LIPIDS

Water-insoluble compounds found in animals and plants

Lipids

- The solubility of lipids in nonpolar organic solvents results from their significant hydrocarbon component.
- Lipids have a variety of structures and functions
 - Fatty Acids
 - Waxes
 - Fats and Oils
 - Membranes
 - Terpenes
 - Steroids

Fatty Acids

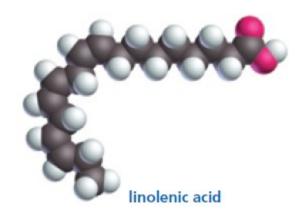
- carboxylic acids with long hydrocarbon chains.
- can be saturated or unsaturated
- The physical properties depend on
 - the length of the hydrocarbon chain and
 - the degree of unsaturation.
- the m.p. of saturated fatty acids increase with increasing molecular weight

Common Naturally Occurring Fatty Acids

16	palmitic acid	hexadecanoic acid	COOH	63
18	stearic acid	octadecanoic acid	COOH	69
20	arachidic acid	eicosanoic acid	COOH	77
16	palmitoleic acid	(9Z)-hexadecenoic acid	COOH	0

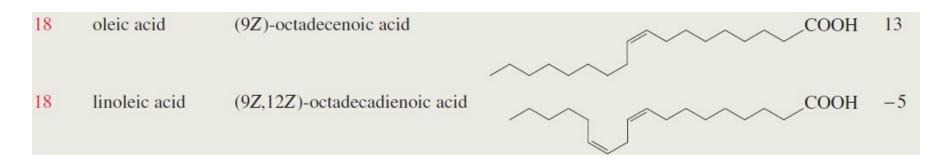
16	palmitoleic acid	(9Z)-hexadecenoic acid	COOH	0
18	oleic acid	(9Z)-octadecenoic acid	COOH	13
18	linoleic acid	(9Z,12Z)-octadecadienoic acid	COOH	-5





- Why unsaturated fatty acids have lower melting points than saturated fatty acids?
- The double bonds in unsaturated fatty acids generally have the cis configuration. This configuration produces a bend in the molecules, which prevents them from packing together as tightly as fully saturated fatty acids.

 The melting points of the unsaturated fatty acids decrease as the number of double bonds increases.



Waxes

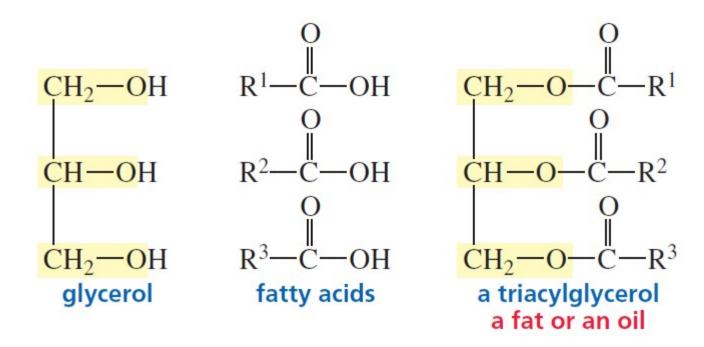
O || CH₃(CH₂)₂₄CO(CH₂)₂₉CH₃ a major component of beeswax structural material of beehives O || CH₃(CH₂)₃₀CO(CH₂)₃₃CH₃ a major component of carnauba wax coating on the leaves of a Brazilian palm

O | CH₃(CH₂)₁₄CO(CH₂)₁₅CH₃ a major component of spermaceti wax from the heads of sperm whales

- esters formed from long-chain carboxylic acids and long-chain alcohols.
- Waxes are common in living organisms.
- feathers of birds, wax secretion to keep fur lubricated, to render exoskeletons waterproof, surfaces of certain leaves and fruits where it serves as a protectant against parasites and minimizes the evaporation of water.

Fats and Oils

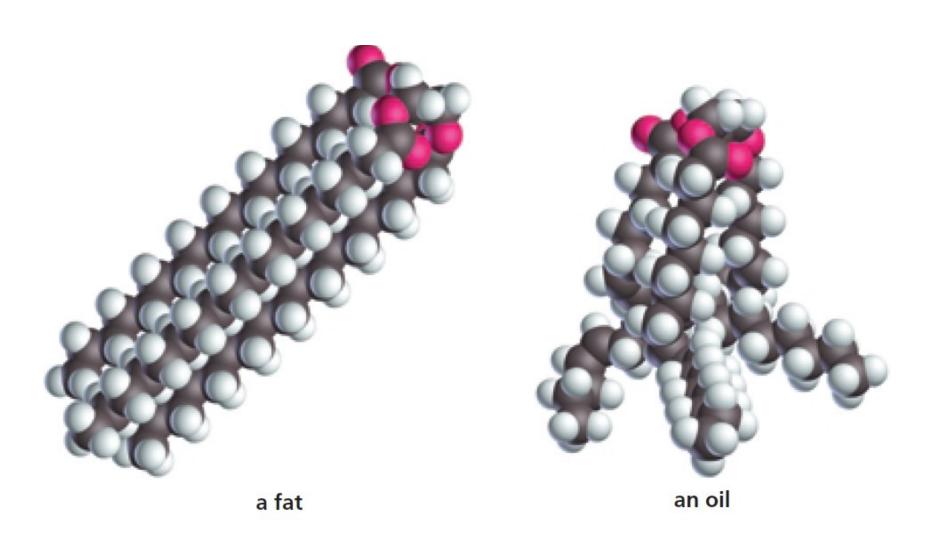
- Triacylglycerols
 - simple triacylglycerol.
 - Mixed triacylglycerols



Fats and Oils

- Fats: Triacylglycerols that are solids or semisolids at room temperature
 - usually obtained from animals and are composed largely of <u>triacylglycerols</u> with either saturated fatty acids or fatty acids with only one double bond.
- Oils: Liquid triacylglycerols
 - typically come from plant products such as corn, soybeans, olives, and peanuts. They are composed primarily of <u>triacylglycerols with unsaturated fatty</u> acids that cannot pack tightly together.

Fats and Oils



Hardening of Oils

- Catalytic hydrogenation of some or all of the double bonds of polyunsaturated oils.
 - Preparation of Margarine by hydrogenating vegetable oils such as soybean oil

RCH=CHCH₂CH=CHCH₂CH=CH
$$\xrightarrow{\text{H}_2}$$
 RCH₂CH₂CH₂CH=CHCH₂CH₂CH₂CH $\xrightarrow{\text{CH}_2}$ CH=CHCH₂CH₂CH₂CH $\xrightarrow{\text{CH}_2}$ CH=CHCH₂CH₂CH₂CH $\xrightarrow{\text{CH}_2}$ CH=CHCH₂CH₂CH₂CH=CHCH₂CH₂CH₂CH₂CH=CHCH₂CH₂CH₂CH₂CH₂CH=CHCH₂CH₂CH₂CH₂CH₂CH=CHCH₂CH₂CH₂CH₂CH=CHCH₂CH₂CH₂CH₂CH=CHCH₂CH₂CH₂CH₂CH=CHCH₂CH₂CH₂CH₂CH=CHCH₂CH₂CH₂CH=CHCH₂CH₂CH₂CH=CHCH₂CH+CH+CH₂CH+CH+CH₂CH+CH₂CH+CH+CH₂CH+CH+CH₂CH+CH+CH₂CH+CH+CH₂CH+CH+CH+CH+CH

Hydrolysis of Fats

 Saponification: Soaps are sodium or potassium salts of fatty acids

$$\begin{array}{c} O \\ CH_2O-C-R^1 \\ O \\ CHO-C-R^2 \\ A \text{ fat or an oil} \end{array} + \begin{array}{c} H_2O \\ H_2OH \\ CH_2OH \\ CH_2OH \\ A \text{ constant } \end{array} + \begin{array}{c} O \\ R^1-C-O^-Na^+ \\ O \\ CH_2OH \\ CH_2OH \\ A \text{ sodium salts of fatty acids} \end{array}$$

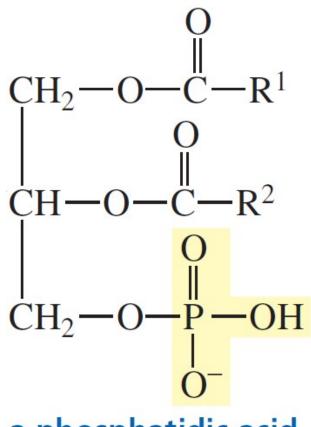
$$\begin{array}{c} O \\ \parallel \\ CH_3(CH_2)_{16}CO^-\,Na^+ \\ \text{sodium stearate} \end{array} \qquad \begin{array}{c} O \\ \parallel \\ CH_3(CH_2)_7CH = CH(CH_2)_7CO^-\,Na^+ \\ \text{sodium oleate} \end{array}$$

Membranes

- some parts of organisms must be separated from other parts (biological system)
- the outside of the cell must be separated from the inside (On a cellular level)
- "Greasy" lipid membranes serve as the barrier
- Example: Phospholipids

Phospholipids

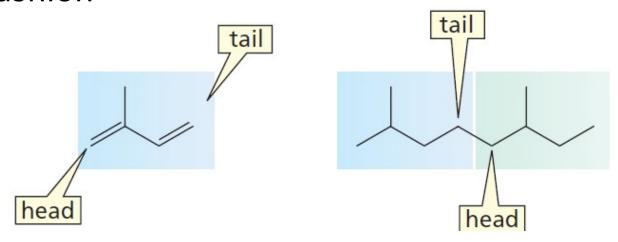
- Phosphoacylglycerols (aka phosphoglycerides)
- a terminal OH group of glycerol is esterified with phosphoric acid
- C-2 carbon of glycerol in phosphoacylglycerols has the R configuration



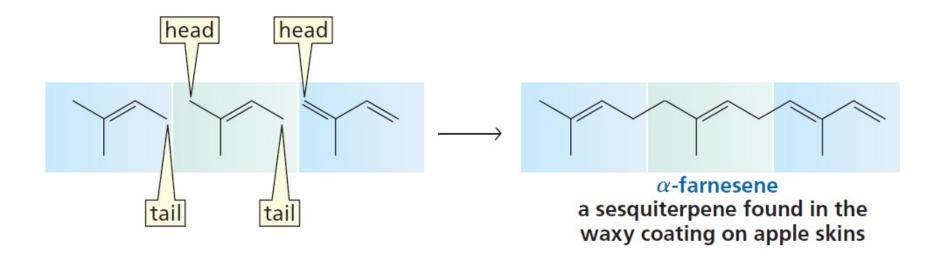
a phosphatidic acid

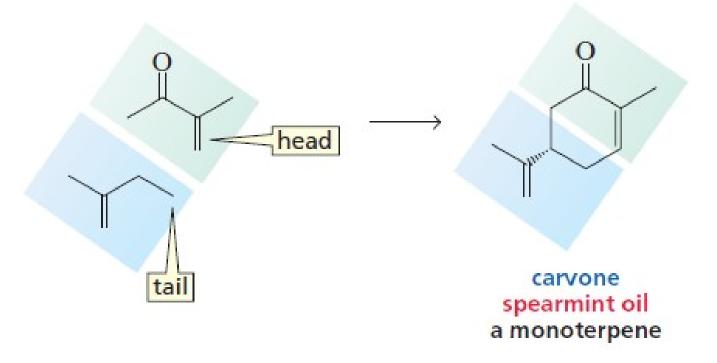
Terpenes

- can be hydrocarbons, or they can contain oxygen and be alcohols, ketones, or aldehydes.
- contain carbon atoms in multiples of 5
 - 10, 15, 20, 25, 30, and 40 carbon atoms
- Oxygen-containing terpenes are sometimes called terpenoids.
- isoprene rule: isoprene units are linked in a head-totail fashion



Isoprene Rule

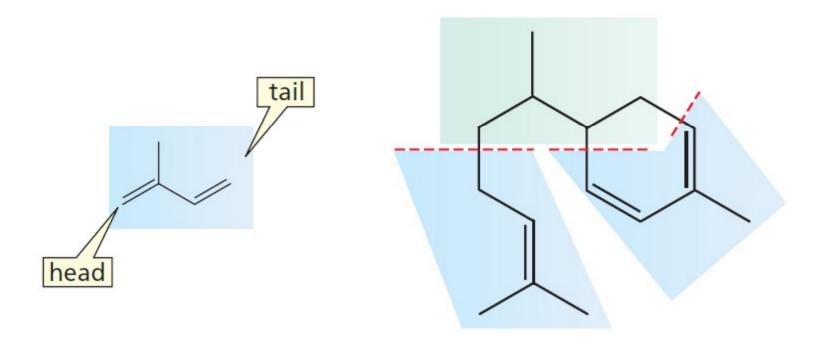




 In the case of cyclic compounds, the linkage of the head of one isoprene unit to the tail of another is followed by an additional linkage to form the ring.

Using the Isoprene Rule

Mark off the isoprene units in zingiberene



Terpenes

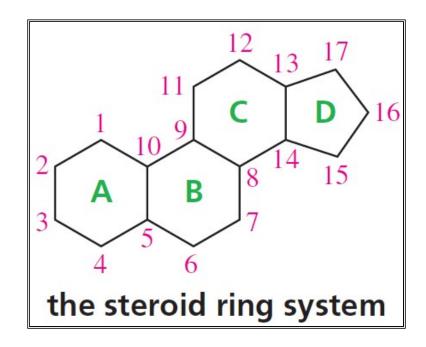
Carbon atoms	Classification	Carbon atoms	Classification
10	monoterpenes	25	sesterterpenes
15	sesquiterpenes	30	triterpenes
20	diterpenes	40	tetraterpenes

Carotenoids

- tetraterpenes.
- Lycopene, the compound responsible for the red coloring of tomatoes and watermelon, and the compound that causes carrots and apricots to be orange, are examples of carotenoids.

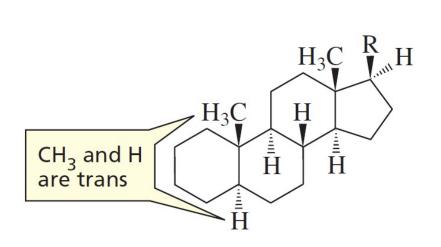
Steroids

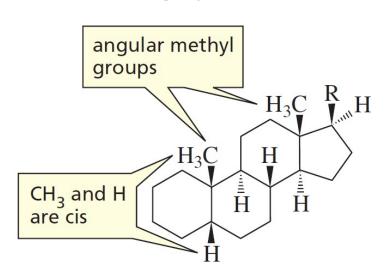
- All steroids contain a **tetracyclic ring system**. The four rings are designated A, B,C, and D.
- A, B, and C are six-membered rings and D is a five-membered ring.

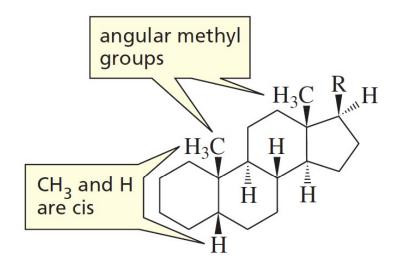


Stereochemistry

- In steroids, the B, C, and D rings are all trans fused. In most naturally occurring steroids, the A and B rings are also trans fused.
- Many steroids have methyl groups at the 10- and 13positions. These are called angular methyl groups.
- When steroids are drawn, both angular methyl groups are shown to be above the plane of the steroid ring system

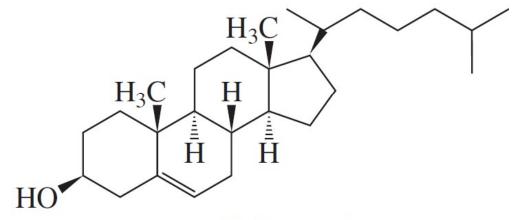






Cholesterol

- The most abundant member of the steroid family in animals and the precursor of all other steroids.
- important component of cell membranes



cholesterol

Number of stereoisomers are possible?

Classification of **Steroid Hormones**

- Glucocorticoids
- Mineralocorticoids
- Androgens
- Estrogens

Glucocorticoids

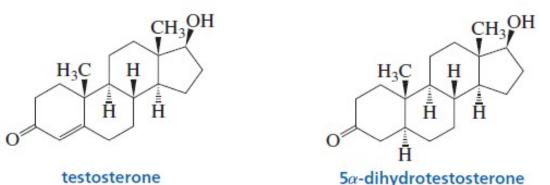
 involved in glucose metabolism, as well as in the metabolism of proteins and fatty acids

Mineralocorticoids

 Mineralocorticoids cause increased reabsorption of Na⁺, Cl⁻, and HCO₃⁻ by the kidneys, leading to an increase in blood pressure.

Androgens and Estrogens

male sex hormones



Female sex hormones

difference between testosterone and progesterone

Synthetic Steroids

- steroids that are not available in nature
- They have the same muscle-building effect as testosterone.
- Steroids that aid in the development of muscle are called **anabolic steroids**.

Curious case of shot put champ

ing been crowned European shot put champion in 1986, Heidi Krieger was one of the stars of the former GDR But having been subjected to a doping program like thousand of other former East German athletes, Krieger realised on her 1990 retirement that the effects of testosterone hormone abuse had left her with all the traits of a man.

She opted for a sex change operation and is today known as Andreas whose birth certificate has been altered and, sporting a moustache, he now owns an army clothes shop in Magdeburg.

The confident, strapping Andreas Krieger, who man of 1.87m shows a copy of competed as a woman (Heidi his photo from his competition days as Heidi, and a timid athletics team, poses with a girl stares out from the image picture of himself in 1987 with short brown hair and broad shoulders hidden in a

have remained as a woman, be- available facilities and equipcause my problems were al- ment, coaching and medical ready there, but they stole my back-up, psychological testing I obtained a new birth certifi story from me," the 44-year-old and dietary supplements.

ty of saying: I do not want to State Plan 14.25 — that set East a plastic bag full of medals take hormones. I was barely Germany apart and was only onto the counter in his clothes 16 years old when my coach 'brought to an end after the col- shop which he won as first gave me those blue pills."

the GDR competed as a sepa- years ago. rate state, the tiny country of 16 million people won 519 athletes were part of the dop- the GDR's doping victims medals at 11 Olympic games ing program which even in- That medal doesn't mean any - 192 of which were gold.



Former German shot putter Krieger) on the East German

East German state ensured ingly foreign in my own body "I don't know if I would their athletes had the best

But it was the scale of state-"I never had the possibili-sponsored doping—known as took life and the man emptie lapse of communism when the woman During the 20-year period Berlin wall came down 20

volved the Stasi, the state's se- thing to me now," he said. A

sure athletes took Turinabo an anabolic steroid which en courages muscle growth.

Each athlete was on an in dex of prescribed hormone and the small country from be hind the iron curtain becam a medal factory.

Krieger was "Athlete No 54" on that list.

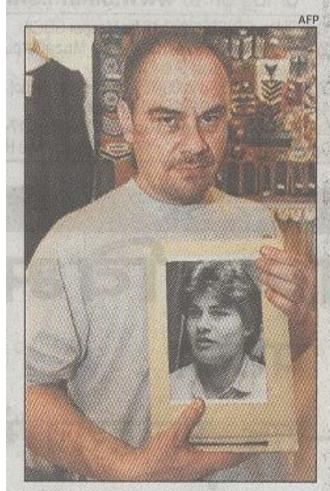
The GDR finished secon on the medals table of severa Olympic Games includin Montreal 1976, Moscow 1980 and Seoul 1988.

At the European Athletic Championships in 1986 held in Stuttgart, Heidi Krieger wo gold in the shot put and An dreas still has the telegram congratulations sent to him b GDR leader Erich Honecke addressed to "My dear friend

But the anger still burn To achieve this success, the "At that time, I felt increas he says, having opted for a sex change operation 12 years ago "I officially became a man an

As Heidi died, so Andrea

Only the gold medal from Stuttgart is missing - he do It is estimated some 10,000 nated it to the association of



Former German shot putter Andreas Krieger, who competed as a woman (Heidi Krieger) on the East German athletics team, poses with a picture of himself in 1987