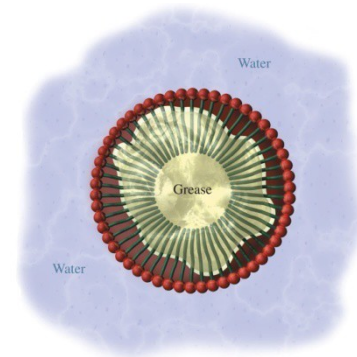


Organic Chemistry, 7th Edition
L. G. Wade, Jr.



Chapter 25

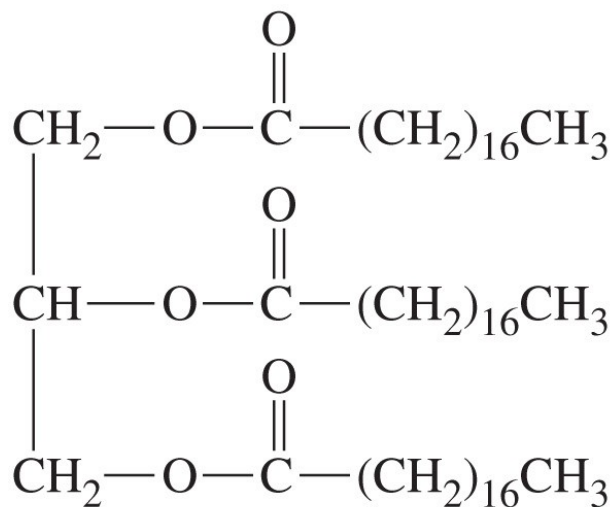
Lipids

Introduction

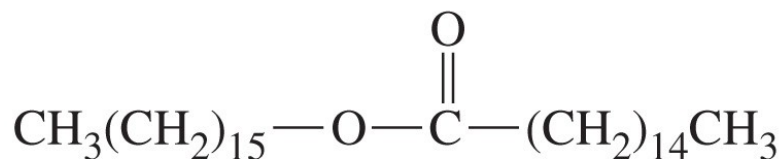
- Lipids are compounds that can be extracted from cells by nonpolar organic solvents.
- Complex lipids are easily hydrolyzed.
 - Long-chain esters called *fatty acids*.
- Simple lipids are not easily hydrolyzed in acid or base.
 - *Steroids*
 - *Prostaglandins*
 - *Terpenes*

Examples of Lipids

Examples of complex lipids

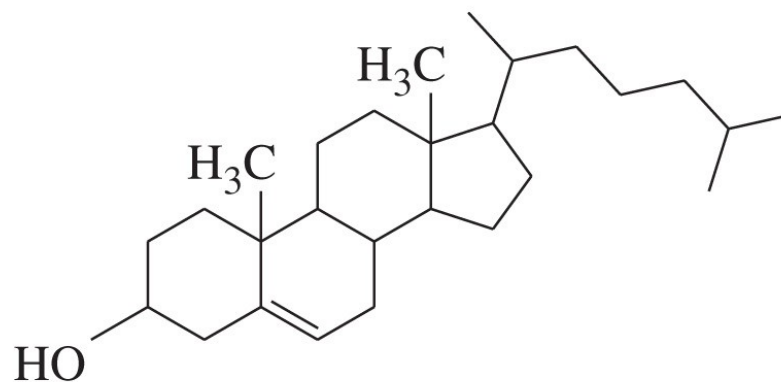


tristearin, a fat

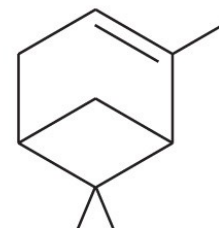


spermaceti (cetyl palmitate), a wax

Examples of simple lipids



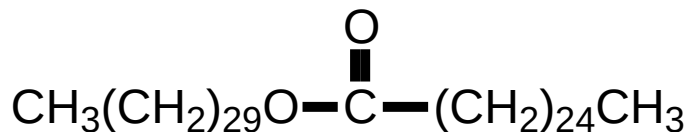
cholesterol, a steroid



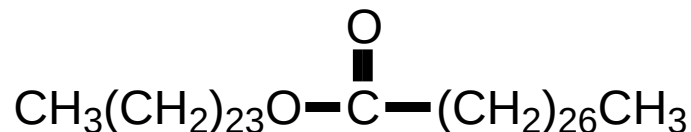
α -pinene, a terpene

Waxes

- Esters of long-chain fatty acids with long-chain alcohols.
- Commonly found in nature.
 - *Spermaceti* is found in the head of the sperm whale.
 - *Beeswax* is a mixture of waxes, hydrocarbons, and alcohols that bees use to make their honeycomb.
 - *Carnauba wax* is a mixture of waxes of high molecular weights.



a component of beeswax



a component of carnauba wax

Fatty Acids

- Unbranched carboxylic acids with 12–20 carbons.
- Most contain an even number of carbons because they are built from acetic acid units.
- Melting points increase with increasing molecular weights.
- Unsaturation greatly lowers the melting point.






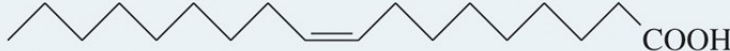
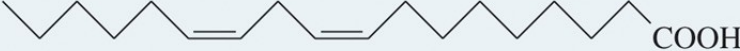

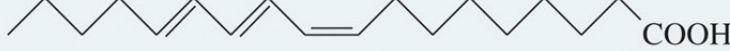
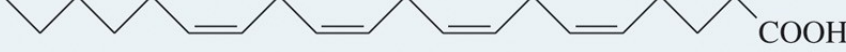
Glycerides

- Fatty acid esters of the triol glycerol.
- Tryglycerides are the most common glycerides and they are used for long-term energy storage in plants and animals.
 - Fats
 - Solid at room temperature.
 - Most are derived from mammals.
 - Oils
 - Liquid at room temperature.
 - Most are derived from plants or cold-blooded animals.

Melting Points of Fatty Acids

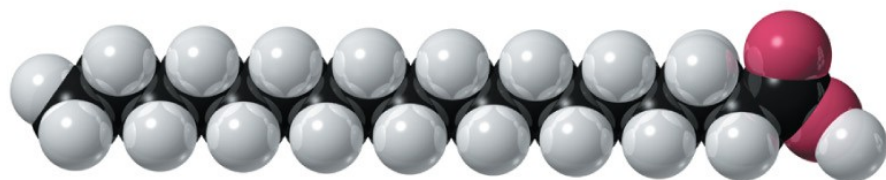
TABLE 25-1

Structures and Melting Points of Some Common Fatty Acids

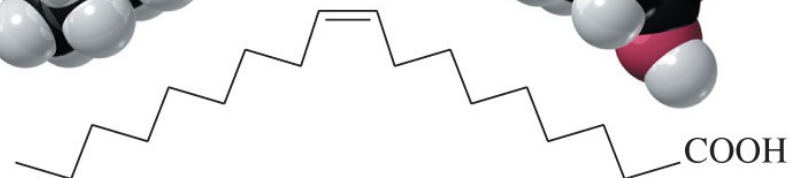
Name	Carbons	Structure	Melting Point (°C)
<i>Saturated acids</i>			
lauric acid	12		44
myristic acid	14		59
palmitic acid	16		64
stearic acid	18		70
arachidic acid	20		76
<i>Unsaturated acids</i>			
oleic acid	18		4
linoleic acid	18		-5
linolenic acid	18		-11
eleostearic acid	18		49
arachidonic acid	20		-49

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Melting Points



stearic acid, mp 70 °C

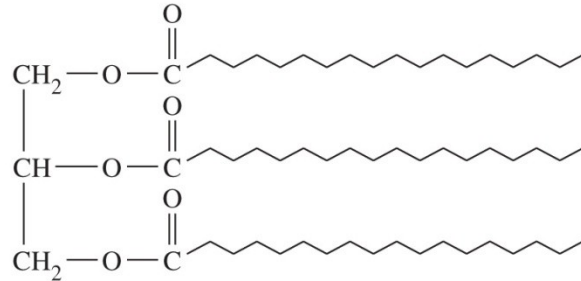


oleic acid, mp 4 °C

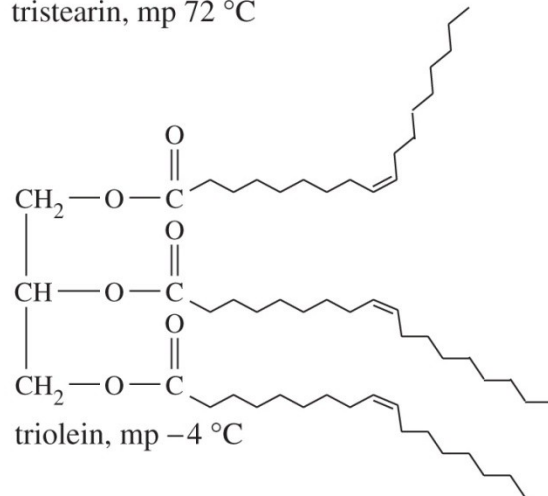
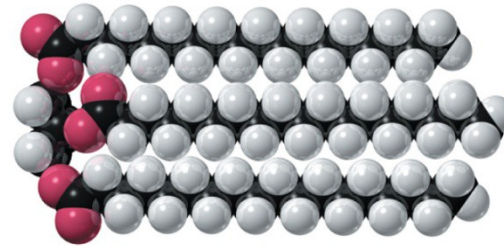
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- The cis double bond in oleic acid lowers the melting point by 66°C.
- A cis double bond bends the molecule, so it cannot pack efficiently.
- A trans double bond has less effect.

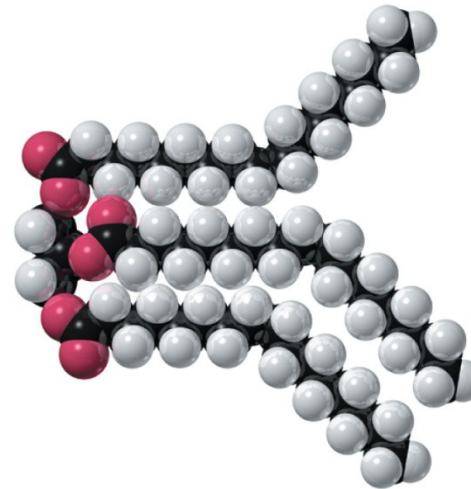
Fats and Oils



tristearin, mp 72 °C



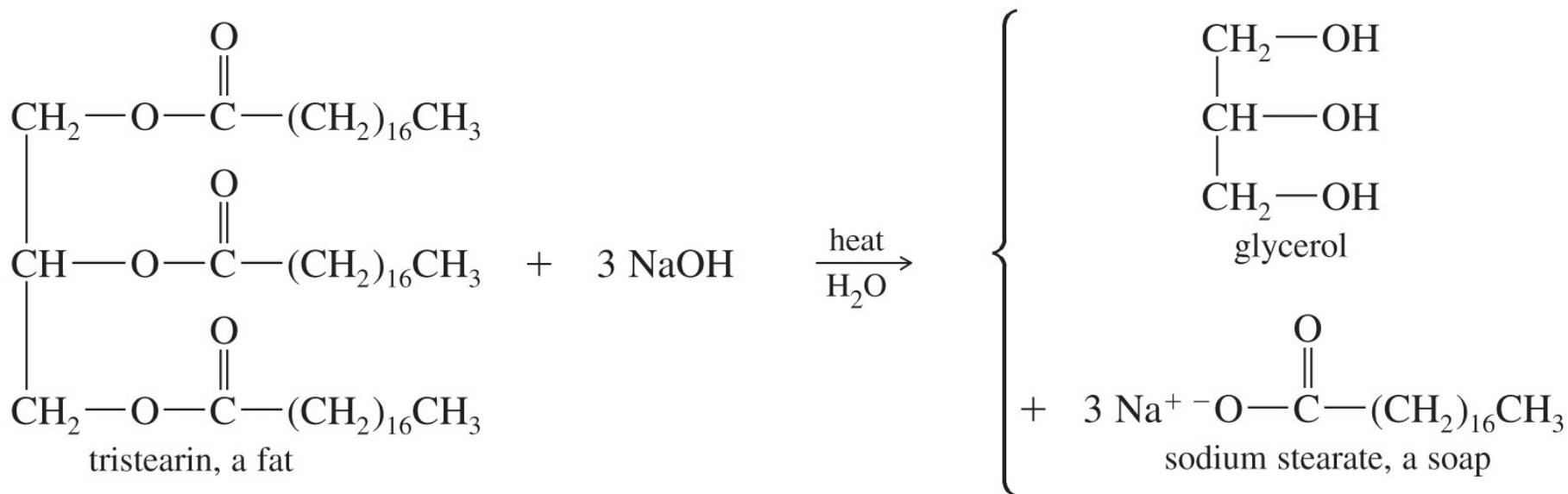
triolein, mp -4 °C



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- Unsaturated triglycerides have lower melting points because their unsaturated fatty acids do not pack as well in a solid lattice.

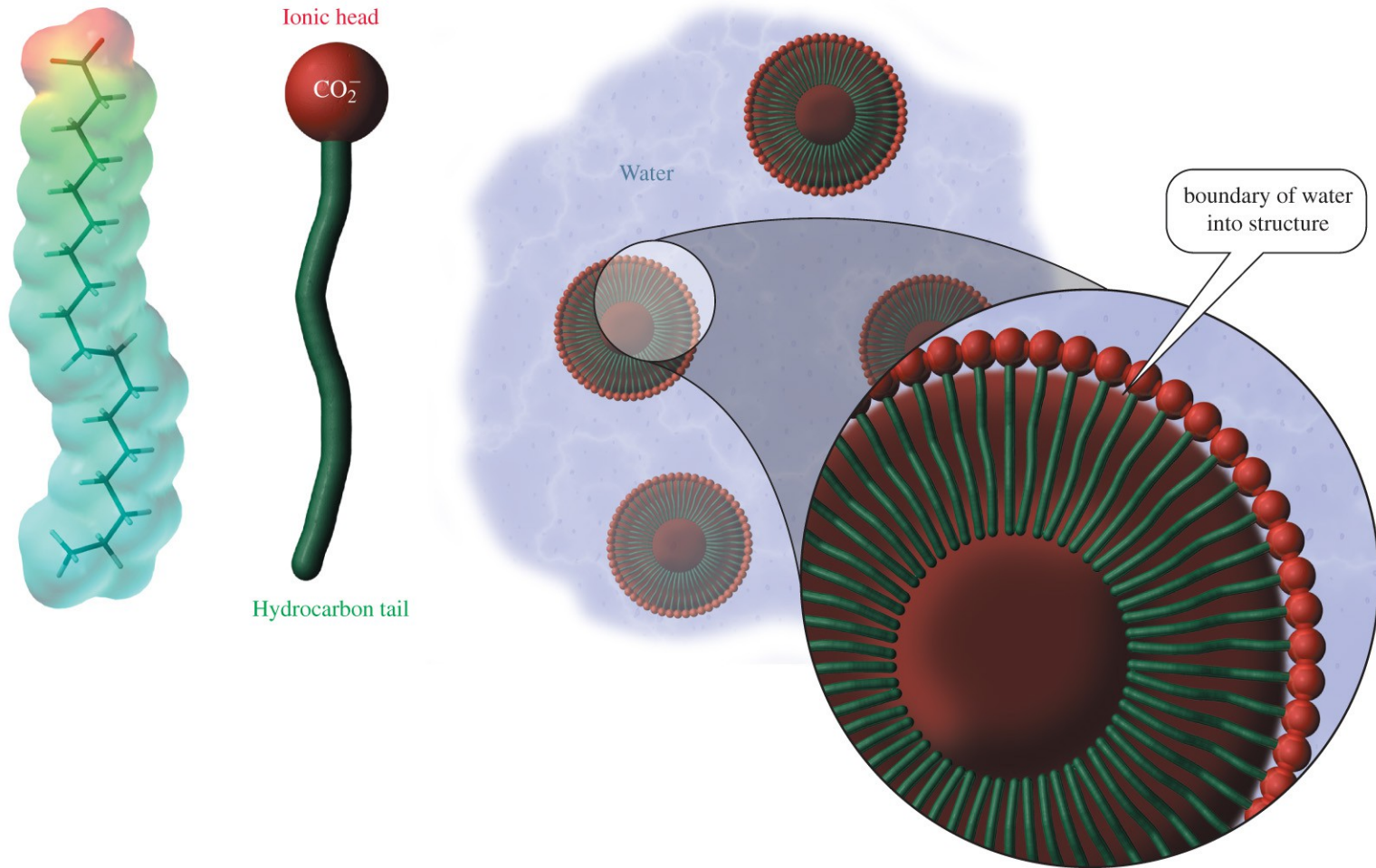
Saponification



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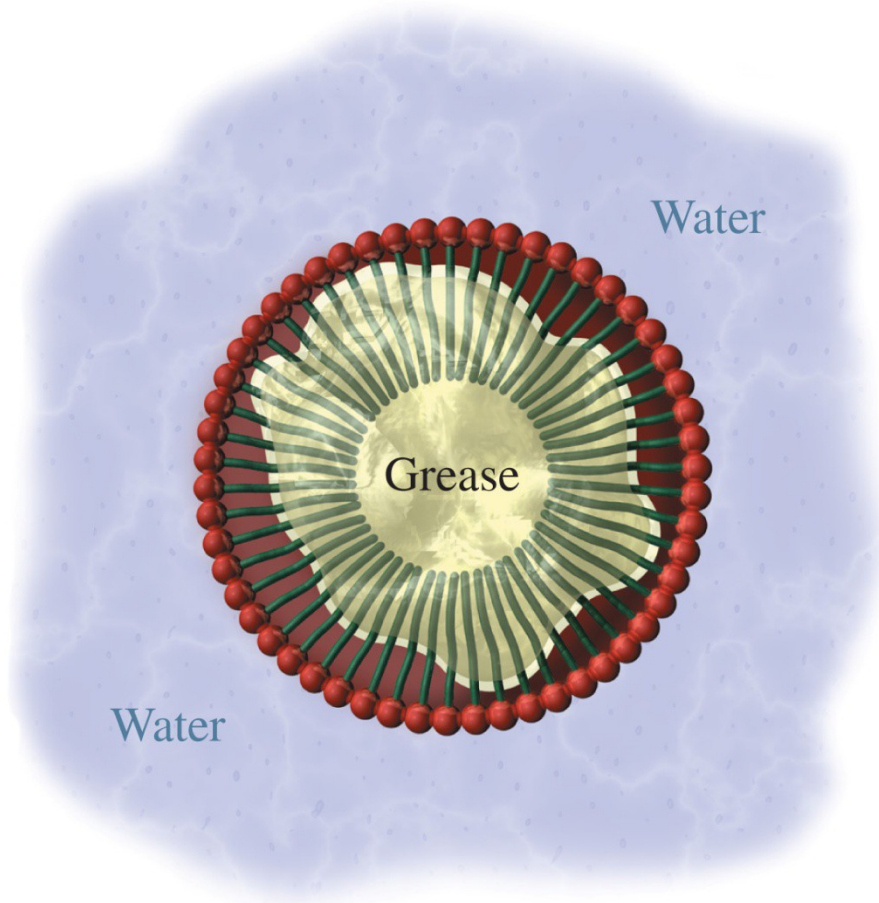
- Base-catalyzed hydrolysis of ester linkages in fats and oils.
- Long-chain carboxylate salts are known as soap.

Soap Structure



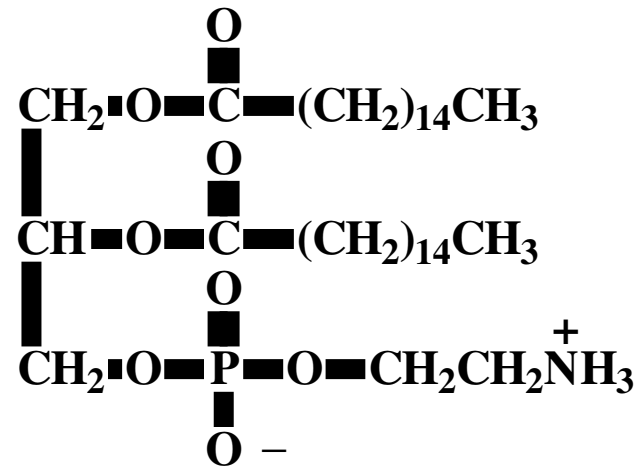
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Grease in Soap Solution



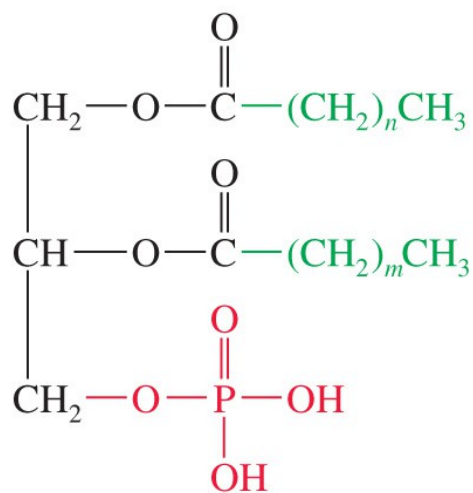
- In water, soap forms a cloudy solution of micelles, with the hydrophilic heads in contact with water and the hydrophobic tails clustered in the interior.
- The Na^+ ions (not shown) are dissolved in the water surrounding the micelle.

Phospholipids

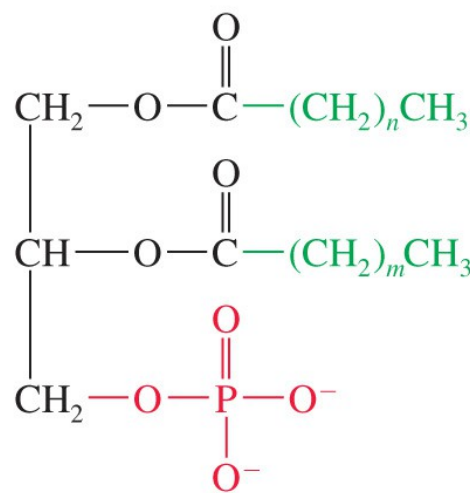


- Contain a phosphate ester bond.
- Phosphoglycerides usually have one phosphoric acid group and two fatty acids.
- The phosphate may have an additional alcohol attached by an ester linkage.

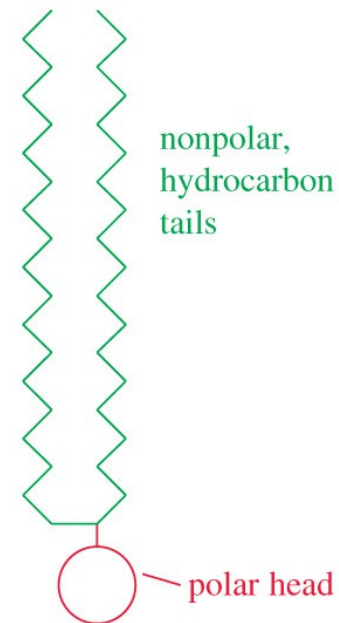
Phosphatidic Acids



a phosphatidic acid



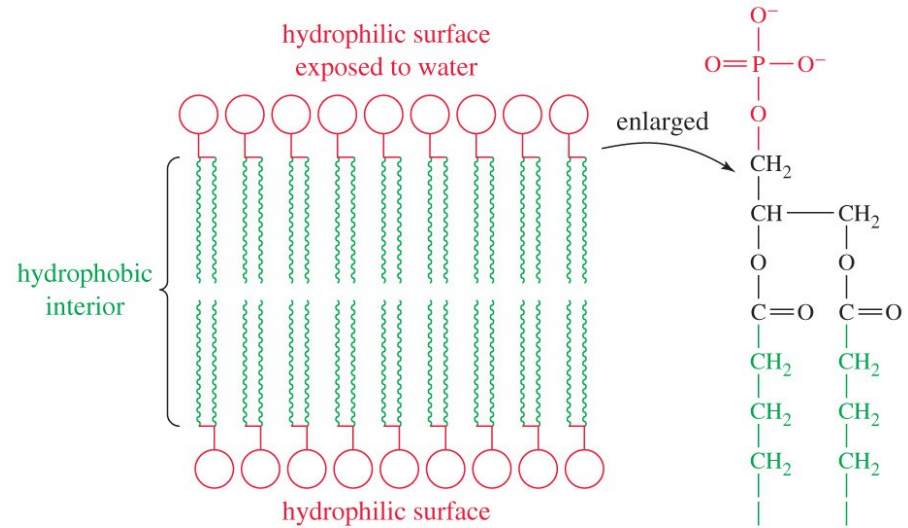
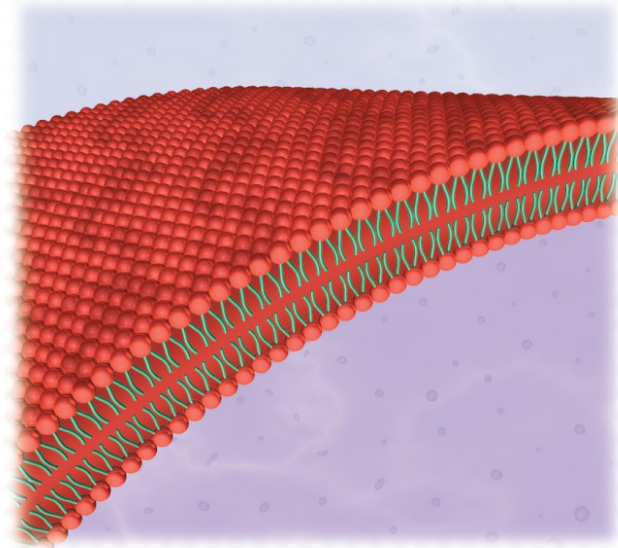
ionized form



schematic representation

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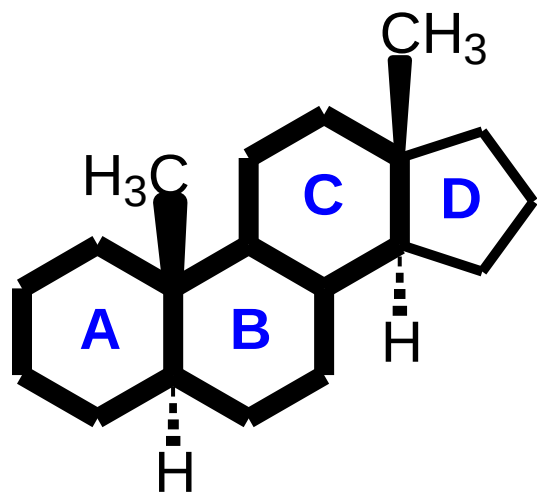
Lipid Bilayer



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- Phosphoglycerides can aggregate into a bilayer membrane with their polar heads exposed to the aqueous solution and the hydrocarbon tails protected within.
- This lipid bilayer is an important part of the cell membrane. It restricts the flow of water and dissolved substances.

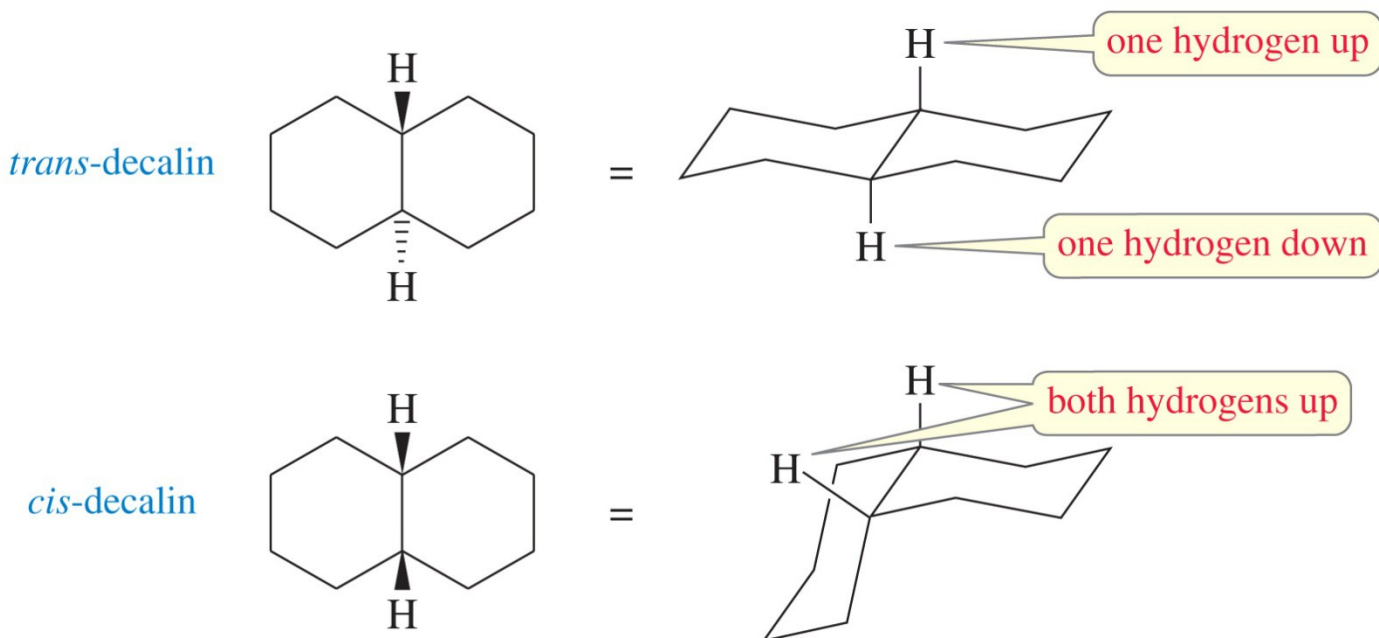
Steroids



androstane

- Polycyclic, usually all trans.
- Common structural features:
 - =O or —OH at C3.
 - Side chain at C17.
 - Double bond from C5 to either C4 or C6.

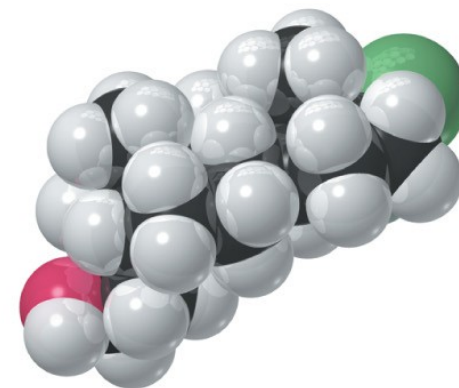
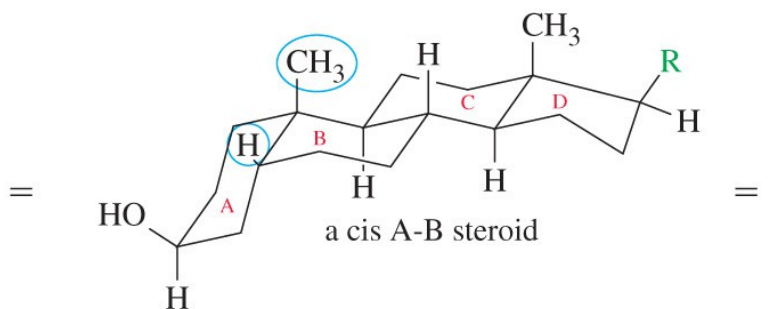
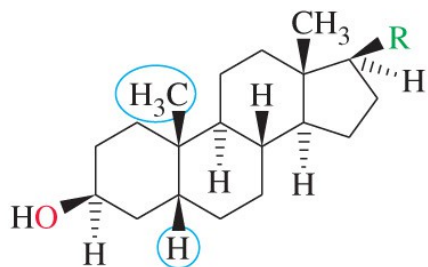
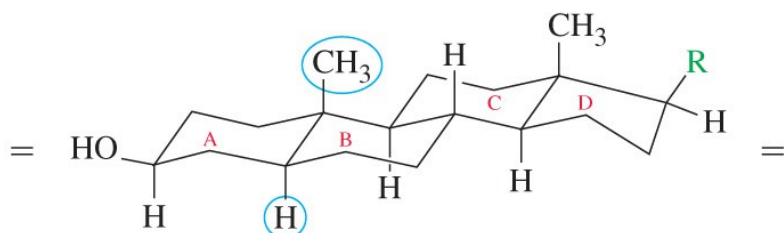
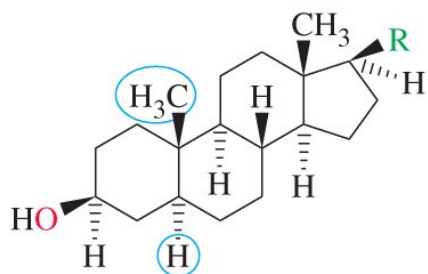
Cis- and Trans-Decalins



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- In ***trans-decalin***, the two bonds to the second ring are trans to one another, and the hydrogens on the junction are also trans.
- In ***cis-decalin***, the bonds to the second ring are cis, and the junction hydrogens are also cis.

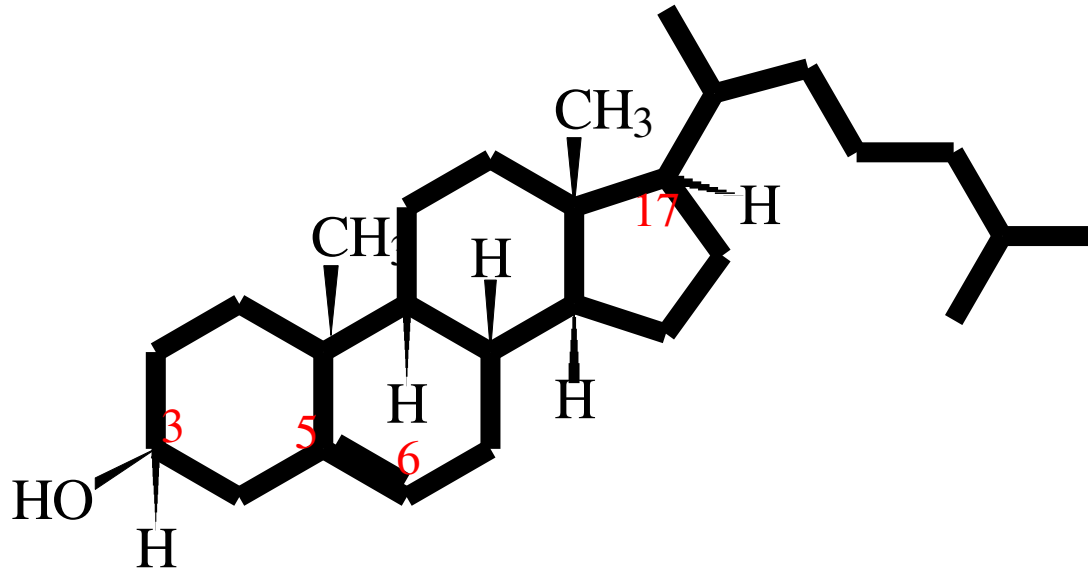
Cis and Trans Steroids



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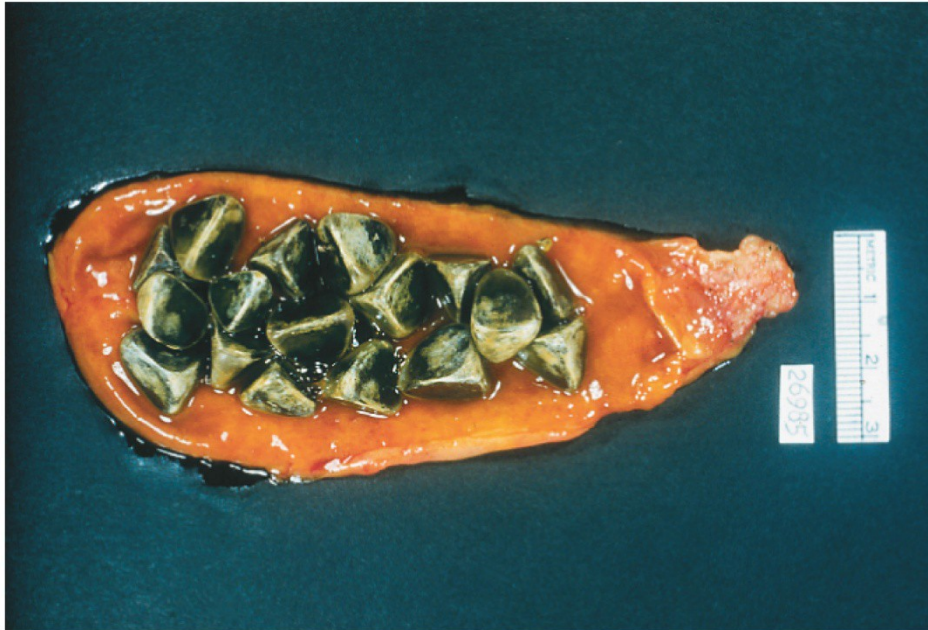
- Common steroids may have either a cis or a trans A-B ring junction. The other junctions are normally trans.

Cholesterol



- Common biological intermediate.
- Probably a precursor to other steroids.
- Side chain at C17 and double bond at C5–C6.

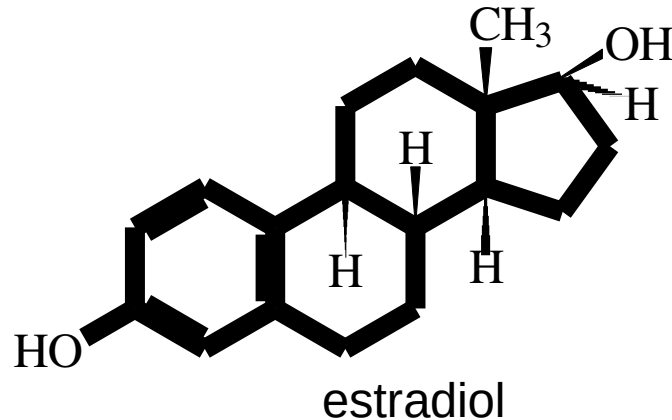
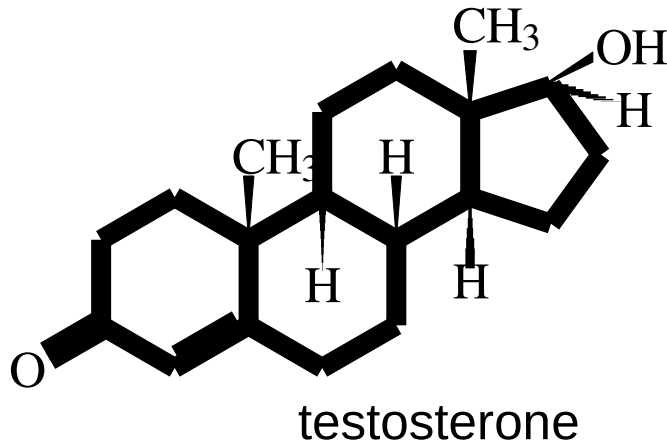
Gallstones



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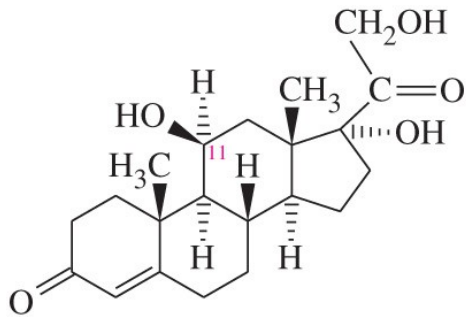
- These gallstones shown here, within the gallbladder, are composed mostly of cholesterol.

Sex Hormones

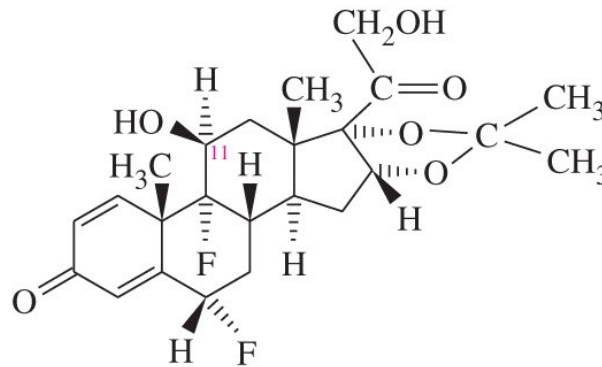


- Female hormone has an aromatic ring and one less methyl group than the male hormone.
- Testosterone is converted to estradiol in the ovaries.

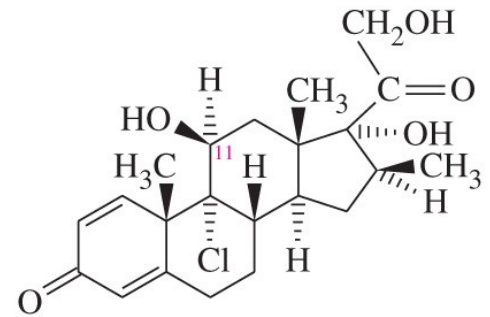
Examples of Steroids



cortisol



fluocinolone acetonide



beclomethasone

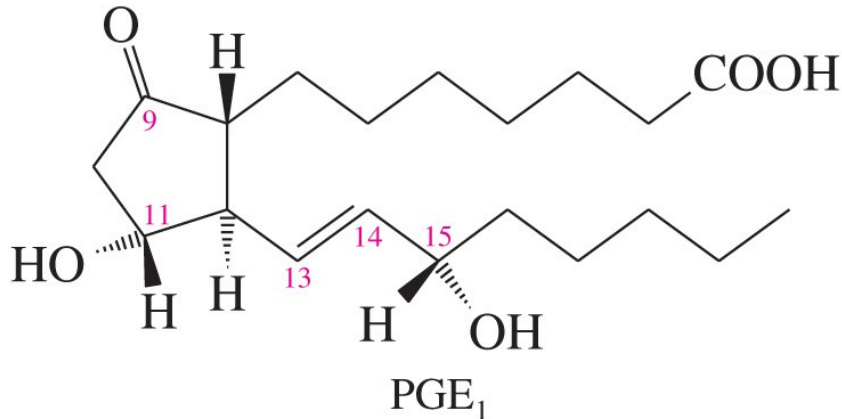
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- Cortisol is the major natural hormone of the adrenal cortex.
- Fluocinolone acetonide is more potent for treating skin inflammation.
- Beclomethasone is more potent for treating asthma.

Prostaglandins

- Biochemical regulators more powerful than steroids.
- Cyclopentane ring with two long side chains trans to each other.
- Most have 20 carbon atoms.
- Derived from arachidonic acid.
- Regulate functions such as:
 - Blood pressure
 - Blood clotting
 - Allergic response
 - Digestive activity
 - Labor onset

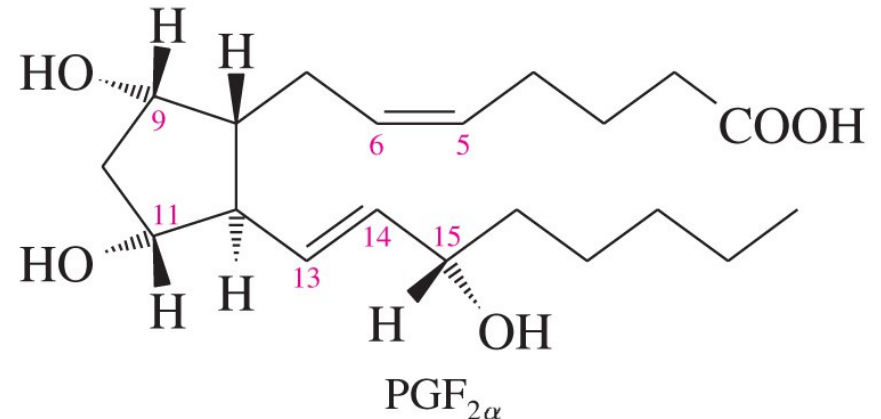
Biosynthesis of Prostaglandins



(PG means prostaglandin;

E means ketone at C9;

1 means one C=C double bond)



(PG means prostaglandin;

F means hydroxyl at C9, and α means down;

2 means two C=C double bonds)

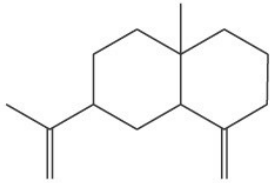
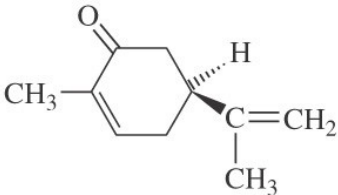
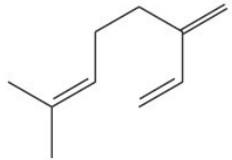
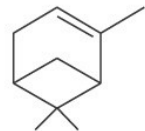
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- Biosynthesis of prostaglandins begins with an enzyme-catalyzed oxidative cyclization of arachidonic acid.

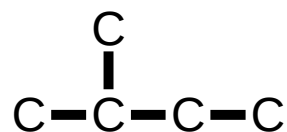
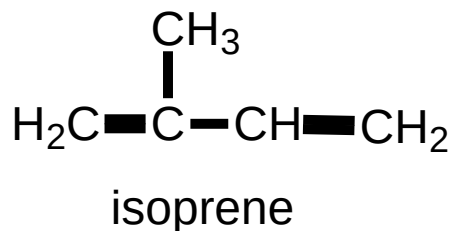
Terpenes

- Composed of five carbon isopentyl (isoprene) groups.
- Isolated from the essential oils of plants.
- Pleasant taste or fragrant aroma and used as flavorings.
- Examples:
 - Anise oil
 - Bay leaves

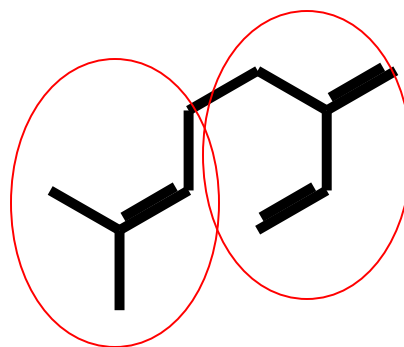
TABLE 25-3 Some Useful Essential Oils

Essential Oil	Source	Major Components
perfume	flowers	mixtures of terpenes and terpenoids
oil of turpentine	evergreens	mixtures of terpenes and terpenoids
oil of celery	celery	 β -selinene, a terpene
caraway oil	caraway seed	 (+)-carvone, a terpene
oil of bay	bay leaves	 myrcene, a terpene
cedar leaf oil	leaves of the “white cedar” (actually a pine)	 α -pinene, a terpene

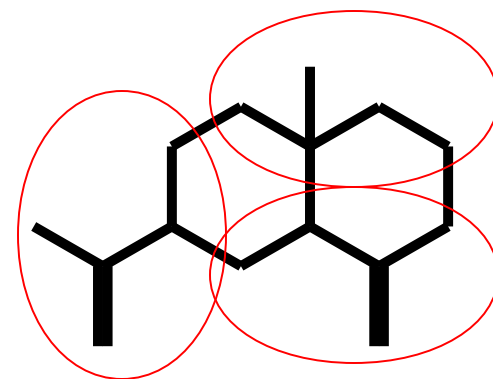
Structure of Terpenes



an isoprene unit
(may have double bonds)



myrcene



-selinene

- Terpenes are composed of two or more isoprene units.
- The isoprene units will maintain its isopentyl, usually with modification of the isoprene double bonds.

Classification

- Terpenes are classified by the number of carbons they contain in groups of ten.
- A monoterpene has ten carbons, two isoprene units.
- A sesquiterpene has 15 carbons, three isoprene units.
- A diterpene has 20 carbons, four isoprene units.

Terpenoids

