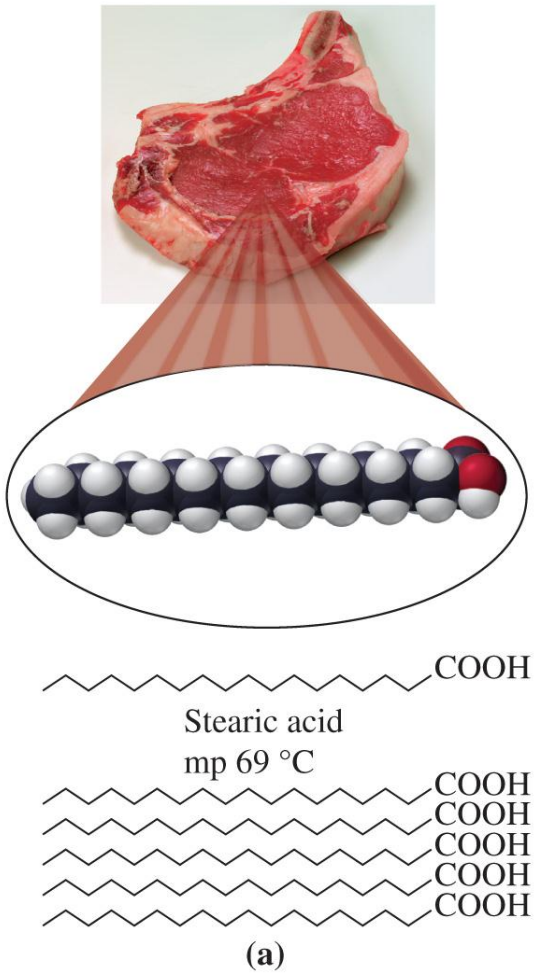
coconut oil, saturated fatty acid

- **monounsaturated,** with one double C=C bond
- **polyunsaturated,** with more than one double C=C bond



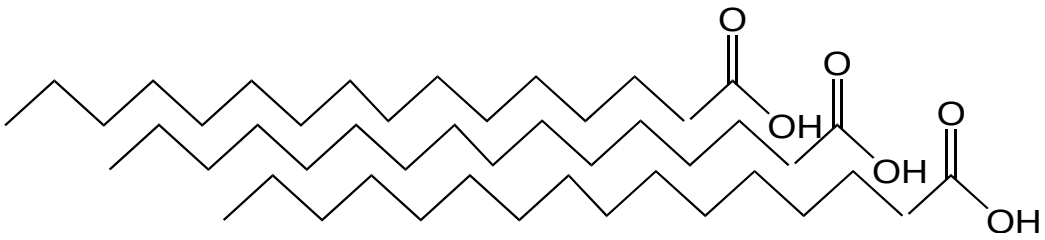
palmitoleic acid, found in butter
monounsaturated fatty acid

Properties of Saturated Fatty Acids



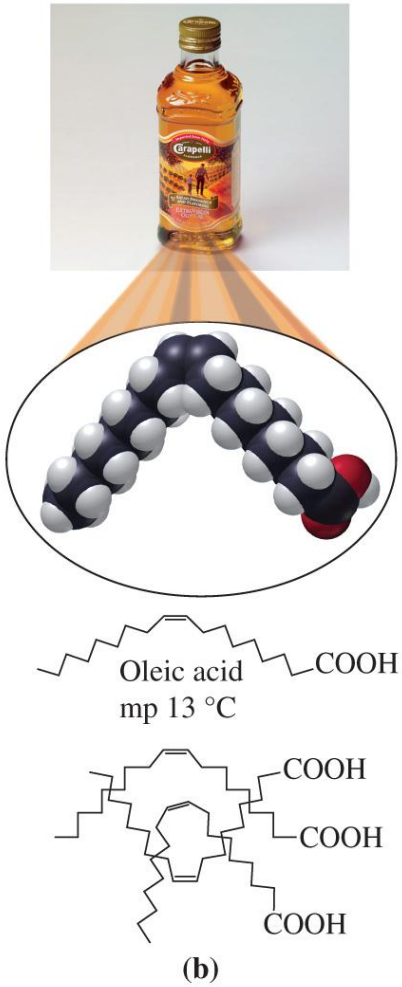
Saturated fatty acids

- contain only single C–C bonds and fit close together in a regular pattern
- have strong attractions between long carbon chains
- have higher melting points and are usually solids at room temperature



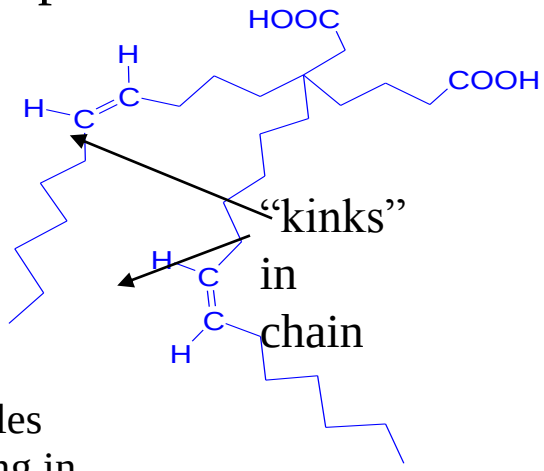
In saturated fatty acids, the molecules fit closely together to give high melting points.

Properties of Unsaturated Fatty Acids



Unsaturated fatty acids

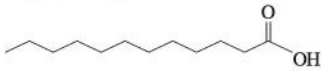
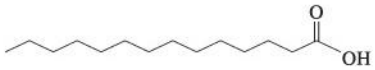
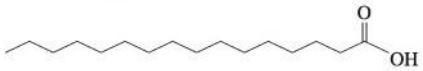
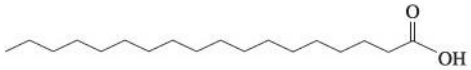
- contain one or more cis double C=C bonds
- have "kinks" in the fatty acid chains
- do not pack closely
- have few attractions between chains
- have low melting points
- are liquids at room temperature



In unsaturated fatty acids, molecules cannot fit closely together, resulting in lower melting points.

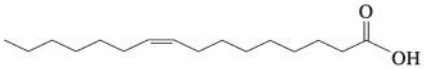
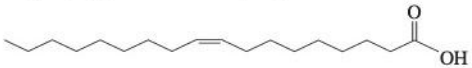
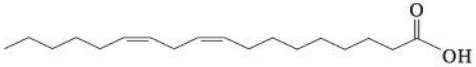
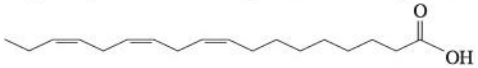
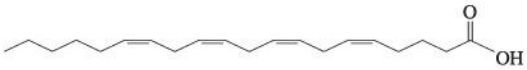
Melting Points of Some Saturated Fatty Acids

TABLE 15.1 Structures and Melting Points of Common Fatty Acids

Name	Carbon Atoms	Source	Melting Point (°C)	Structures
Saturated				
Lauric acid	12	Coconut	43	$CH_3—(CH_2)_{10}—COOH$ 
Myristic acid	14	Nutmeg	54	$CH_3—(CH_2)_{12}—COOH$ 
Palmitic acid	16	Palm	62	$CH_3—(CH_2)_{14}—COOH$ 
Stearic acid	18	Animal fat	69	$CH_3—(CH_2)_{16}—COOH$ 

Melting Points of Some Unsaturated Fatty Acids

TABLE 15.1 Structures and Melting Points of Common Fatty Acids

Name	Carbon Atoms	Source	Melting Point (°C)	Structures
Monounsaturated				
Palmitoleic acid	16	Butter	0	$CH_3—(CH_2)_5—CH{=}CH—(CH_2)_7—COOH$ 
Oleic acid	18	Olives, corn	13	$CH_3—(CH_2)_7—CH{=}CH—(CH_2)_7—COOH$ 
Polyunsaturated				
Linoleic acid	18	Soybean, safflower, sunflower	−9	$CH_3—(CH_2)_4—CH{=}CH—CH_2—CH{=}CH—(CH_2)_7—COOH$ 
Linolenic acid	18	Corn	−17	$CH_3—CH_2—CH{=}CH—CH_2—CH{=}CH—CH_2—CH{=}CH—(CH_2)_7—COOH$ 
Arachidonic acid	20	Meat, eggs, fish	−50	$CH_3—(CH_2)_3—(CH_2—CH{=}CH)_4—(CH_2)_3—COOH$ 

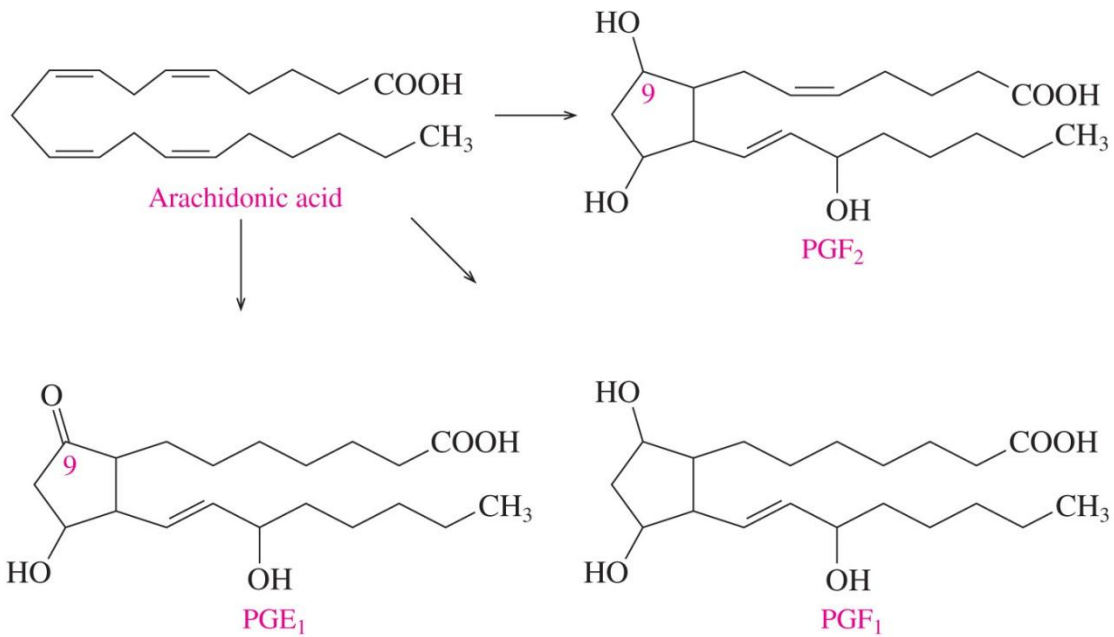
Prostaglandins

Prostaglandins

- are hormone-like substances produced in cells
- are also known as eicosanoids, formed from arachidonic acid, the polyunsaturated fatty acid with 20 carbon atoms
- differ by the substituents attached to the five-carbon ring
- have many functions, such as lower or raising blood pressure and stimulating contraction and relaxation of uterine smooth muscle

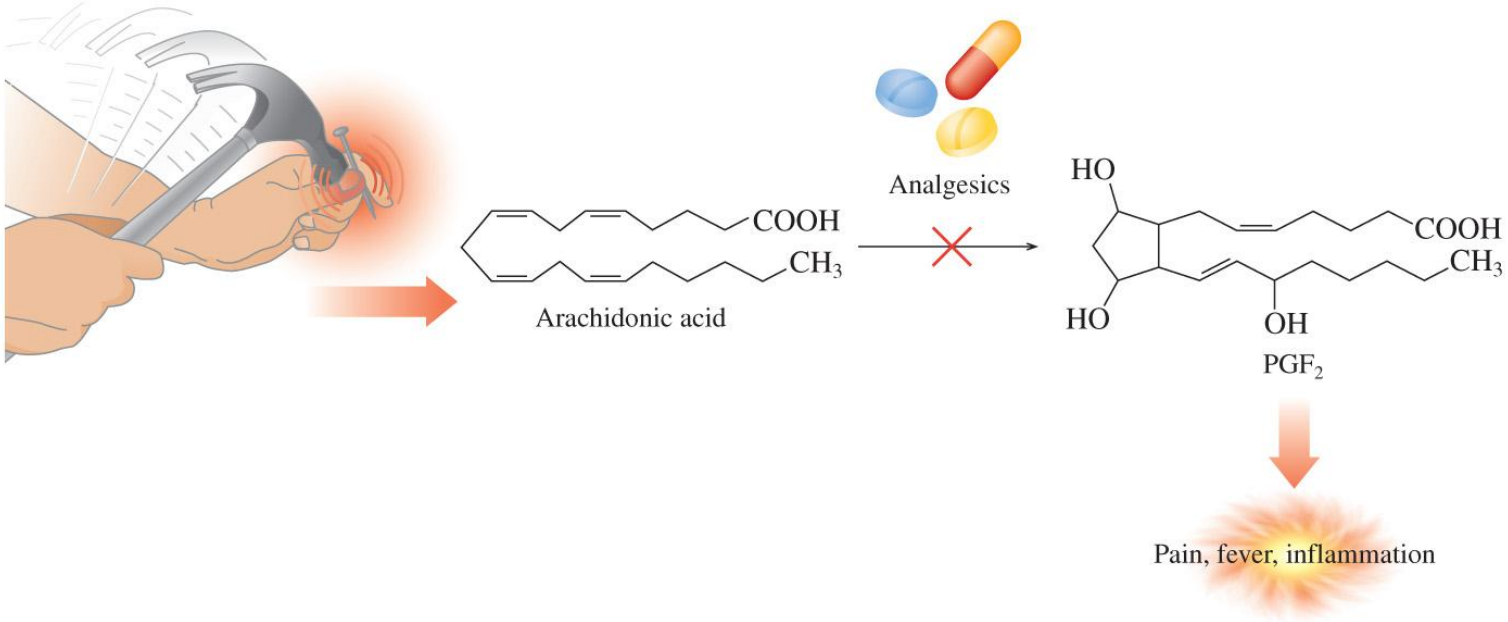
Prostaglandins

When tissues are injured, arachidonic acid is converted to prostaglandins such as PGE and PGF that produce inflammation and pain in the area.



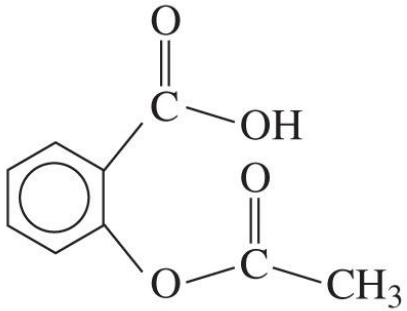
Prostaglandins: NSAIDs

The treatment of pain, fever, and inflammation is based on inhibiting the enzymes that convert arachidonic acid to prostaglandins.

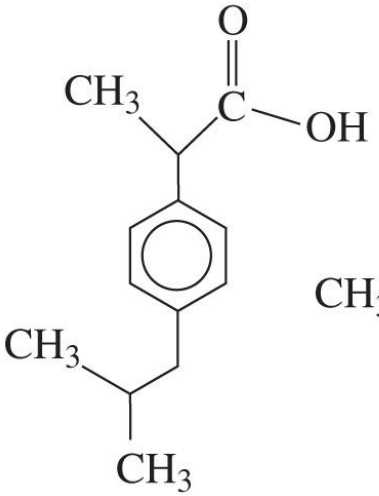


Prostaglandins: NSAIDs

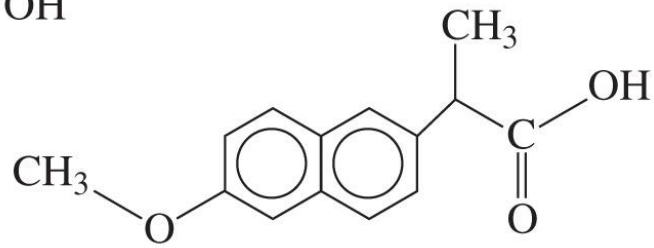
Nonsteroidal anti-inflammatory drugs (NSAIDs) block production of prostaglandins, decreasing pain and inflammation.



Aspirin (acetylsalicylic acid)



Ibuprofen (Advil, Motrin)



Naproxen (Aleve, Naprosyn)

Omega-3 Fatty Acids

Unsaturated fats such as those in vegetable oils and fish are recognized as more beneficial to health than saturated fats.

Vegetables contain omega-6 acids, meaning the first double bond occurs at carbon 6. Examples of omega-6 acids are linoleic and arachidonic acids.

Fish have high levels of omega-3 acids, meaning the first double bond occurs at carbon 3. Examples of omega-3 acids include linolenic, eicosapentaenoic, and docosahexaenoic acids.

Cold-water fish are a source of omega-3 fatty acids.

Omega-3 and Omega-6 Fatty Acids

Omega-6 Fatty Acids

Linoleic acid (LA) $CH_3—(CH_2)_4—CH{=}CH—CH_2—CH{=}CH—(CH_2)_7—COOH$

1 6

Arachidonic acid (AA) $CH_3—(CH_2)_4—(CH{=}CH—CH_2)_4—(CH_2)_2—COOH$

1 6

Omega-3 Fatty Acids

Linolenic acid (ALA) $CH_3—CH_2—(CH{=}CH—CH_2)_3—(CH_2)_6—COOH$

1 3

Eicosapentaenoic acid (EPA) $CH_3—CH_2—(CH{=}CH—CH_2)_5—(CH_2)_2—COOH$

1 3

Docosahexaenoic acid (DHA) $CH_3—CH_2—(CH{=}CH—CH_2)_6—CH_2—COOH$

1 3

Waxes

Waxes are

- esters of saturated fatty acids and long-chain alcohols
- coatings that prevent loss of water by leaves of plants

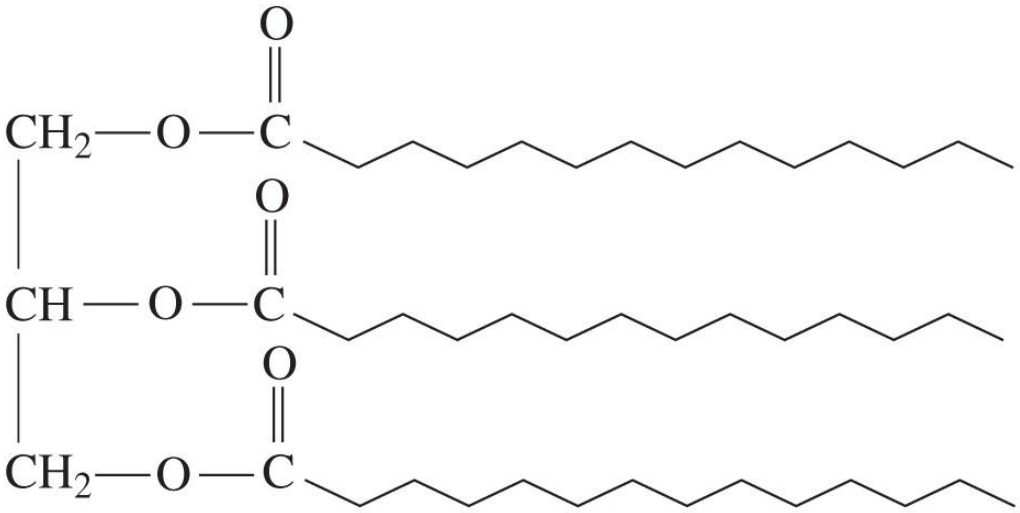
TABLE 15.2 Some Typical Waxes

Type	Condensed Structural Formula	Source	Uses
Beeswax	$CH_3—(CH_2)_{14}—\overset{\overset{\displaystyle O}{\|}}{C}—O—(CH_2)_{29}—CH_3$	Honeycomb	Candles, shoe polish, wax paper
Carnauba wax	$CH_3—(CH_2)_{24}—\overset{\overset{\displaystyle O}{\|}}{C}—O—(CH_2)_{29}—CH_3$	Brazilian palm tree	Waxes for furniture, cars, floors, shoes
Jojoba wax	$CH_3—(CH_2)_{18}—\overset{\overset{\displaystyle O}{\|}}{C}—O—(CH_2)_{19}—CH_3$	Jojoba bush	Candles, soaps, cosmetics

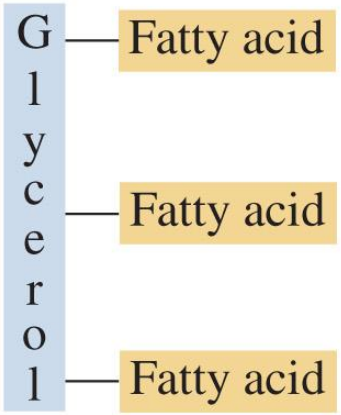
Fats and Oils: Triacylglycerols

Fats and oils are

- also called triacylglycerols
- esters of glycerol
- produced by esterification
- formed when the hydroxyl groups of glycerol react with the carboxyl groups of fatty acids
- In a **triacylglycerol**, glycerol forms ester bonds with three fatty acids.

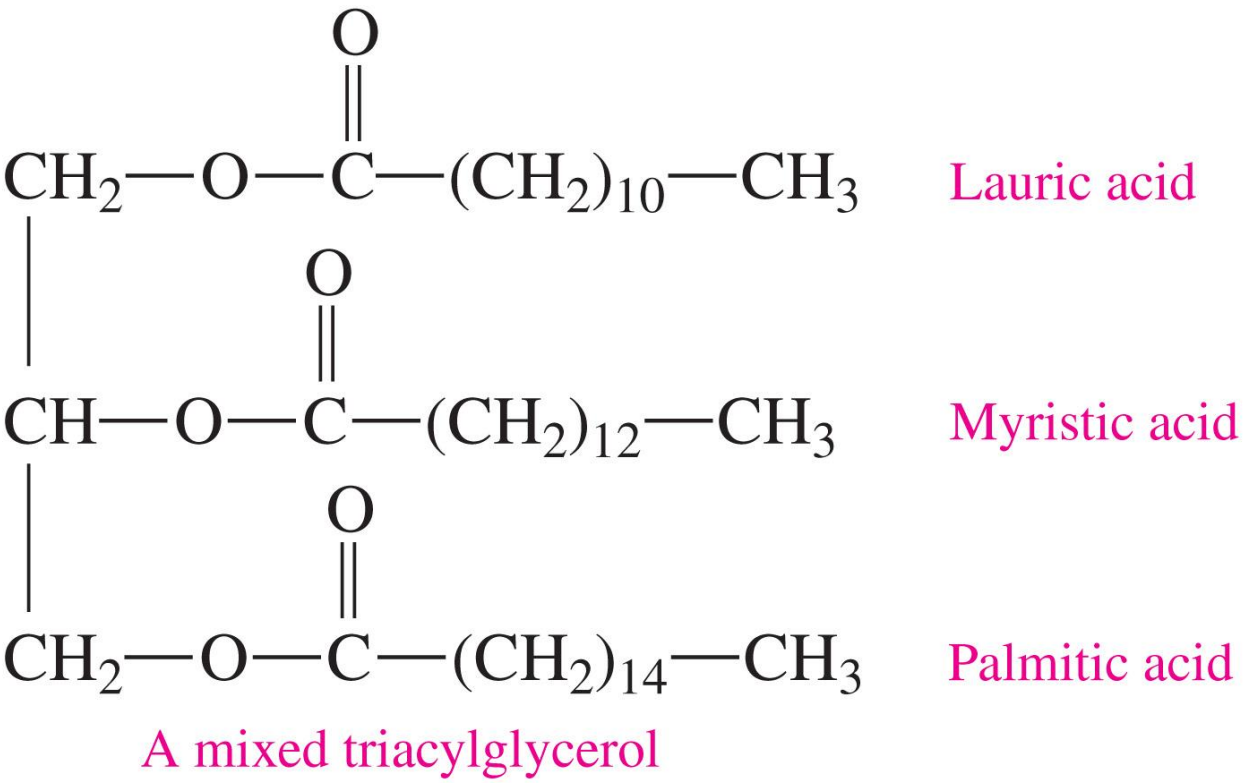


Triacylglycerol



Triacylglycerols

Triacylglycerol may contain different fatty acids.



Melting Points of Fats and Oils

A **fat**

- is usually solid at room temperature
- is prevalent in meats, whole milk, butter, and cheese

An **oil**

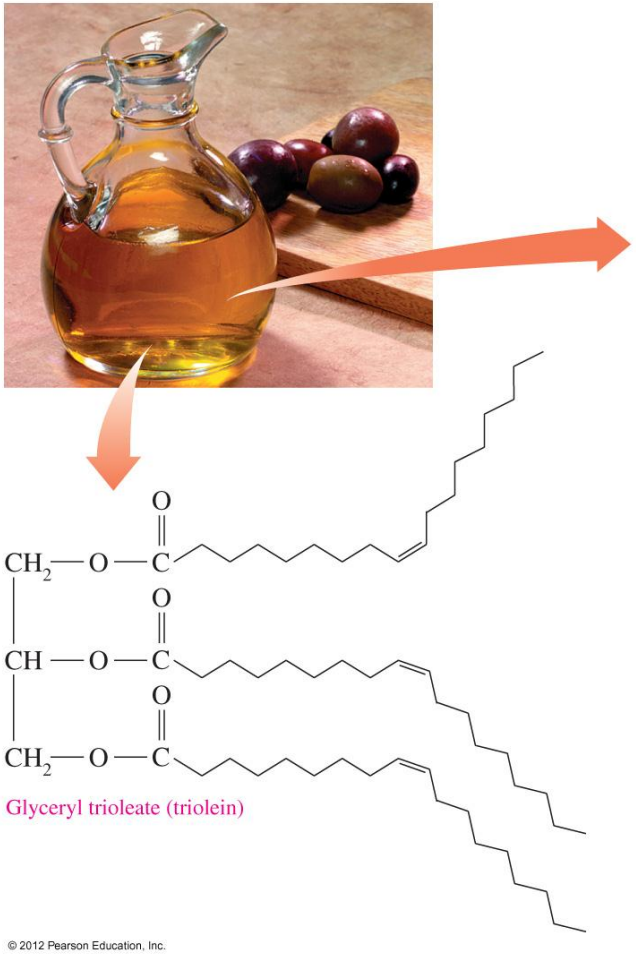
- is usually liquid at room temperature
- is prevalent in plants such as olive and safflower

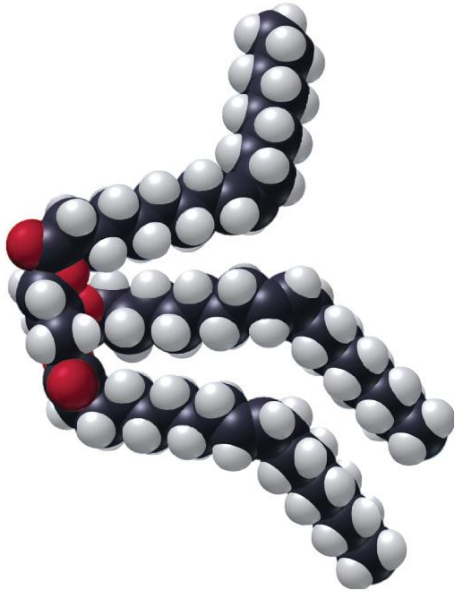
Oils with Unsaturated Fatty Acids

Oils

- have more unsaturated fats
- have cis double bonds that cause “kinks” in the fatty acid chains
- with “kinks” in the chains do not allow the triacylglycerol molecules to pack closely
- have lower melting points than saturated fatty acids
- are liquids at room temperature

Diagram of Triacylglycerol with Unsaturated Fatty Acids

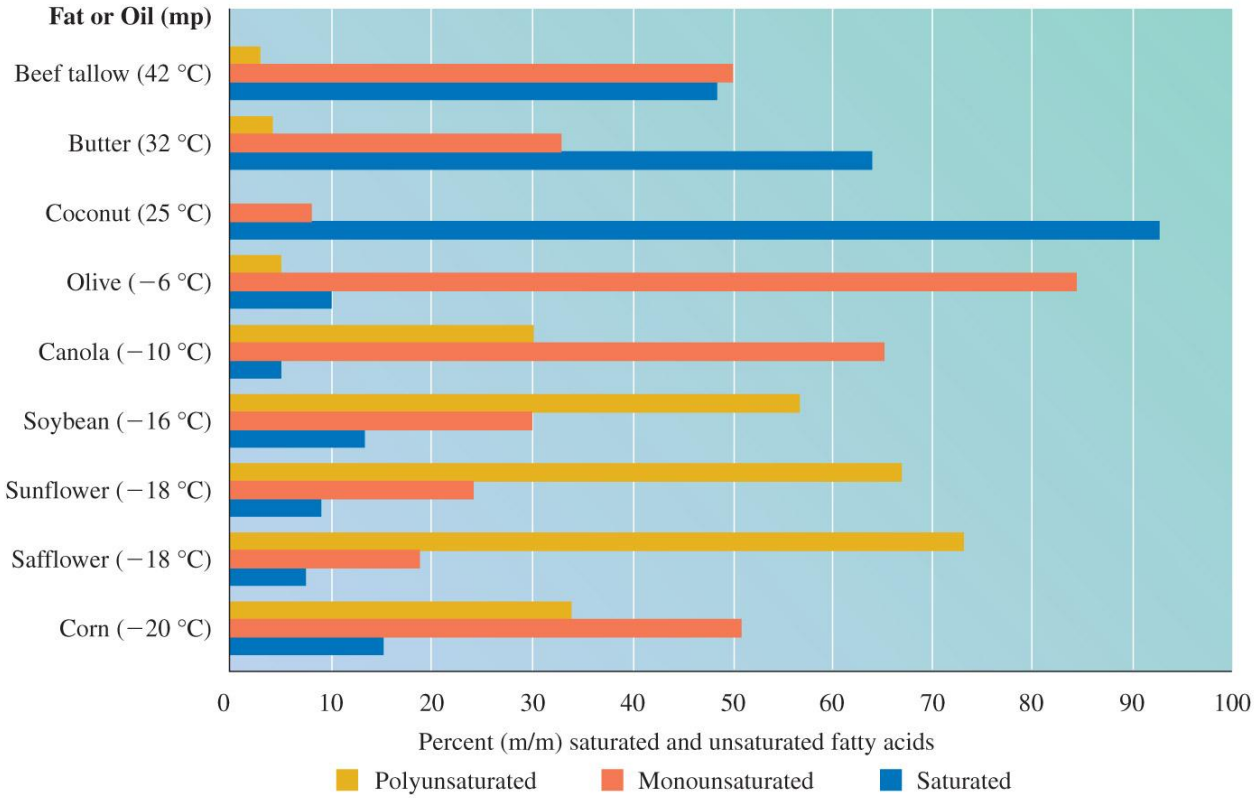




Unsaturated fatty acid chains with kinks cannot pack closely while those with saturated fatty acid chains can. This close packing leads to higher melting points for saturated fats than unsaturated fats.

Percent Saturated and Unsaturated Fatty Acids in Fats and Oils

Vegetable oils have low melting points because they have a higher percentage of unsaturated fatty acids than do animal fats.



Chemical Properties of Triacylglycerols

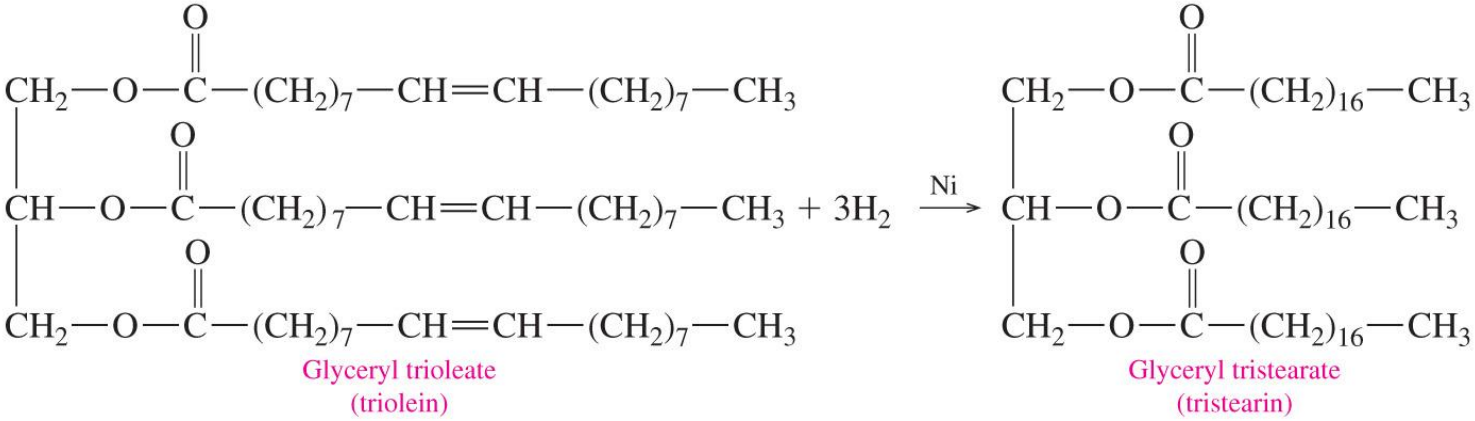
The chemical reactions of triacylglycerols are similar to those of alkenes and esters. In

- **hydrogenation**, double bonds in unsaturated fatty acids react with H_2 in the presence of a Ni or Pt catalyst
- **hydrolysis**, ester bonds are split by water in the presence of an acid, a base, or an enzyme

Hydrogenation of Oils

The **hydrogenation** of oils

- adds hydrogen (H_2) to the carbon atoms of double bonds
- converts double bonds to single bonds increases the melting point
- produces solids, such as margarine and shortening

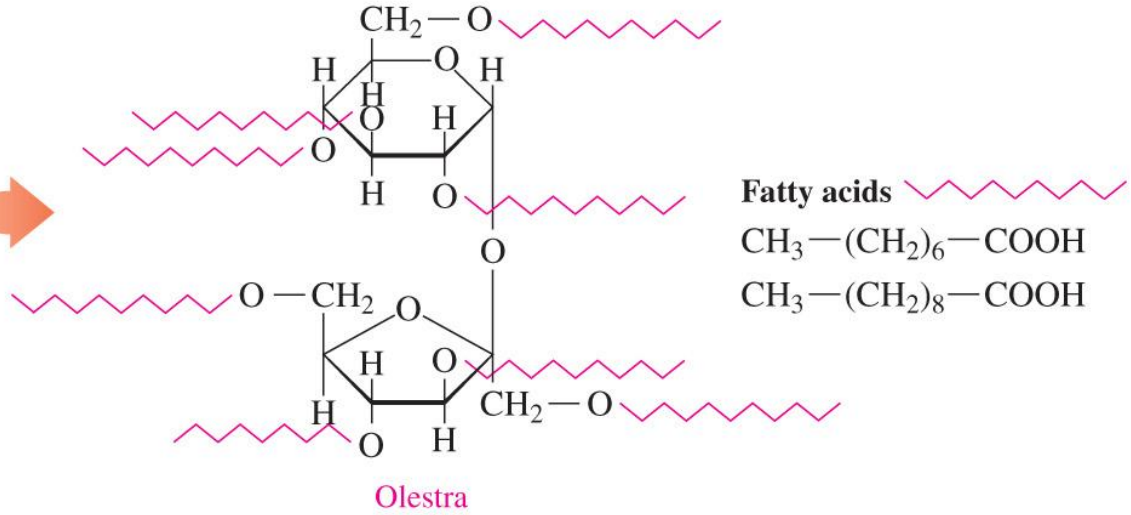


When hydrogen adds to all the double bonds of glyceryl trioleate (triolein) using a nickel catalyst, the product is the saturated fat glyceryl tristearate (tristearin).

Olestra, a Fat Substitute

Olestra is

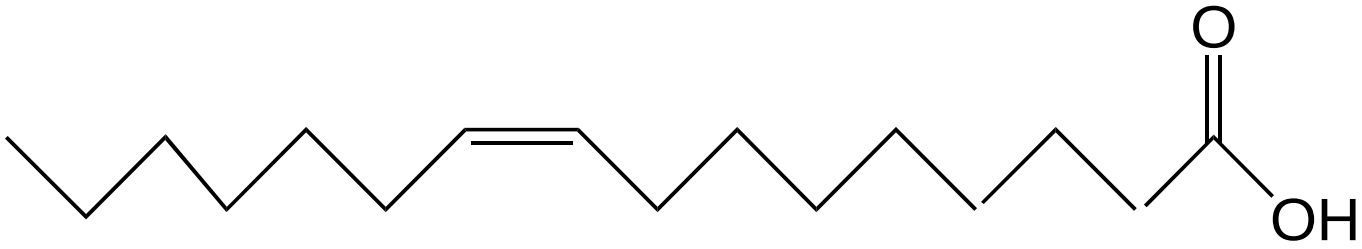
- used in foods as an artificial fat
- sucrose linked by ester bonds to several long-chain fatty chains
- not broken down in the intestinal tract



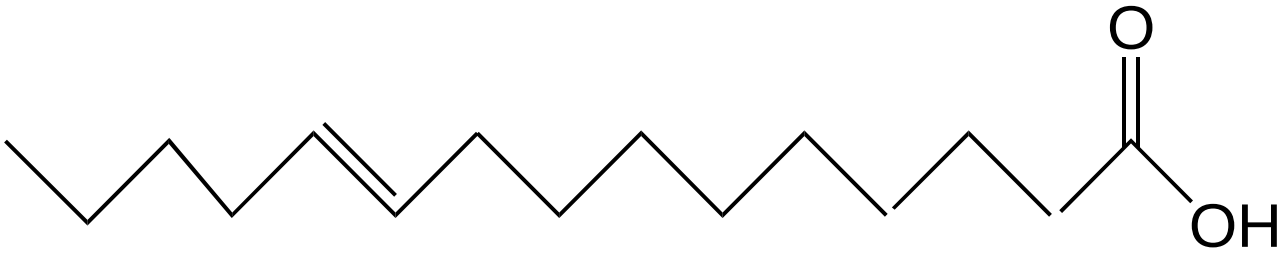
Cis and Trans Fatty Acids

Unsaturated fatty acids can be

- cis, with bulky groups on same side of C=C



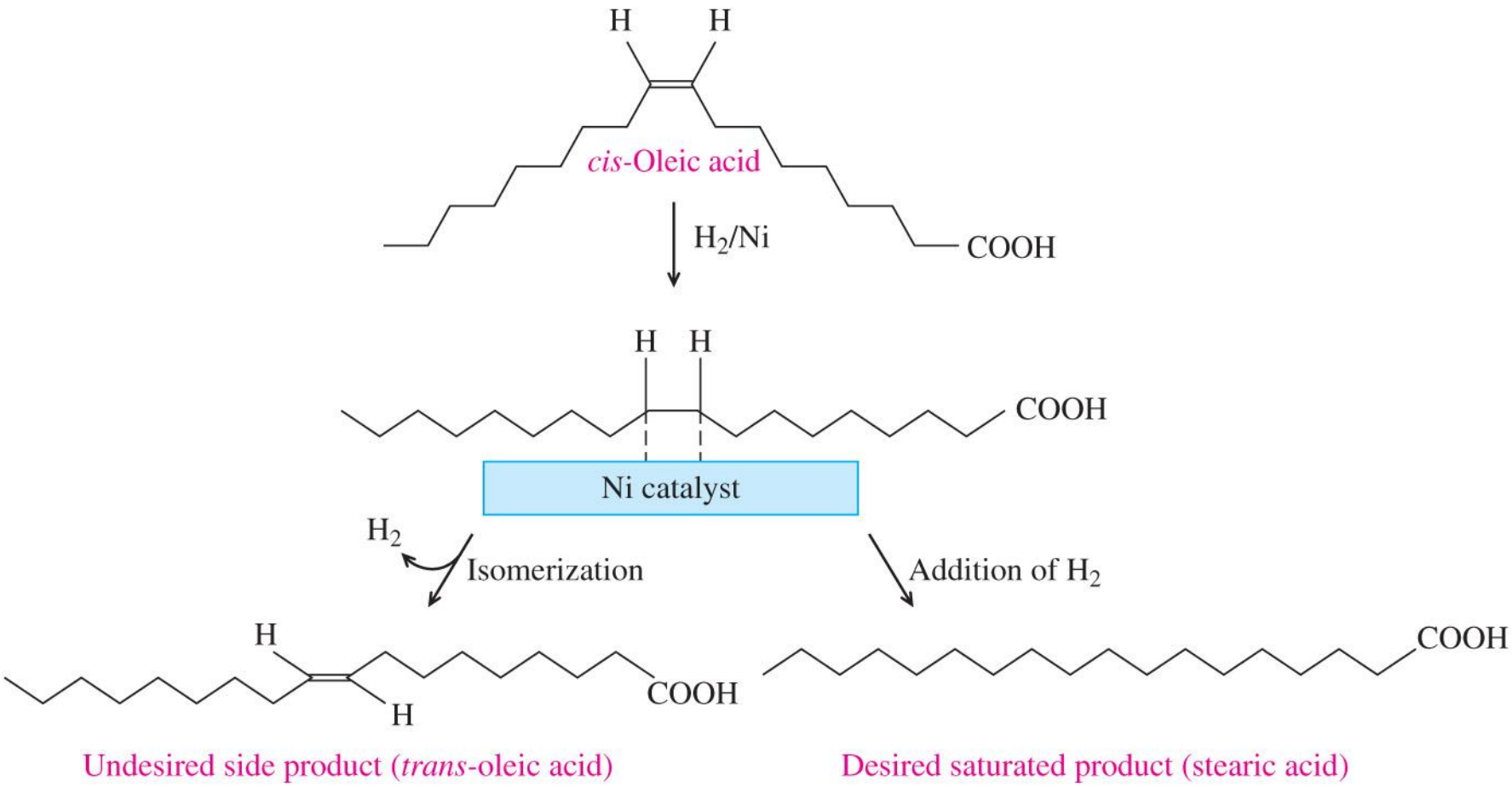
- trans, with bulky groups on opposite sides of C=C



Hydrogenation and Trans Fatty Acids

- Most naturally occurring fatty acids have cis double bonds.
- During hydrogenation, some cis double bonds are converted to trans double bonds.
- In the body, trans fatty acids behave like saturated fatty acids.
- It is estimated that 2–4% of our total calories are in the form of trans fatty acids.
- Several studies reported that trans fatty acids raise LDL-cholesterol and lower HDL-cholesterol.

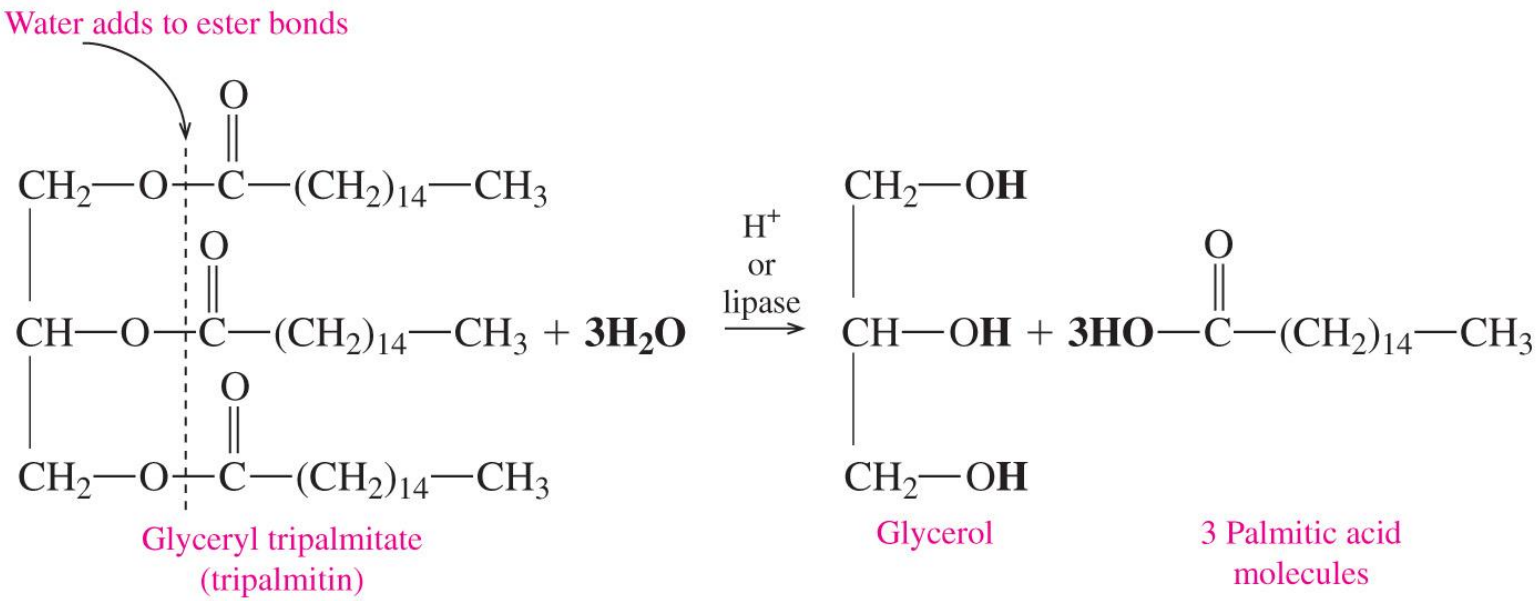
Hydrogenation of Unsaturated Fats



Hydrolysis

In **hydrolysis**,

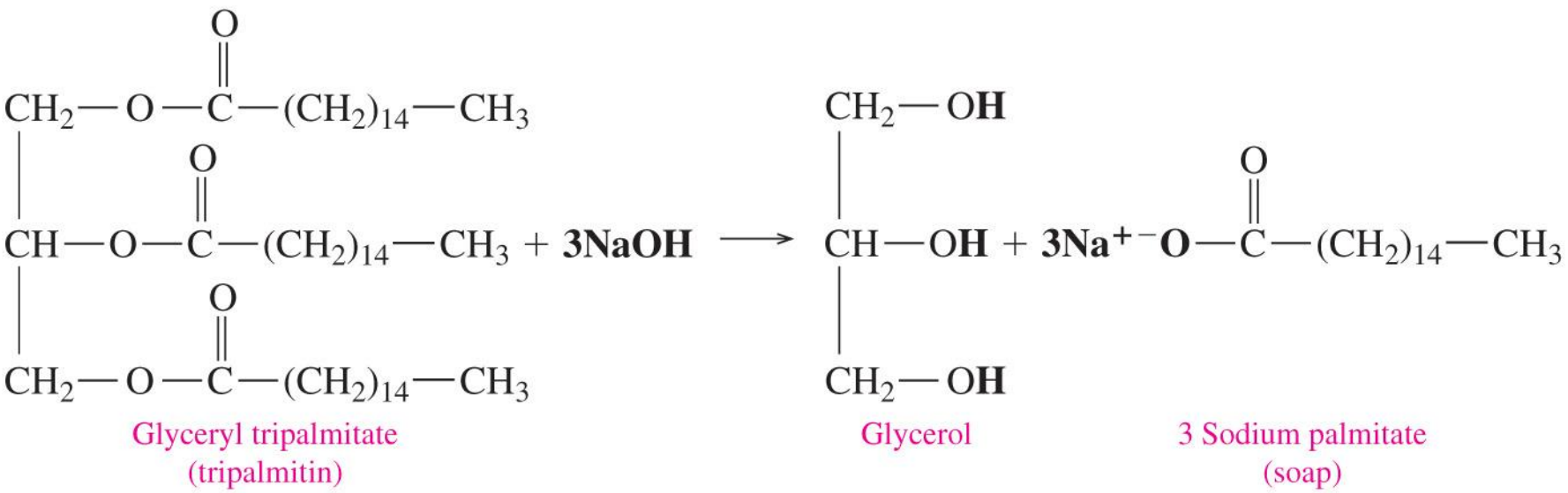
- triacylglycerols split into glycerol and three fatty acids
- an acid or enzyme catalyst is required



Saponification and Soap

Saponification

- is the reaction of a fat with a strong base
- splits triacylglycerols into glycerol and the salts of fatty acids
- is the process of forming “soaps” (salts of fatty acids)
- with KOH gives softer soaps



Summary of Organic and Lipid Reactions

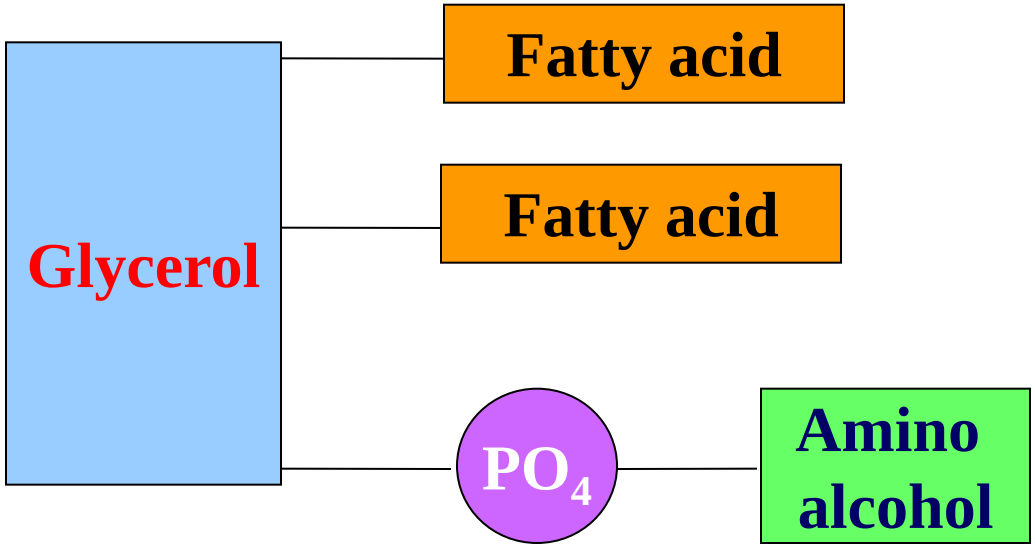
TABLE 15.3 Summary of Organic and Lipid Reactions

Reaction	Organic Reactants and Products	Lipid Reactants and Products
Esterification	Carboxylic acid + alcohol $\xrightarrow{H^+, \text{Heat}}$ ester + water	3 Fatty acids + glycerol $\xrightarrow{\text{Enzyme}}$ triacylglycerol (fat) + 3 water
Hydrogenation	Alkene (double bond) + hydrogen $\xrightarrow{\text{Pt}}$ alkane (single bonds)	Unsaturated fat (double bonds) + hydrogen $\xrightarrow{\text{Ni}}$ saturated fat (single bonds)
Hydrolysis	Ester + water $\xrightarrow{H^+, \text{Heat}}$ carboxylic acid + alcohol	Triacylglycerol (fat) + 3 water $\xrightarrow{\text{Enzyme}}$ 3 fatty acids + glycerol
Saponification	Ester + sodium hydroxide $\longrightarrow$ sodium salt of carboxylic acid + alcohol	Triacylglycerol (fat) + 3 sodium hydroxide $\longrightarrow$ 3 sodium salts of fatty acid (soaps) + glycerol

Glycerophospholipids

Glycerophospholipids are

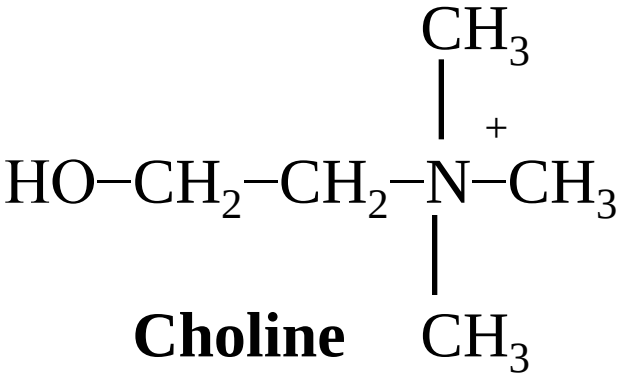
- the most abundant lipids in cell membranes
- composed of glycerol, two fatty acids, phosphate, and an amino alcohol



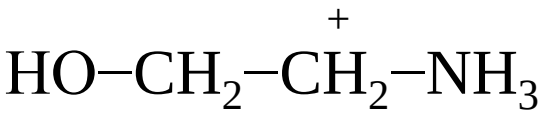
Polarity of Glycerophospholipids

Amino alcohols found in **glycerophospolipids**

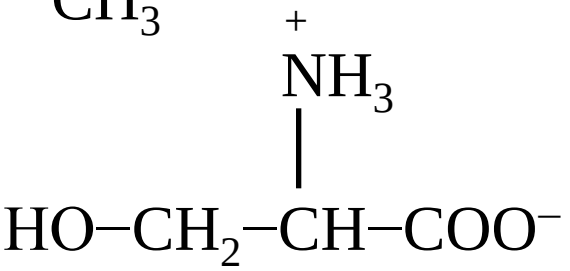
- have two nonpolar fatty acid chains, a phosphate group, and a polar amino alcohol
- are ionized at physiological pH of 7.4



Choline



Ethanolamine

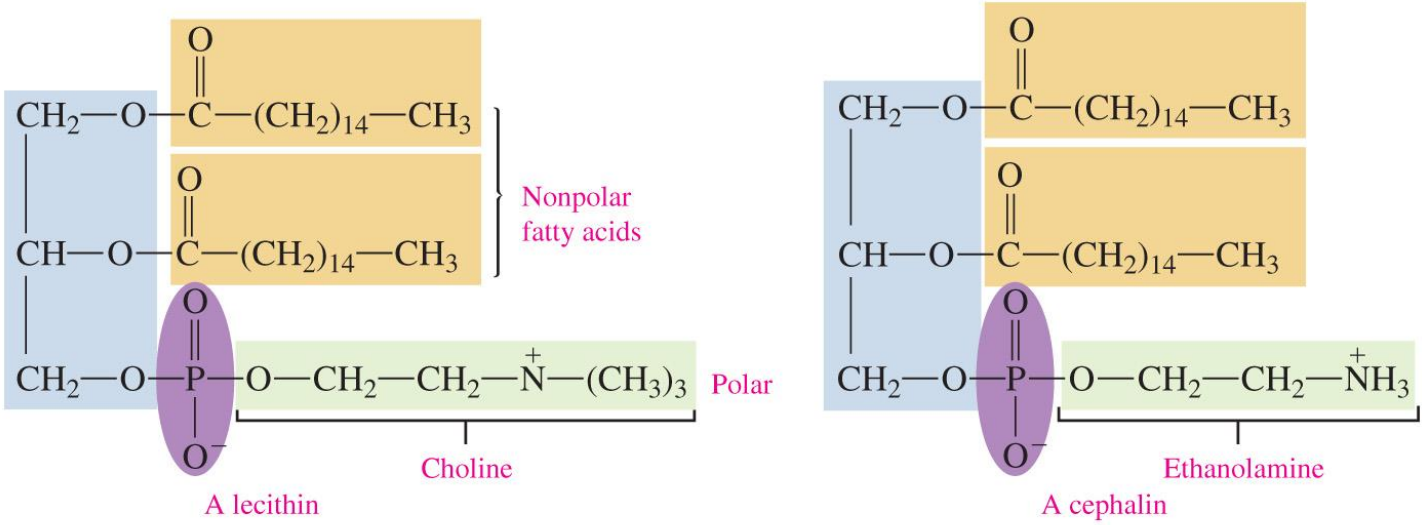


Serine

Lecithin and Cephalin

Lecithin and **cephalin** are types of glycerophospholipids that are

- abundant in brain and nerve tissues
- found in egg yolk, wheat germ, and yeast

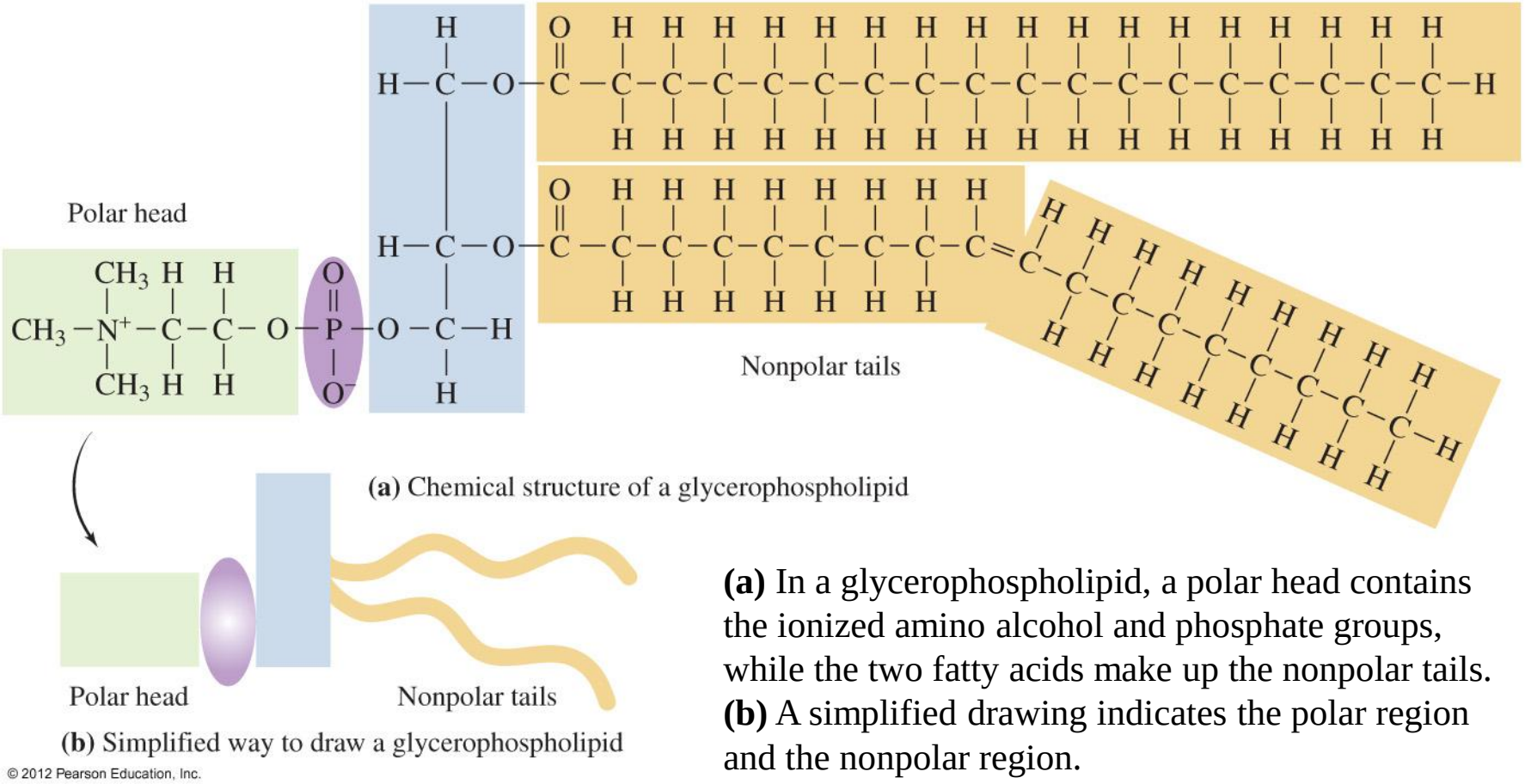


Structure and Polarity of a Glycerophospholipid

Glycerophospholipids

- have both polar and nonpolar regions that allow them to interact with polar and nonpolar substances
- have a polar head containing the ionized amino alcohol and phosphate portion, which is strongly attracted to water
- have a hydrocarbon tail portion only soluble in nonpolar substances such as lipids
- are the most abundant lipids in cell membranes and play an important role in cellular permeability

Structure and Polarity of a Glycerophospholipid

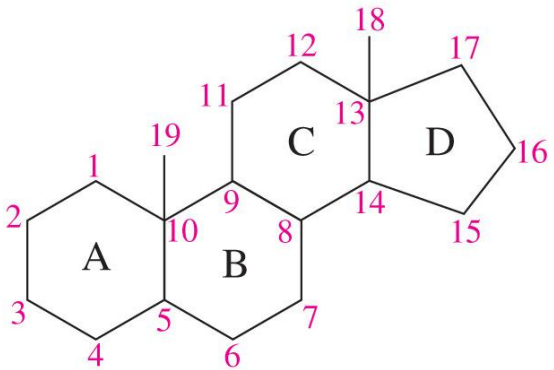


(a) In a glycerophospholipid, a polar head contains the ionized amino alcohol and phosphate groups, while the two fatty acids make up the nonpolar tails. **(b)** A simplified drawing indicates the polar region and the nonpolar region.

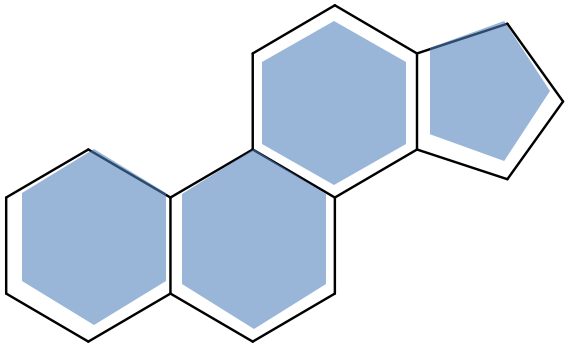
Steroid Nucleus

A **steroid nucleus** consists of

- three cyclohexane rings and one cylopentane ring fused together
- rings designated as A, B, C, and D
- numbered carbon atoms beginning in ring A



Steroid numbering system

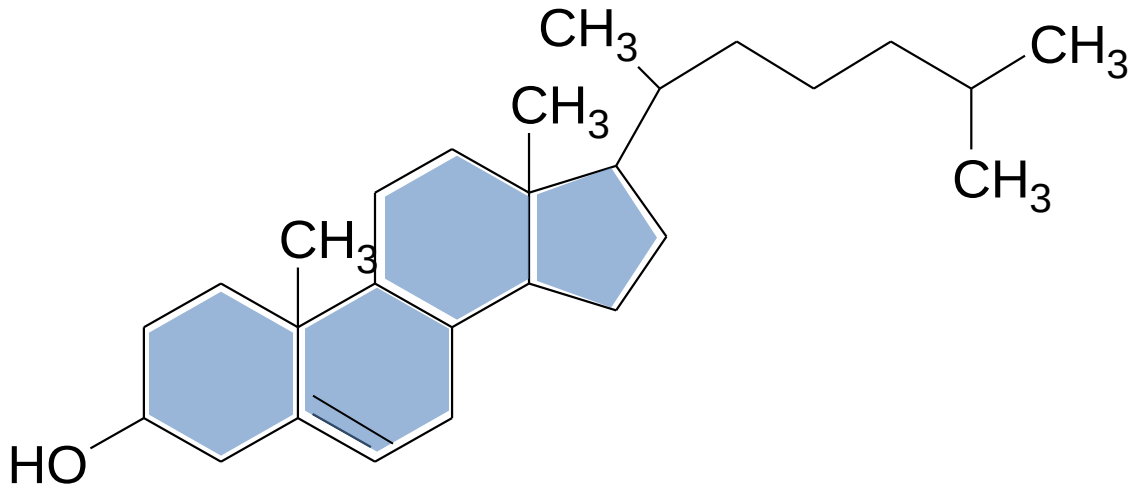


steroid nucleus

Cholesterol

Cholesterol

- is the most abundant steroid in the body
- has methyl groups (carbons 10, 13) an alkyl chain (carbon 17), and an –OH group (carbon 3) attached to the steroid nucleus



Cholesterol in the Body

Cholesterol

- is obtained from meats, milk, and eggs
- is synthesized in the liver
- is needed for cell membranes, brain and nerve tissue, steroid hormones, and vitamin D
- clogs arteries when high levels form plaque

A normal, open artery.

(a)

(b)

An artery clogged by cholesterol plaque

Cholesterol in Foods

Cholesterol

- is considered elevated if plasma cholesterol exceeds 200 mg/dL
- is synthesized in the liver and obtained from foods
- increases in the liver when high levels of saturated fat are consumed

Cholesterol in Foods

TABLE 15.4 Cholesterol Content of Some Foods

Food	Serving Size	Cholesterol (mg)
Liver (beef)	3 oz	370
Large egg	1	200
Lobster	3 oz	175
Fried chicken	$3\frac{1}{2}$ oz	130
Hamburger	3 oz	85
Chicken (no skin)	3 oz	75
Fish (salmon)	3 oz	40
Whole milk	1 cup	35
Butter	1 tablespoon	30
Skim milk	1 cup	5
Margarine	1 tablespoon	0

Learning Check

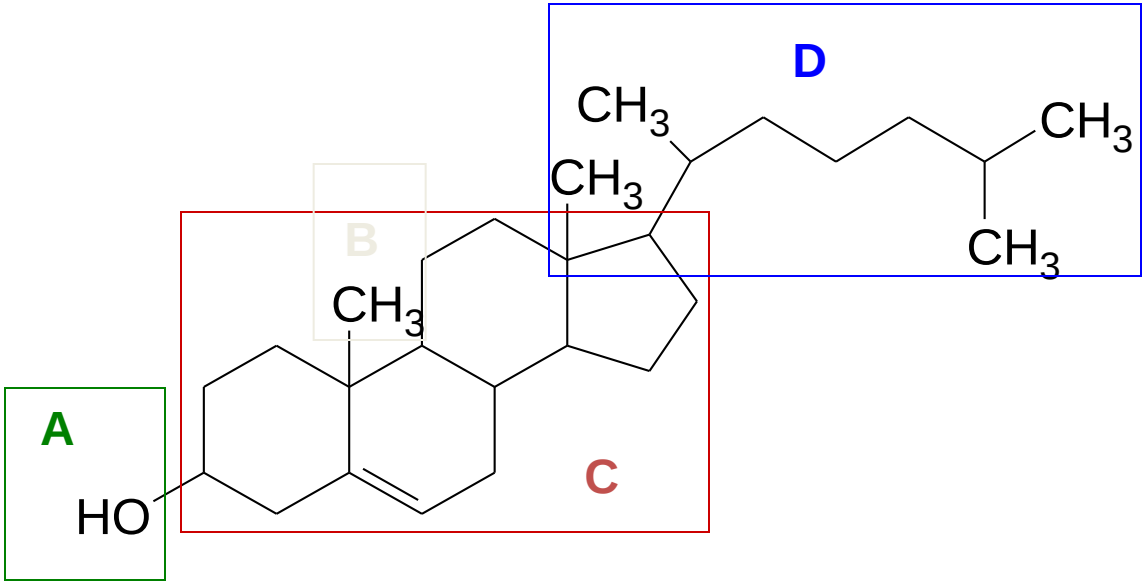
Match the components of the cholesterol molecule with the following:

___ carbon chain

___ hydroxyl group

___ steroid nucleus

___ methyl group



Solution

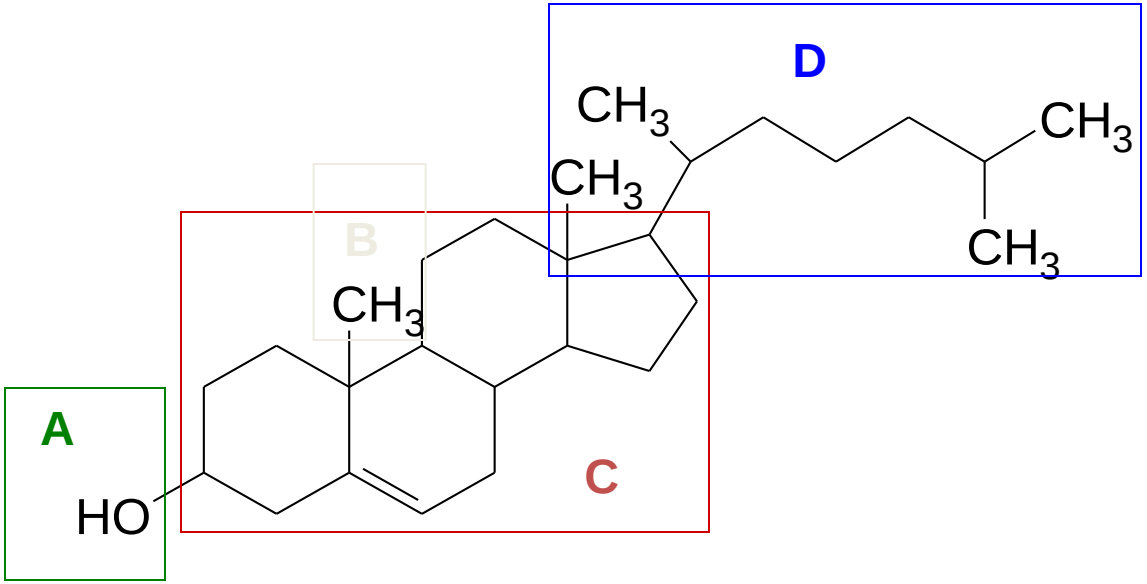
Match the components of the cholesterol molecule with the following:

D carbon chain

A hydroxyl group

C steroid nucleus

B methyl group



Bile Salts

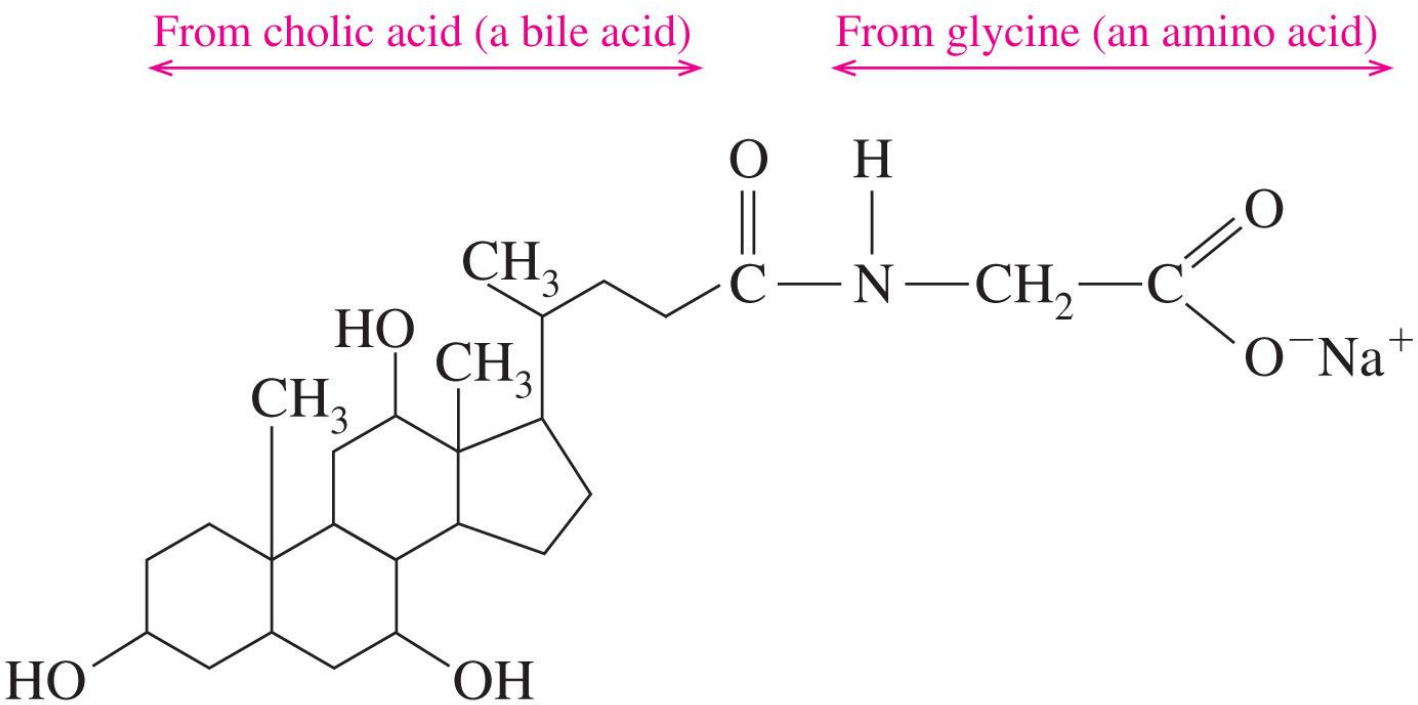
Bile salts

- are synthesized in the liver from cholesterol and stored in the gallbladder
- have polar and nonpolar regions that act like soaps to make fat soluble in water
- help in absorption of cholesterol

When large amounts of cholesterol accumulate in the gallbladder, gallstones are formed.

Gallstones form in the gallbladder when cholesterol levels are high.

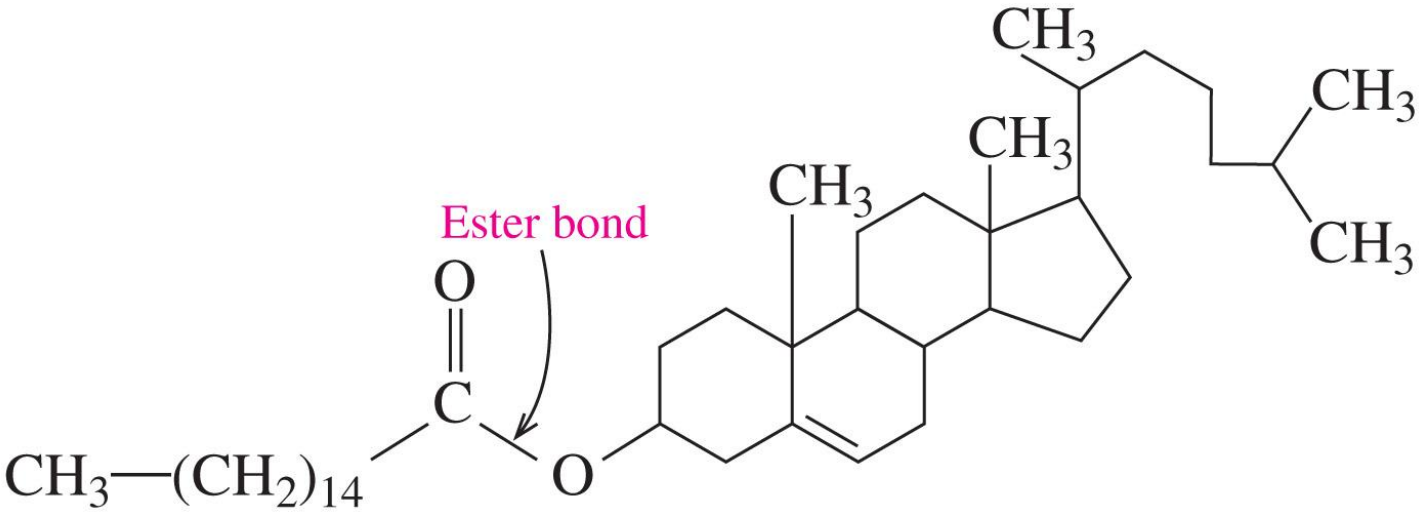
Bile Salts



Sodium glycocholate (a bile salt)

Lipoproteins: Lipid Transport

Lipids are nonpolar and made more soluble by combining them with glycerophospholipids and proteins to form water-soluble complexes called lipoproteins.

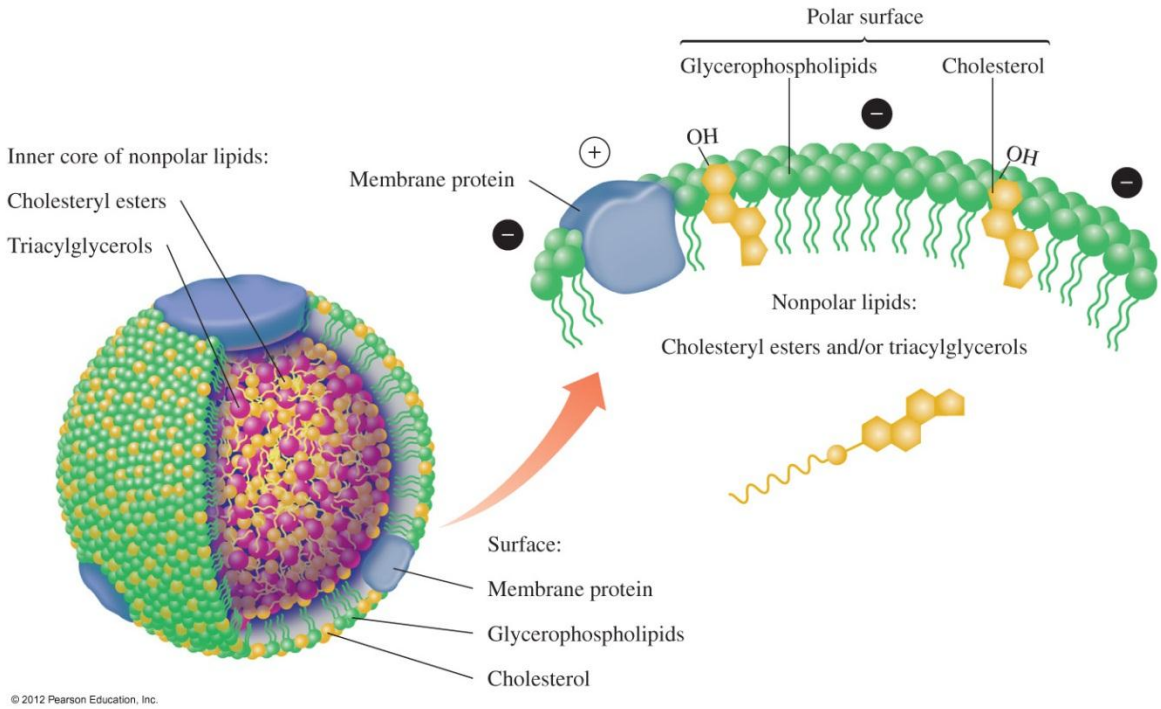


Cholesteryl ester

Lipoproteins

Lipoproteins

- surround nonpolar lipids with polar lipids and protein for transport to cells
- are soluble in water because the surface consists of polar lipids



Types of Lipoproteins

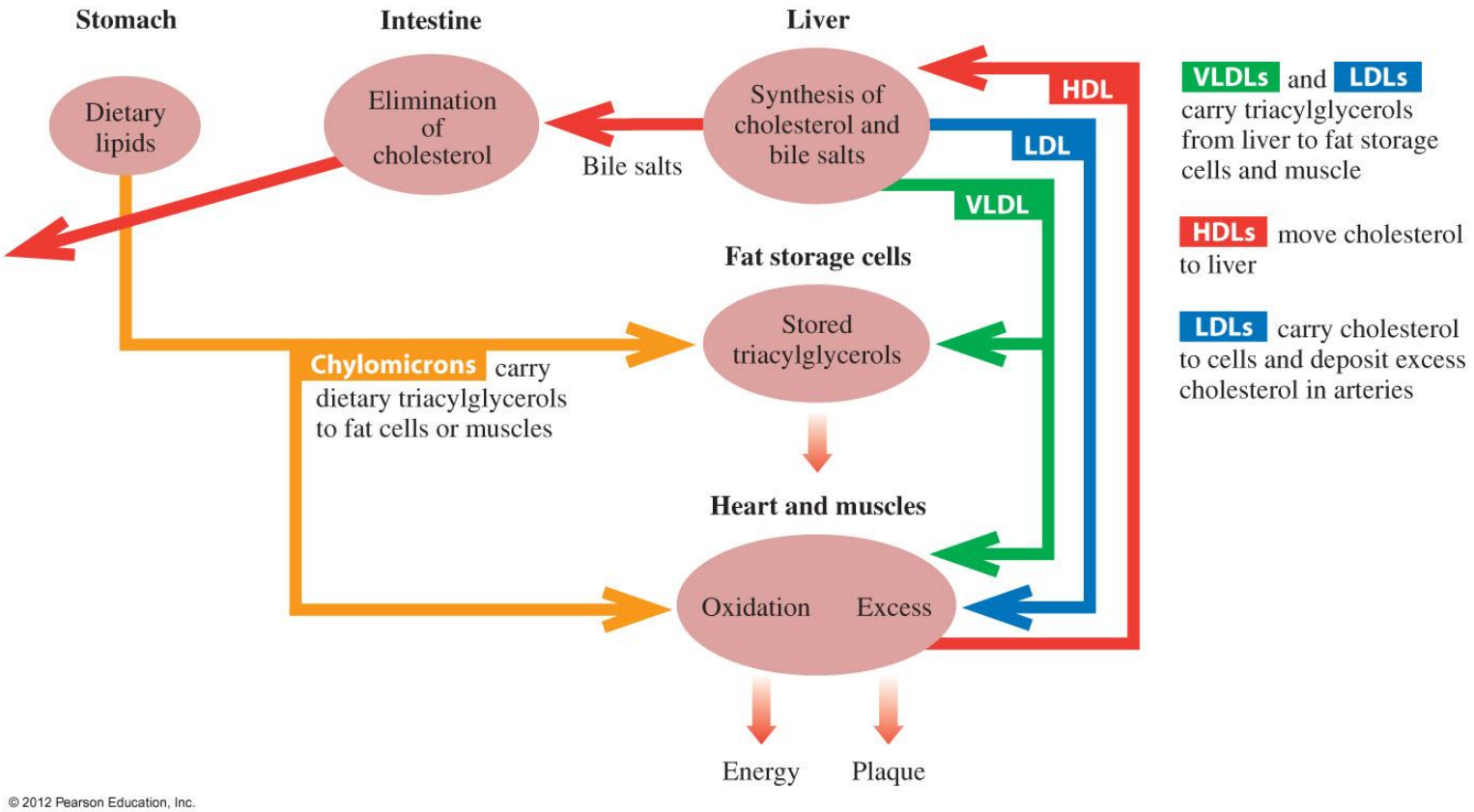
Lipoproteins

- differ in density, composition, and function
- include low-density lipoproteins (LDLs) and high-density lipoproteins (HDLs)

TABLE 15.5 Composition and Properties of Plasma Lipoproteins

	Chylomicron	VLDL	LDL	HDL
Density (g/mL)	<0.95	0.950–1.006	1.006–1.063	1.063–1.210
Composition (% by mass)				
Triacylglycerol	86	55	6	4
Phospholipids	7	18	22	24
Cholesterol	2	7	8	2
Cholesteryl esters	3	12	42	15
Protein	2	8	22	55

Transport of Lipoproteins in the Body



Lipoproteins such as HDLs and LDLs transport nonpolar lipids and cholesterol to cells and the liver.

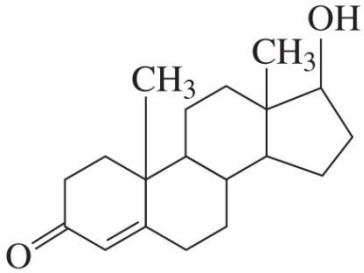
Steroid Hormones

Steroid hormones are

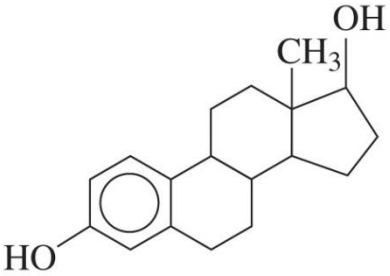
- chemical messengers that serve as a communication system for the body
- produced from cholesterol
- sex hormones
  - androgens in males (testosterone and androsterone)
  - estrogens in females (estradiol)
- adrenal corticosteroids from adrenal glands
  - mineralocorticoids (electrolyte balance)
  - glucocorticoids (regulate glucose level)

Sex Hormones

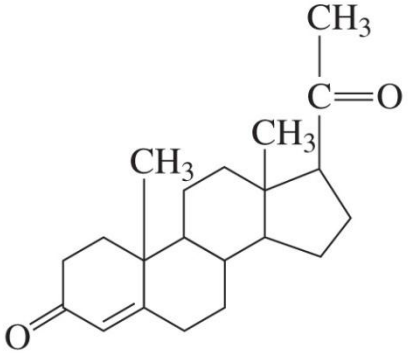
Sex hormones include sex hormones such as androgens (testosterone) in males and estrogens (estradiol) in females.



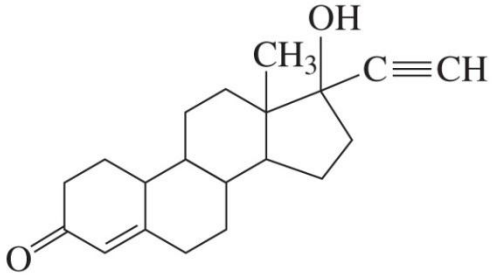
Testosterone (androgen)
(produced in testes)



Estradiol (estrogen)
(produced in ovaries)



Progesterone
(produced in ovaries)



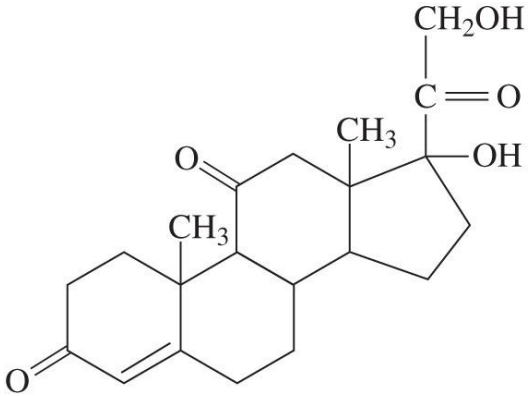
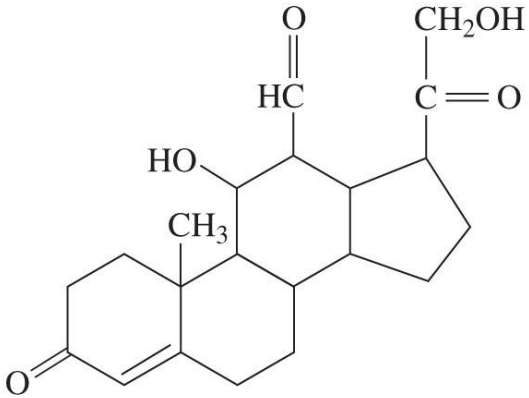
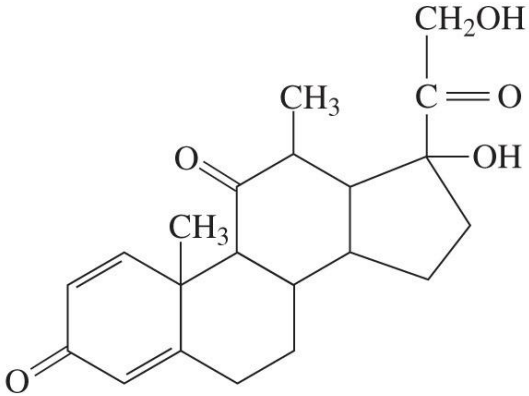
Norethindrone
(synthetic progestin)

Adrenal Corticosteroids

Steroid hormones called **adrenal corticosteroids**

- are produced by the adrenal glands located on the top of each kidney
- include *aldosterone*, which regulates electrolytes and water balance by the kidneys
- include *cortisone*, a glucocorticoid, which increases blood glucose level and stimulates the synthesis of glycogen in the liver

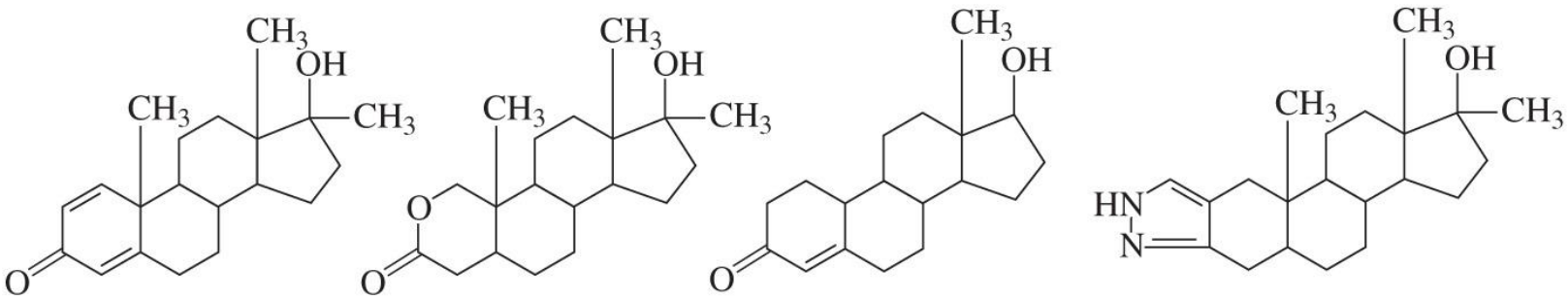
Adrenal Corticosteroids

Corticosteroids		
 Cortisone (produced in adrenal gland)	 Aldosterone (mineralocorticoid) (produced in adrenal gland)	 Prednisone (synthetic corticoid)
Biological Effects		
Increases the blood glucose and glycogen levels from fatty acids and amino acids	Increases the reabsorption of Na^+ in kidneys; retention of water	Reduces inflammation; treatment of asthma and rheumatoid arthritis

Anabolic Steroids

Anabolic steroids

- are derivatives of testosterone
- are used illegally to increase muscle mass
- have side effects including fluid retention, hair growth, sleep disturbance, and liver damage



Cell Membranes

Cell membranes

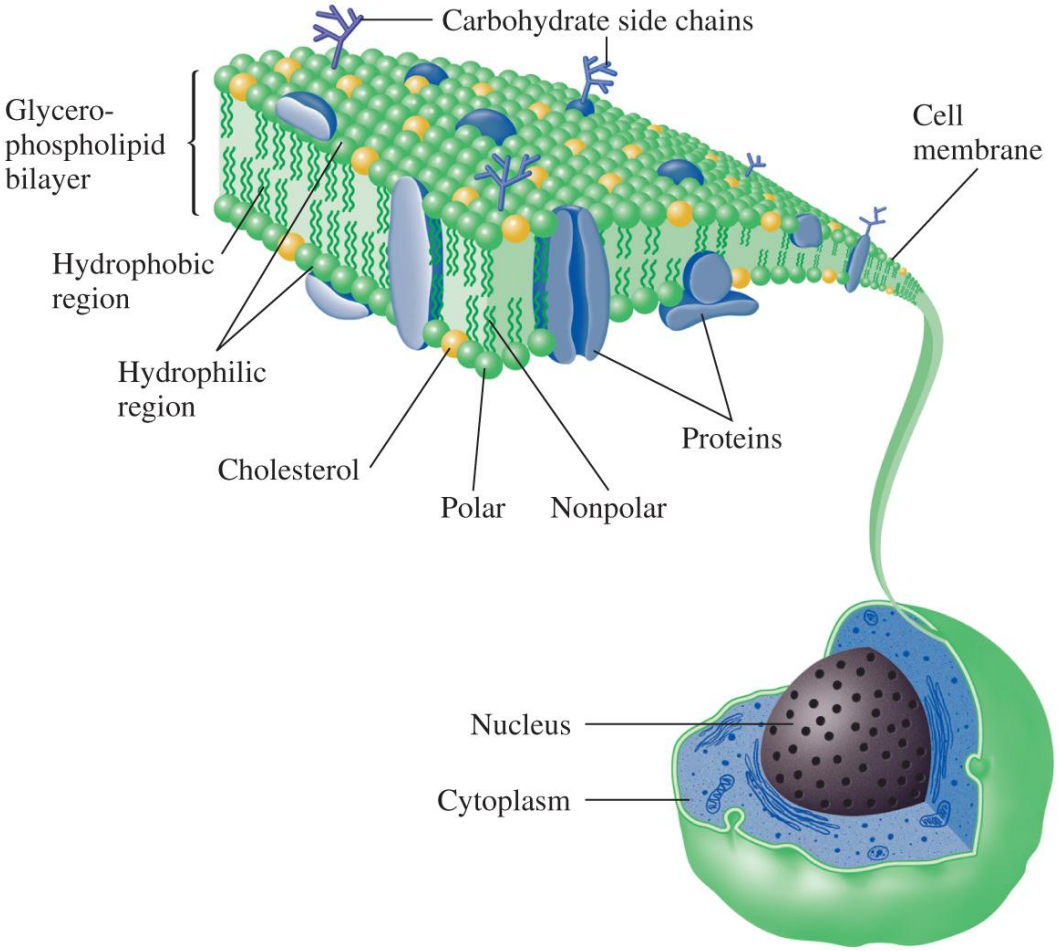
- separate cellular contents from the external environment
- consist of a lipid bilayer made of two rows of phospholipids
- have an inner portion made of the nonpolar tails of phospholipids with the polar heads at the outer and inner surfaces

Fluid Mosaic Model of Cell Membranes

The **lipid bilayer**

- contains proteins, carbohydrates, and cholesterol
- has unsaturated fatty acids that make cell membranes fluid-like rather than rigid
- has proteins and carbohydrates on the surface that communicate with hormones and neurotransmitters

Fluid Mosaic Model of Cell Membranes



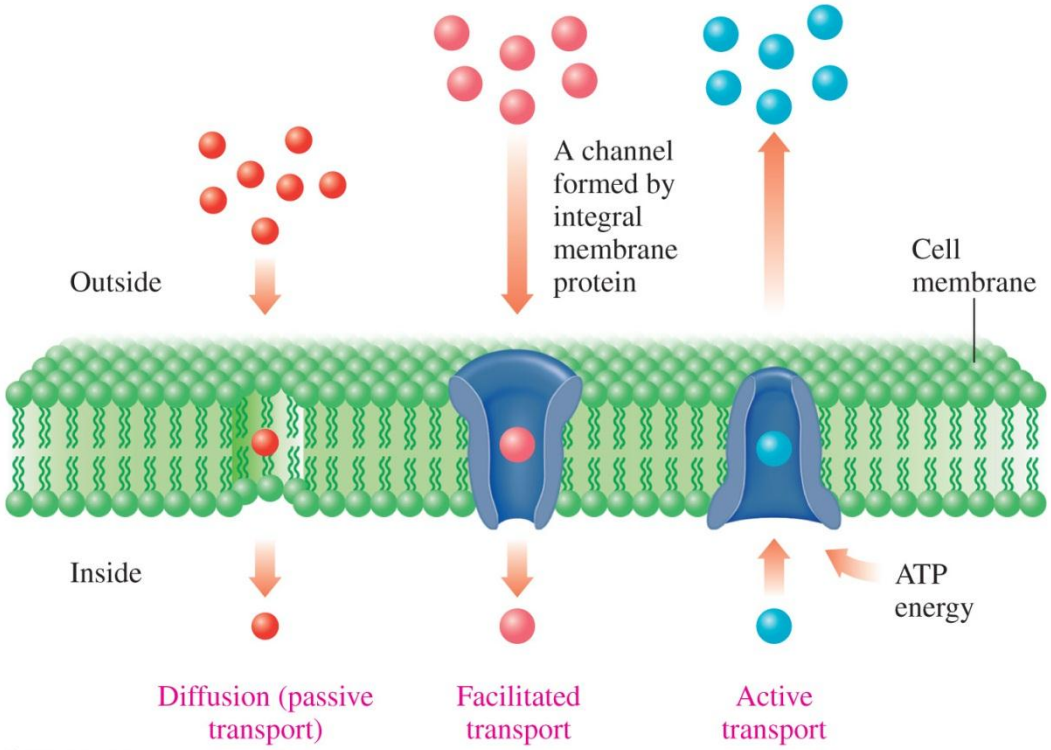
Transport through Cell Membranes

The transport of substances through cell membranes involves

- **diffusion (passive transport),** which moves particles from a higher to a lower concentration
- **facilitated transport**, which uses protein channels to increase the rate of diffusion
- **active transport**, which moves ions against a concentration gradient

Transport Pathways through Cell Membranes

Substances are transported across a cell membrane by diffusion, facilitated transport, or active transport.



Lipids: Concept Map