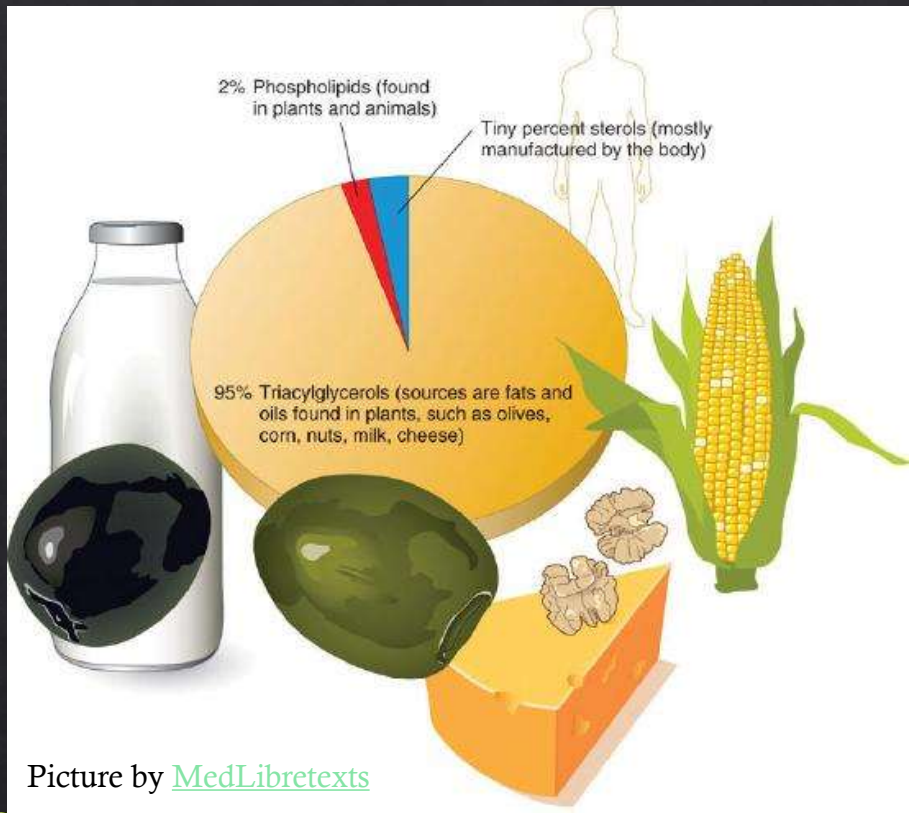
Lipids

Lipids

- Low solubility
- Structural role
- Long term storage of energy



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Lipids

Storage of energy

- reduced compounds: lots of available energy
- hydrophobic nature: good packing

Insulation from environment

- low thermal conductivity
- high heat capacity (can "absorb" heat & prevent evaporation)
- mechanical protection (can absorb shocks)

Lipids

Water repellant
hydrophobic nature: keeps surface of the organism dry

- prevents excessive wetting (birds)
- prevents loss of water via evaporation

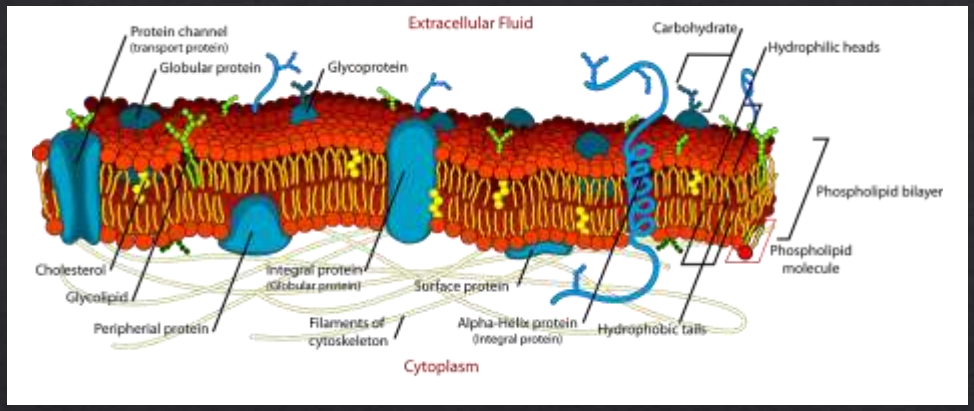
Buoyancy control and acoustics in marine mammals

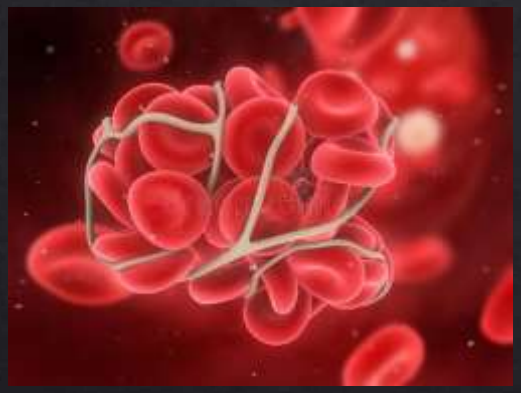
- increased density while diving deep (helps sinking?)
- spermaceti organ may focus sound energy (?)

Lipids

Membrane structure

- main structure of cell membranes



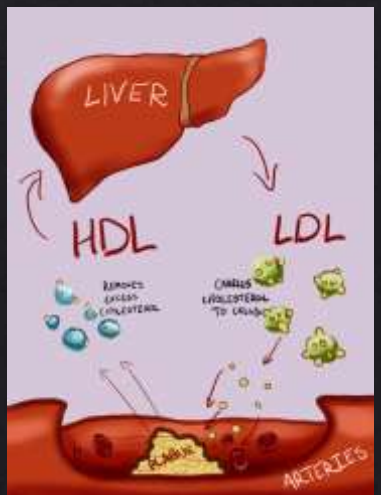


Cofactors for enzymes

- vitamin K: blood clot formation
- coenzyme Q: ATP synthesis in mitochondria

Signaling molecules

- paracrine hormones (act locally)
- steroid hormones (act body-wide)
- growth factors
- vitamins A and D (hormone precursors)



Picture from SITN

Lipids

Antioxidants

- vitamin E

Dr. Dan Sudia/Science Source

Richard Day/VIREO

Pigments

- color of tomatoes, carrots, pumpkins, some birds

Classification of Lipids

Two major categories based on the structure and function:

1. Lipids that contain fatty acids (complex lipids)
   - can be further separated into: storage lipids and membrane lipids
2. Lipids that do not contain fatty acids: cholesterol, vitamins, pigments, etc.

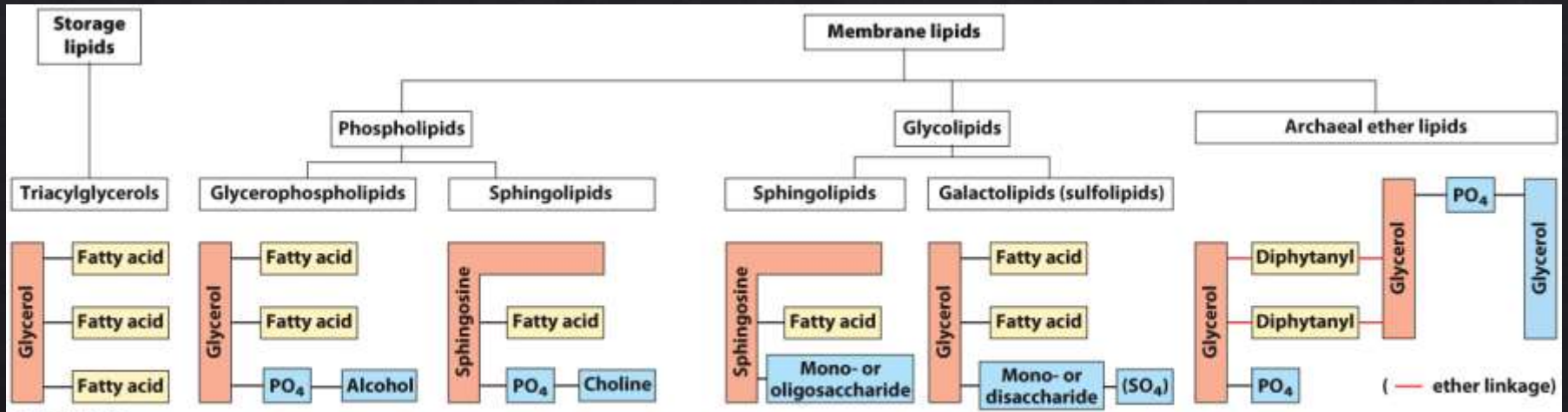


Figure 10-6

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Classification of Lipids

TABLE 10-2 Eight Major Categories of Biological Lipids

Category	Category code	Examples
Fatty acids	FA	Oleate, stearoyl-CoA, palmitoylcarnitine
Glycerolipids	GL	Di- and triacylglycerols
Glycerophospholipids	GP	Phosphatidylcholine, phosphatidylserine, phosphatidyethanoloamine
Sphingolipids	SP	Sphingomyelin, ganglioside GM2
Sterol lipids	ST	Cholesterol, progesterone, bile acids
Prenol lipids	PR	Farnesol, geraniol, retinol, ubiquinone
Saccharolipids	SL	Lipopolysaccharide
Polyketides	PK	Tetracycline, erythromycin, aflatoxin B_1

Table 10-2
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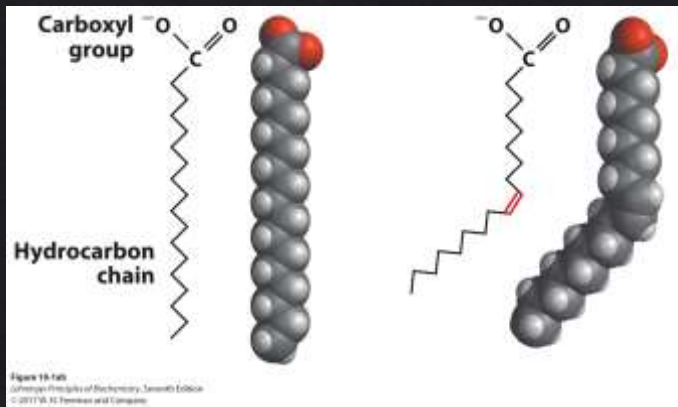
Fatty Acids

- Carboxylic acids with hydrocarbon chains containing between 4 to 36 carbons
  - Almost all natural fatty acids have an even number of carbons.
  - Most natural fatty acids are unbranched.
- Saturated: no double bonds between carbons in the chain
- Monounsaturated: one double bond between carbons in the alkyl chain
- Polyunsaturated: more than one double bond in the alkyl chain
- Solubility decreases with chain length
- Melting point
  - Increases with chain length
  - Decreases with the n° of double bonds



Melting point and double bonds

- Saturated fatty acids pack in a fairly orderly way.
  - extensive favorable interactions
- Unsaturated cis fatty acids pack less orderly due to the kink.
  - less-extensive favorable interactions
- It takes less thermal energy to disrupt disordered packing of unsaturated fatty acids.
  - Unsaturated cis fatty acids have a lower melting point.

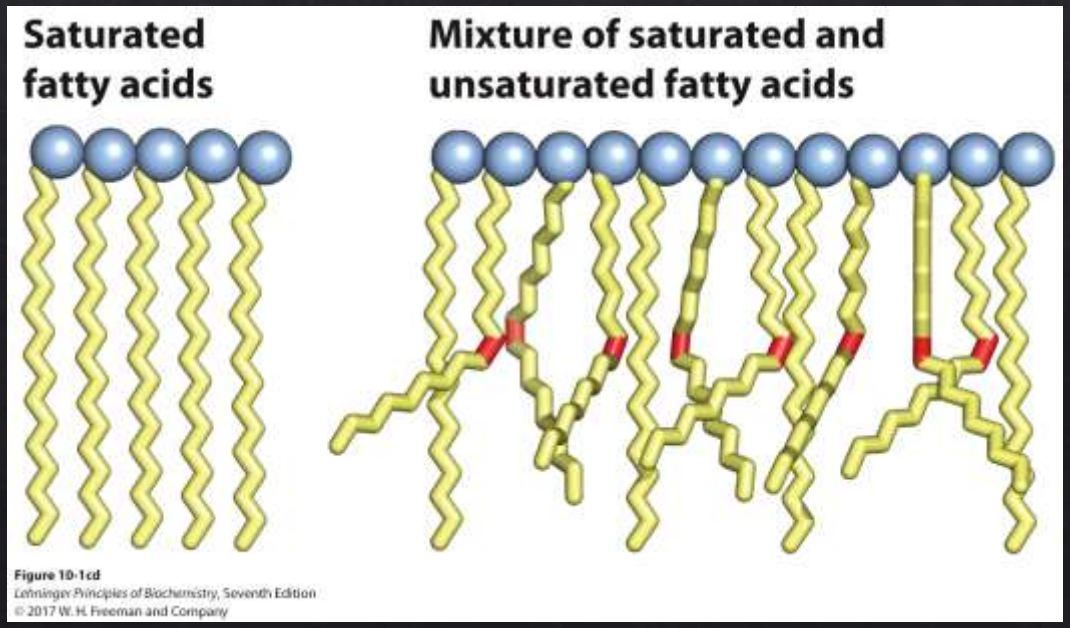


Figure 10-1cd
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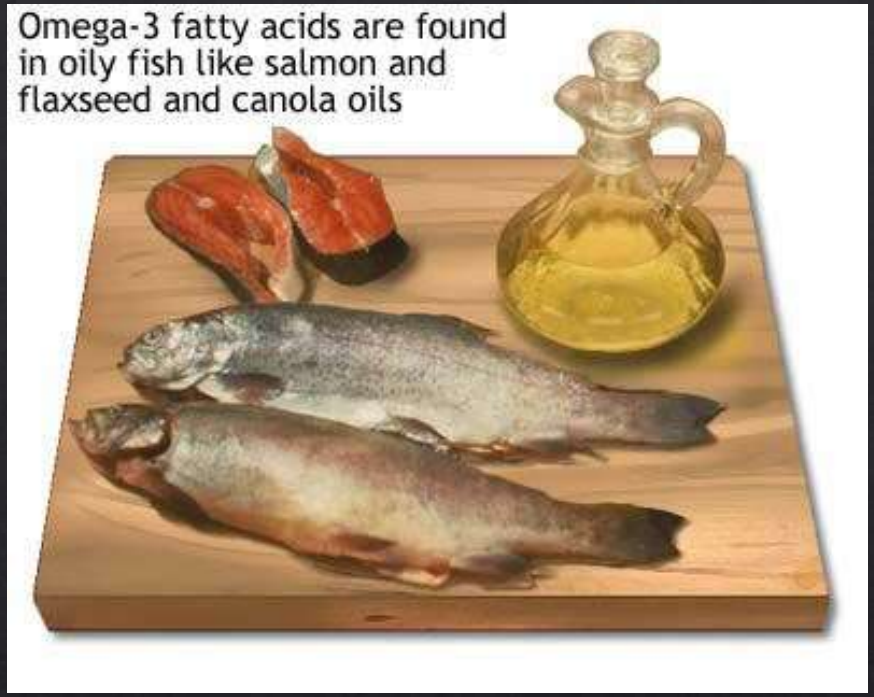
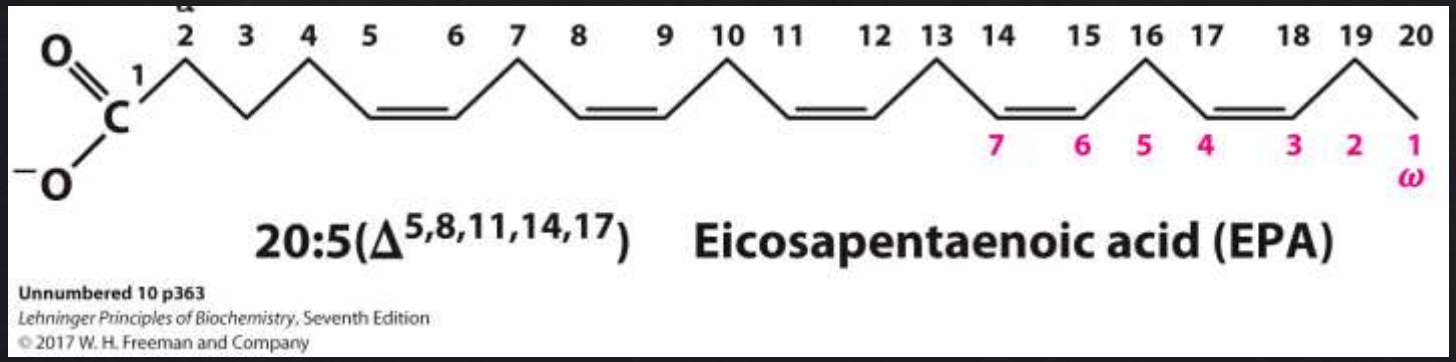
Fatty Acids

Omega-3 fatty acids are essential nutrients.

- Humans need them but cannot synthesize them.
- They include ALA, DHA, and EPA (DHA and EPA can be synthesized from ALA)



Picture from Progressive Charlestown



Fatty Acids nomenclature

TABLE 10-1 Some Naturally Occurring Fatty Acids: Structure, Properties, and Nomenclature

Carbon skeleton	Structure[a]	Systematic name[b]	Common name (derivation)	Melting point (°C)	Solubility at 30 °C (mg/g solvent)	
					Water	Benzene
16:1(Δ^9)	$CH_3(CH_2)_5CH{=}CH(CH_2)_7COOH$	*cis*-9-Hexadecenoic acid	Palmitoleic acid	1 to −0.5		
18:1(Δ^9)	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	*cis*-9-Octadecenoic acid	Oleic acid (Latin *oleum*, "oil")	13.4		
18:2($\Delta^{9,12}$)	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$	*cis*-,*cis*-9,12-Octadecadienoic acid	Linoleic acid (Greek *linon*, "flax")	1–5		
18:3($\Delta^{9,12,15}$)	$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$	*cis*-,*cis*-,*cis*-9,12,15-Octadecatrienoic acid	α-Linolenic acid	−11		
20:4($\Delta^{5,8,11,14}$)	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_3COOH$	*cis*-,*cis*-,*cis*-,*cis*-5,8,11,14-Icosatetraenoic acid	Arachidonic acid	−49.5		

[a] All acids are shown in their nonionized form. At pH 7, all free fatty acids have an ionized carboxylate. Note that numbering of carbon atoms begins at the carboxyl carbon.

[b] The prefix *n*- indicates the "normal" unbranched structure. For instance, "dodecanoic" simply indicates 12 carbon atoms, which could be arranged in a variety of branched forms; "*n*-dodecanic" specifies the linear, unbranched form. For unsaturated fatty acids, the configuration of each double bond is indicated; in biological fatty acids the configuration is almost always cis.

Table 10-1 part 2

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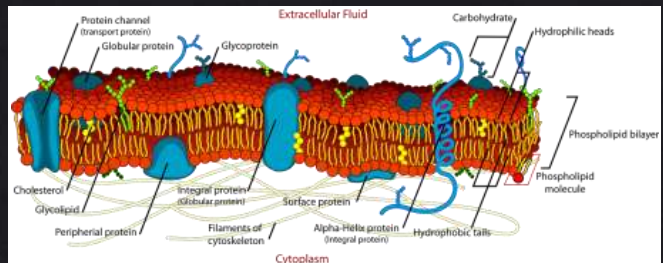
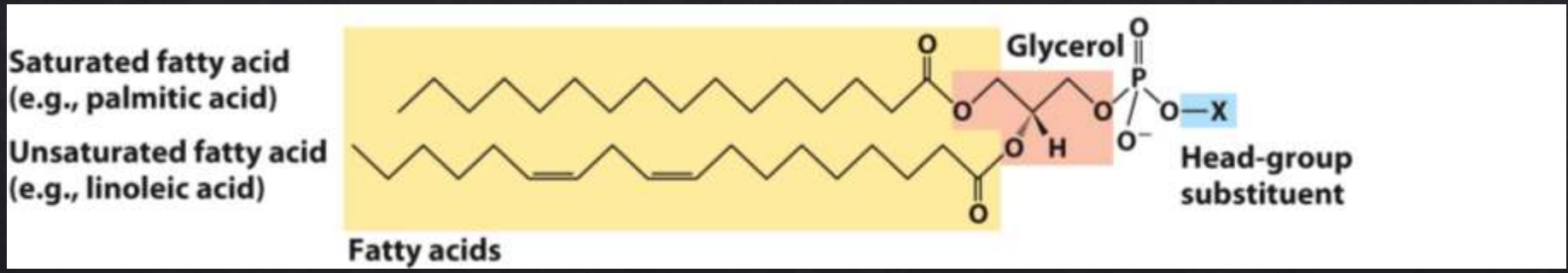
Structural lipids in membranes

- Contain polar head groups and nonpolar tails (usually attached fatty acids)
- Diversification can come from:
  - modifying a different backbone
  - changing the fatty acids
  - modifying the head groups
- The properties of head groups determine the surface properties of membranes.
- Different organisms have different membrane lipid head group compositions.
- Different tissues have different membrane lipid head group compositions.



General Structure of Glycerophospholipids

- Unsaturated fatty acids are commonly found connected to C2 of glycerol-3-phosphate.
- The highly polar phosphate group may be further esterified by an alcohol; such substituent groups are called the head groups.
- Head-groups can be charged (+ or -) or neutral – functional.



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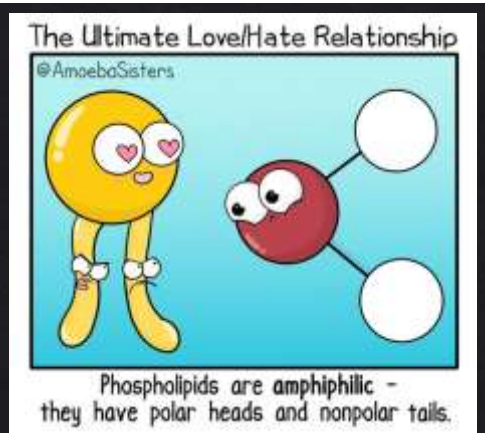
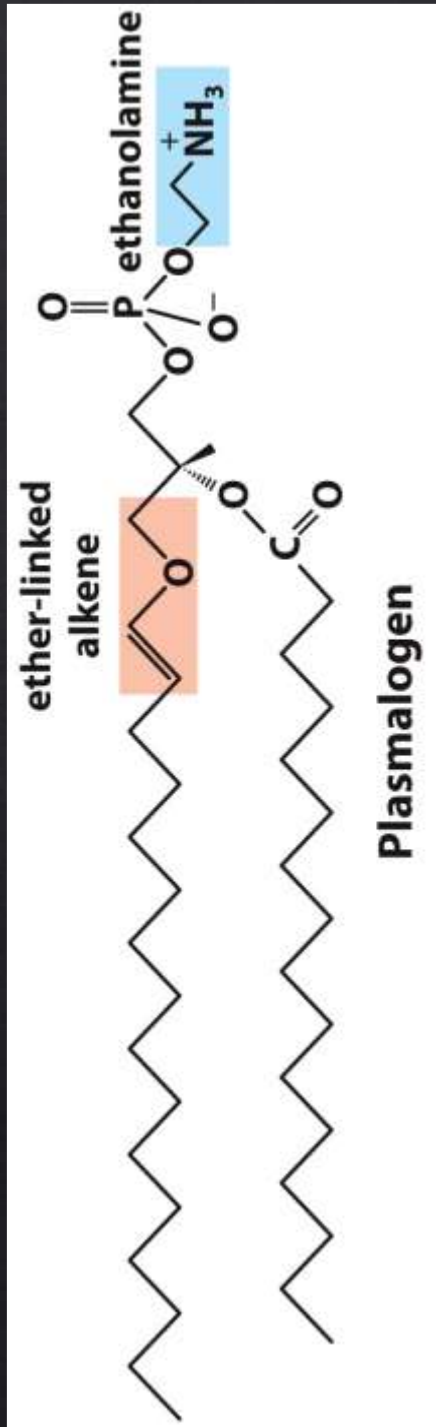


Ether lipids: plasmalogen

- Most phospholipids have ester bonds, some have ether bonds
- Common in vertebrate heart tissue
- Also found in some protozoa and anaerobic bacteria
- Function is not well understood
  - resistant to cleavage by common lipases but cleaved by few specific lipases
  - Increase membrane rigidity?
  - Sources of signaling lipids?
  - May be antioxidant?



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Ether lipids: platelets-activating factor

- Aliphatic ether analog of phosphatidylcholine
- Acetic acid has esterified position C2
- First signaling lipid to be identified
- Stimulates aggregation of blood platelets
- Plays role in mediation of inflammation

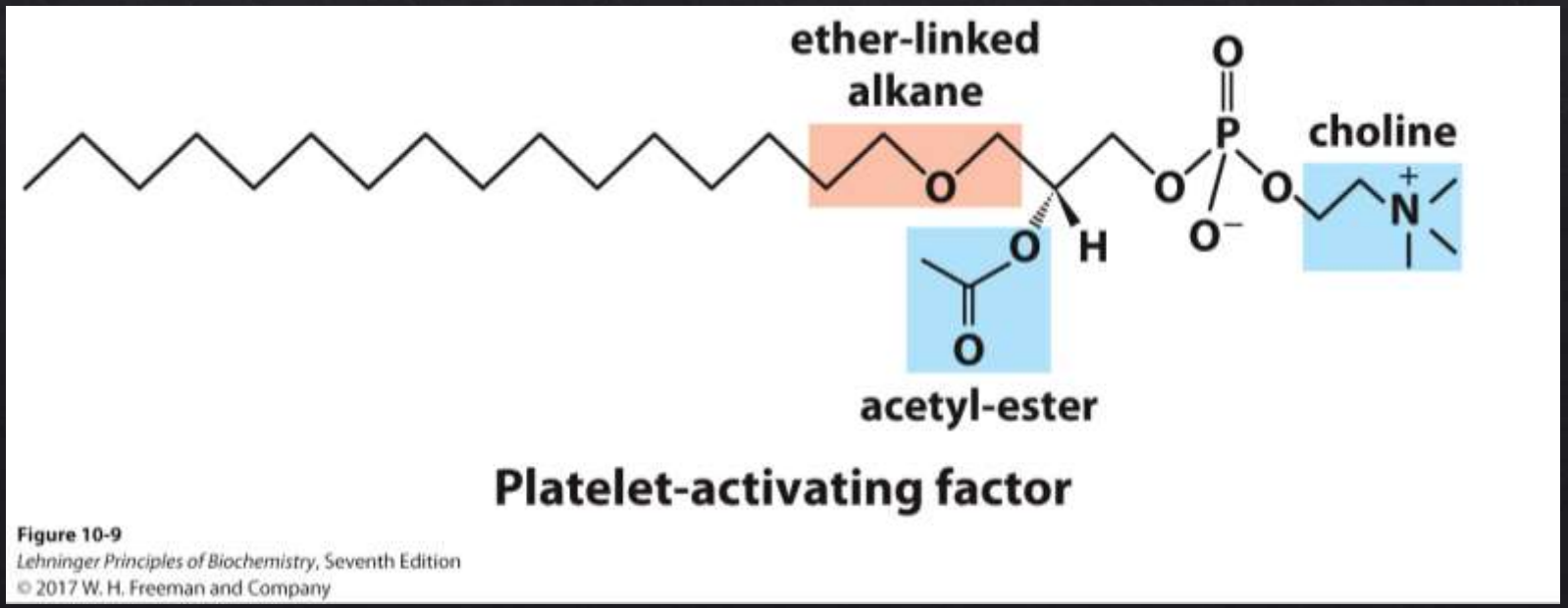

Figure 10-9
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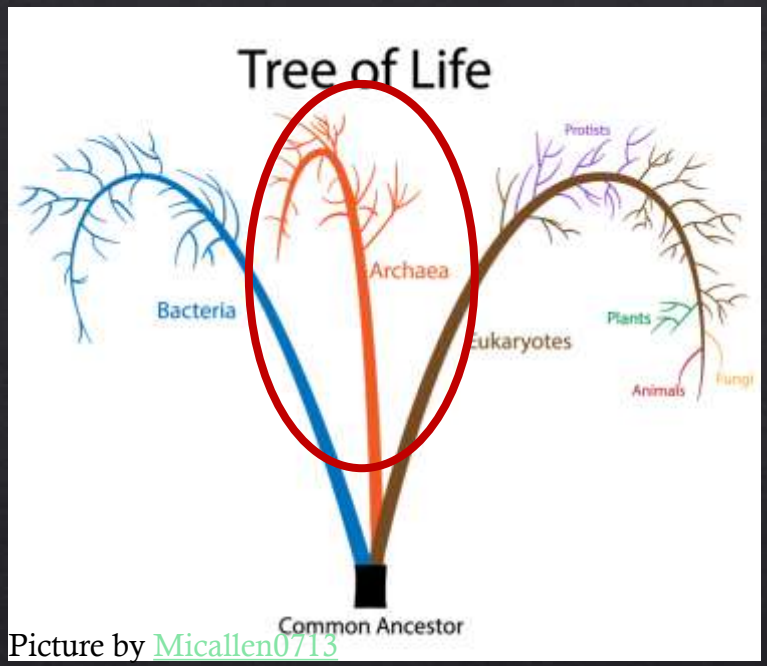
Other ether lipids

- Organisms living in extreme environments
- Longer chain
- Two polar heads
- Glycerol is a different steroisomer



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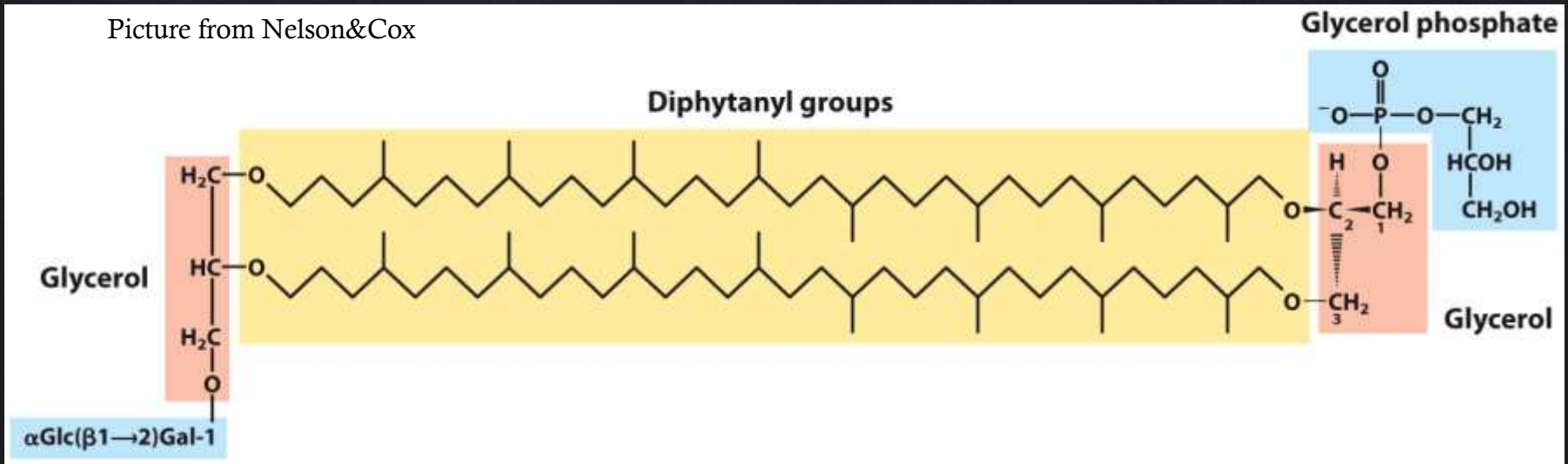
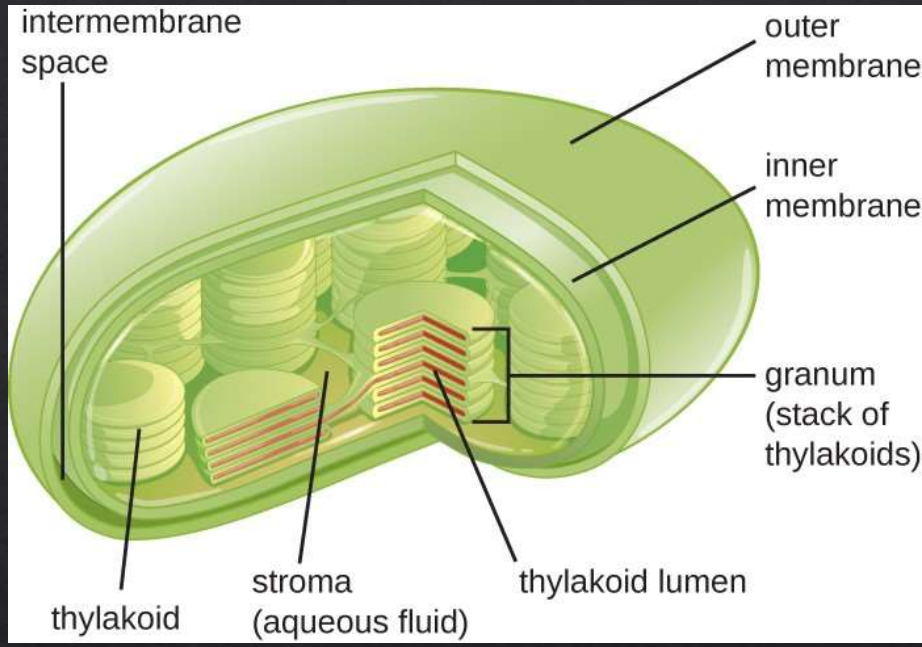


Galactolipids

- Predominate in plant cells (thylakoids)
- Plant membranes also contain sulfolipids
- Adaptation to shortage of phosphate?



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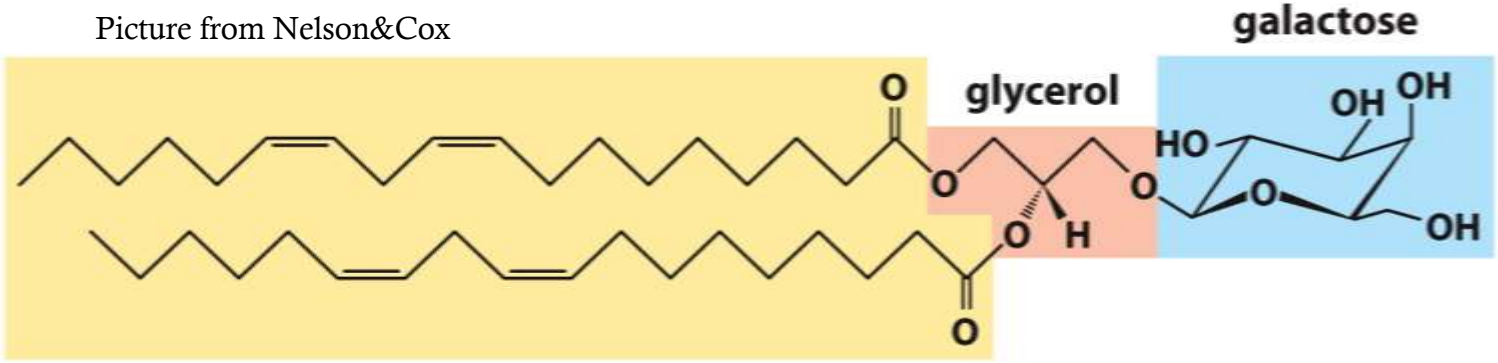
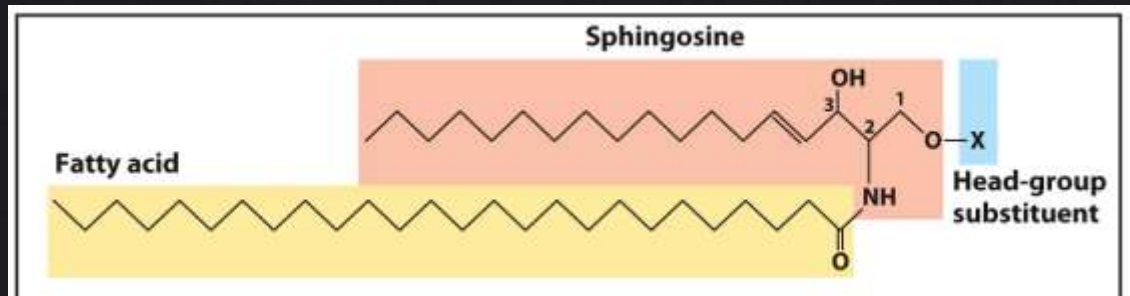


Monogalactosyldiacylglycerol (MGDG)

Sphingolipids

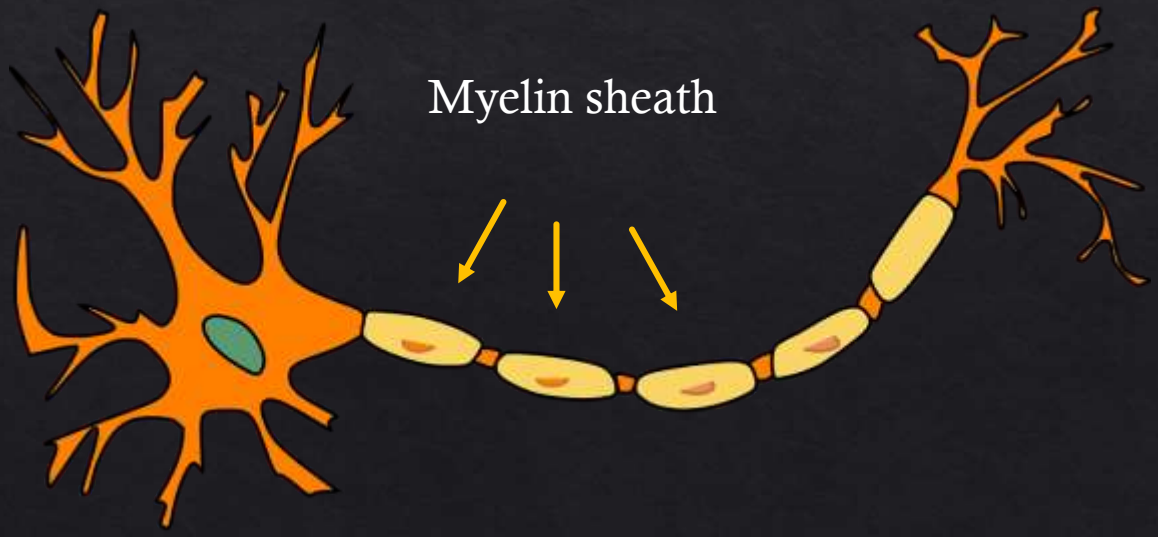
- The backbone of sphingolipids is a long-chain amino alcohol sphingosine, not glycerol.
- A fatty acid is joined to sphingosine via an amide linkage, rather than an ester linkage as usually seen in lipids.
- A polar head group is connected to sphingosine by a glycosidic or phosphodiester linkage.
- The sugar-containing glycosphingolipids are found largely in the outer face of plasma membranes.



Picture from Nelson&Cox

Sphingomyelin

- Ceramide (sphingosine + amide-linked fatty acid) + phosphocholine attached to the alcohol
- Sphingomyelin is abundant in myelin sheath that surrounds some nerve cells in animals.




5 minute

Glycosphingolipids and blood groups

- Blood groups are partly determined by the sugars on the head groups in glycosphingolipids.
- The structure of sugar is determined by an expression of specific glycosyltransferases.
  - Individuals with no active glycosyltransferase will have the **O antigen**.
  - Individuals with a glycosyltransferase that transfers an *N*-acetylgalactosamine group have **A blood group**.
  - Individuals with a glycosyltransferase that transfers a galactose group have **B blood group**.

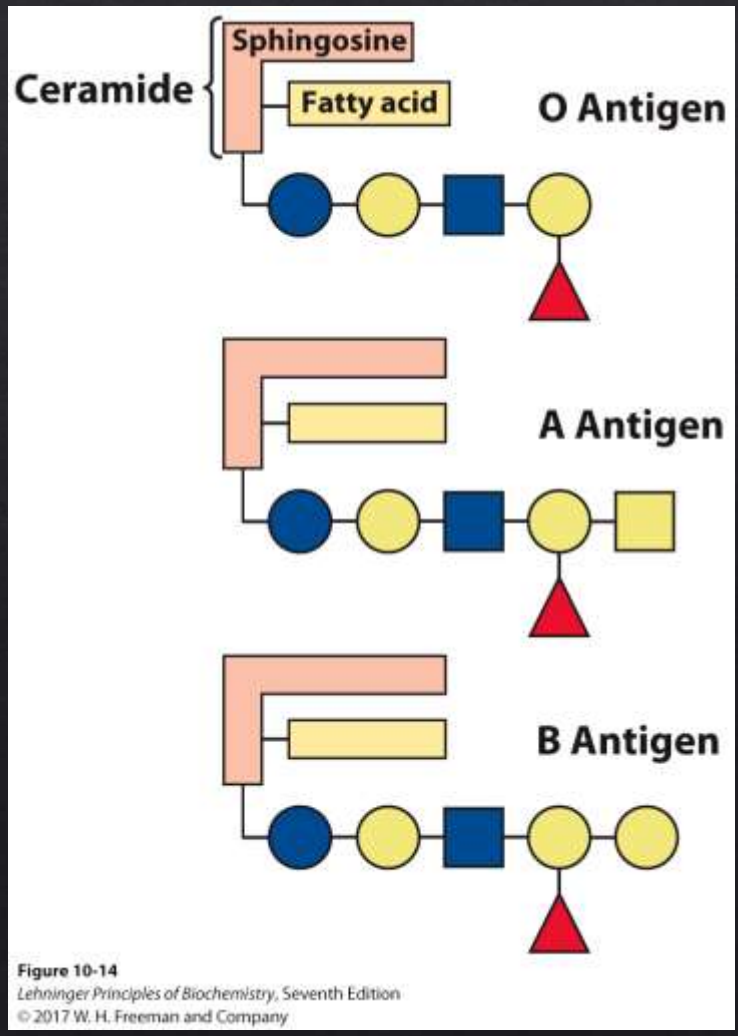


Figure 10-14
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Structural and signaling lipids are degraded in the lysosome

- Most cells continually degrade and replace their membrane lipids.
- Phospholipids are degraded by phospholipases A–D.
  - Each phospholipase cleaves a specific bond.

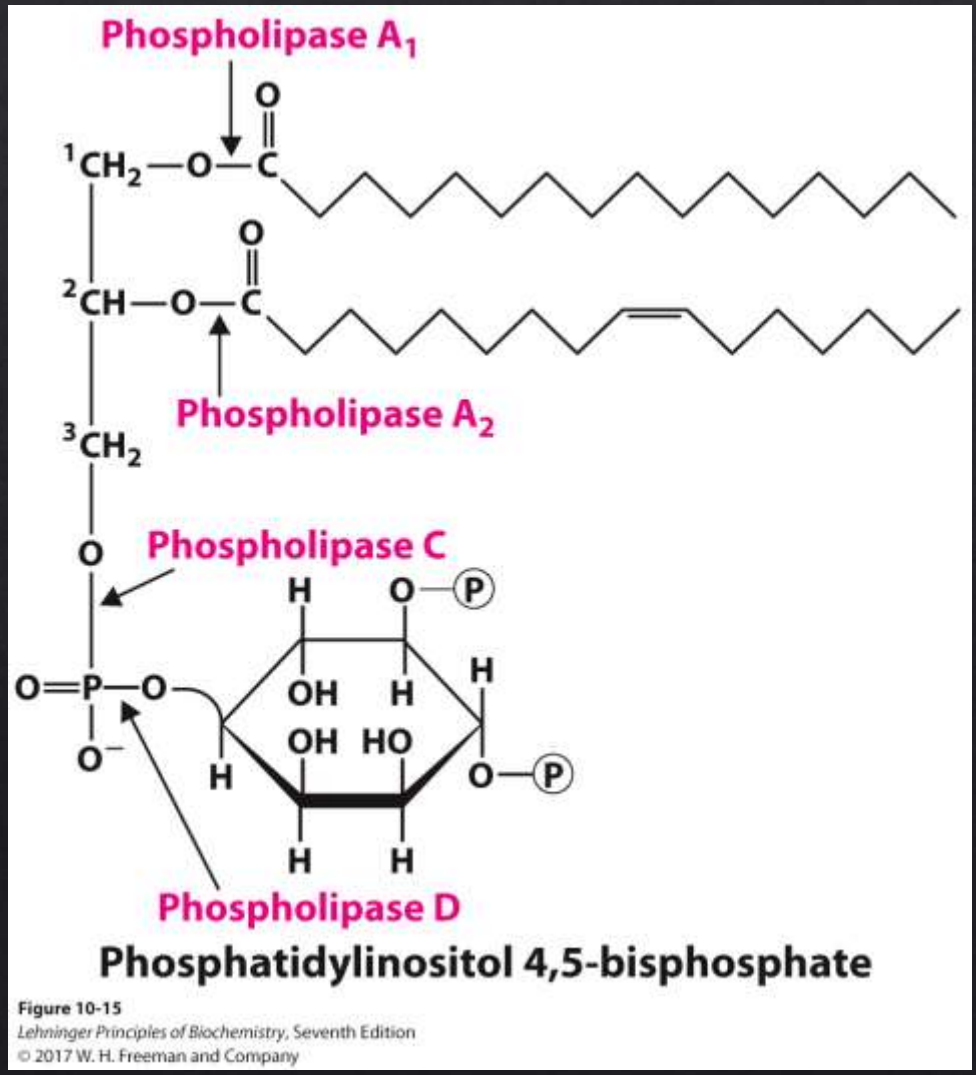

Figure 10-15
Lehninger Principles of Biochemistry, Seventh Edition

Sterols

- Sterol
  - steroid nucleus: four fused rings
  - hydroxyl group (polar head) in the A-ring
  - various nonpolar side chains
- The tetracycle structure of sterols is almost planar.

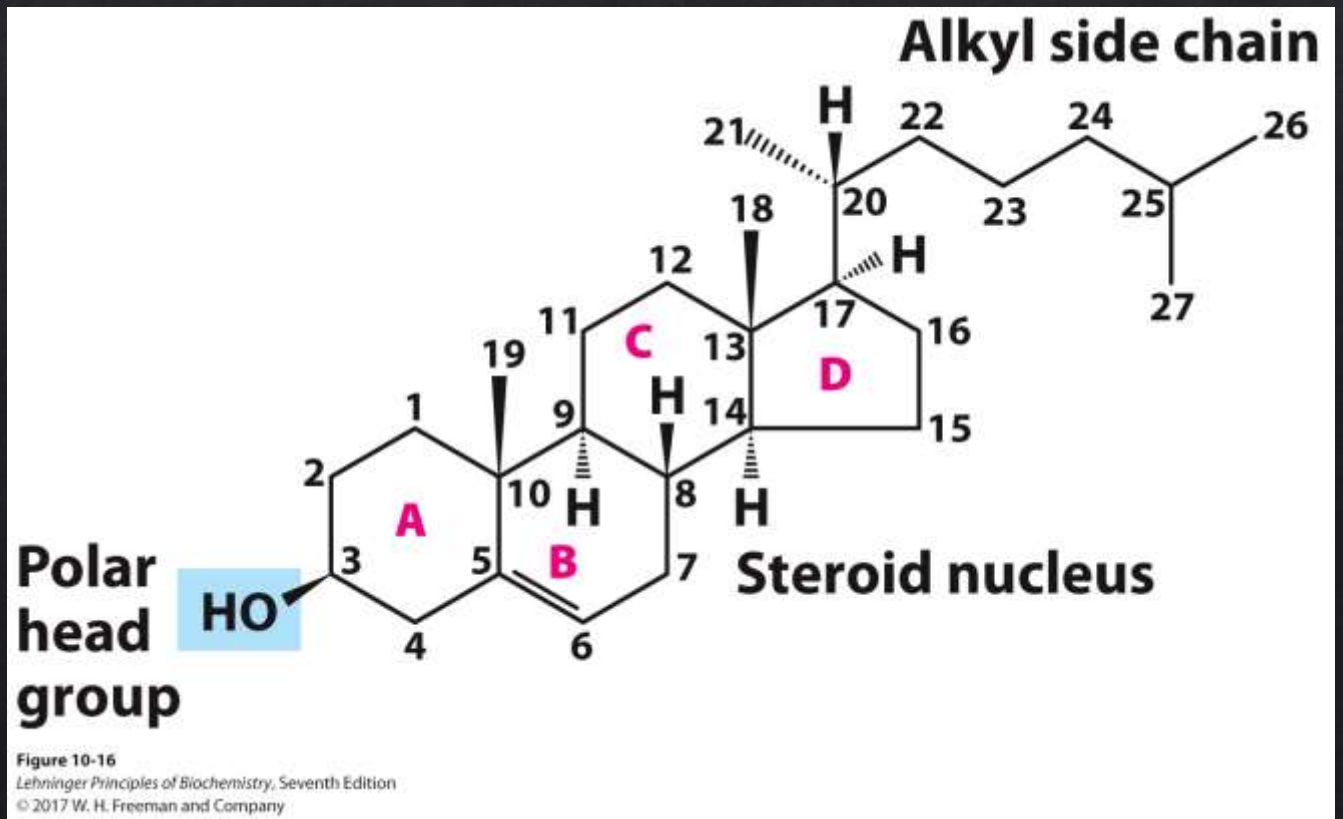

Figure 10-16
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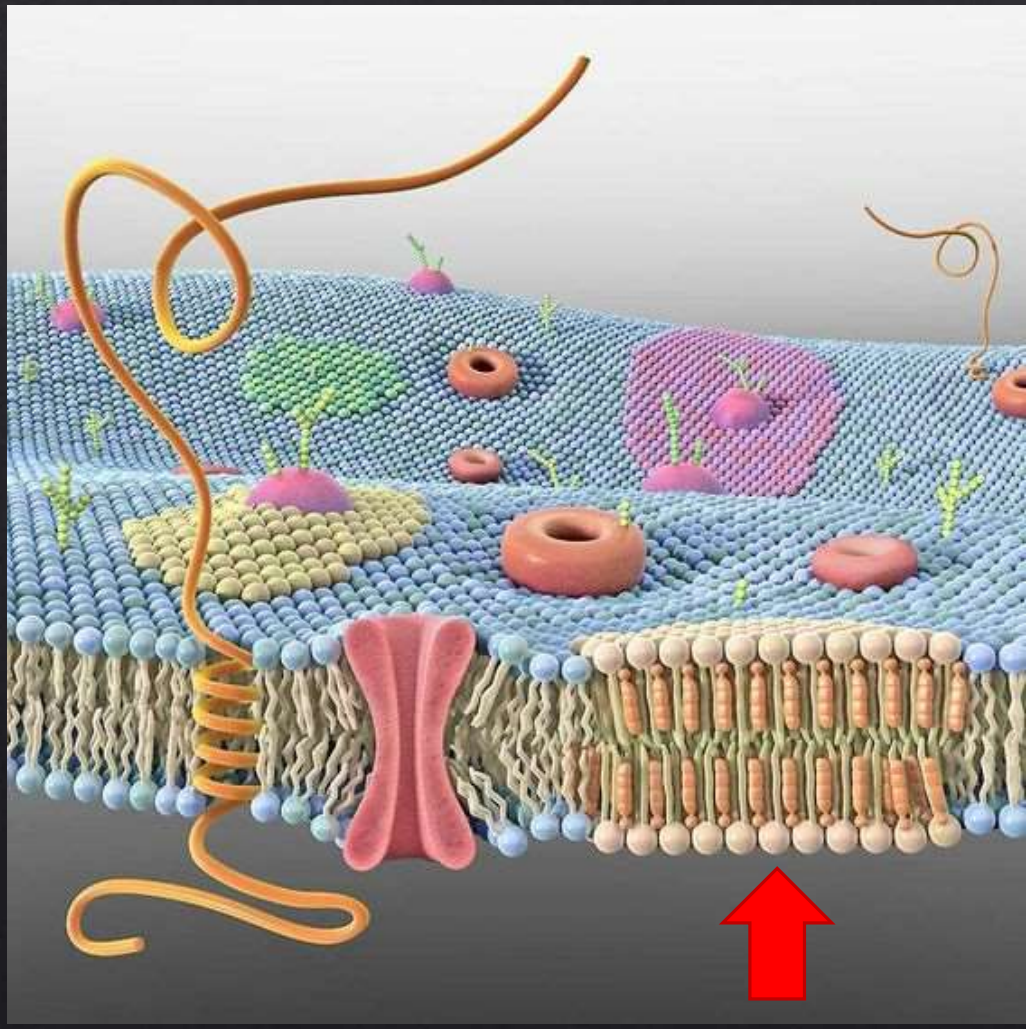
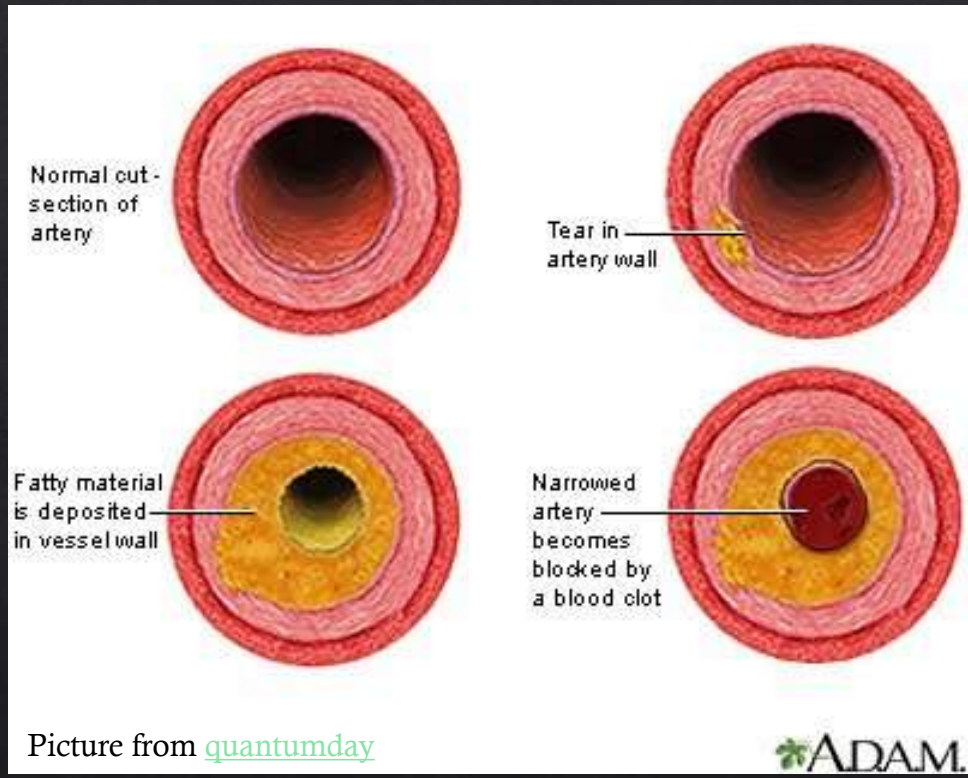
Cholesterol

- Cholesterol and related sterols are present in the membranes of most eukaryotic cells.
  - modulate fluidity and permeability
  - thicken the plasma membrane
  - no sterols in most bacteria
- Mammals obtain cholesterol from food or synthesize it *de novo* in the liver.



Cholesterol

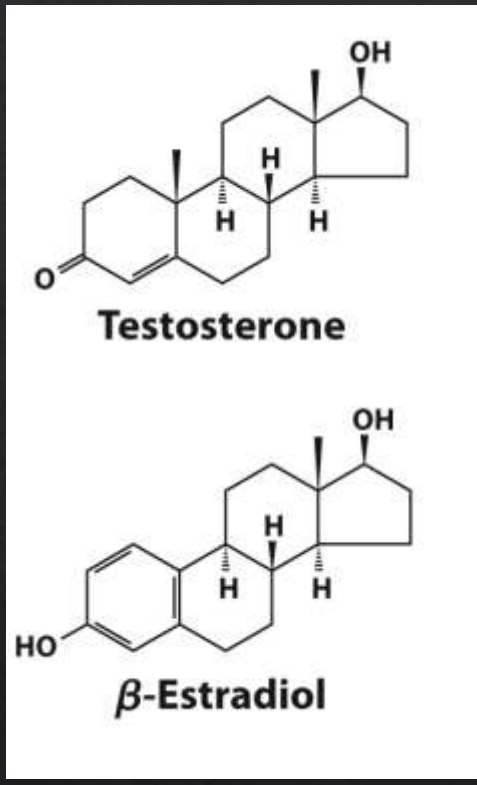
- Cholesterol, bound to proteins, is transported to tissues via blood vessels.
  - Cholesterol in low-density lipoproteins tends to deposit and clog arteries.
- Many hormones are derivatives of sterols.



Picture from quantumday

Steroid hormones

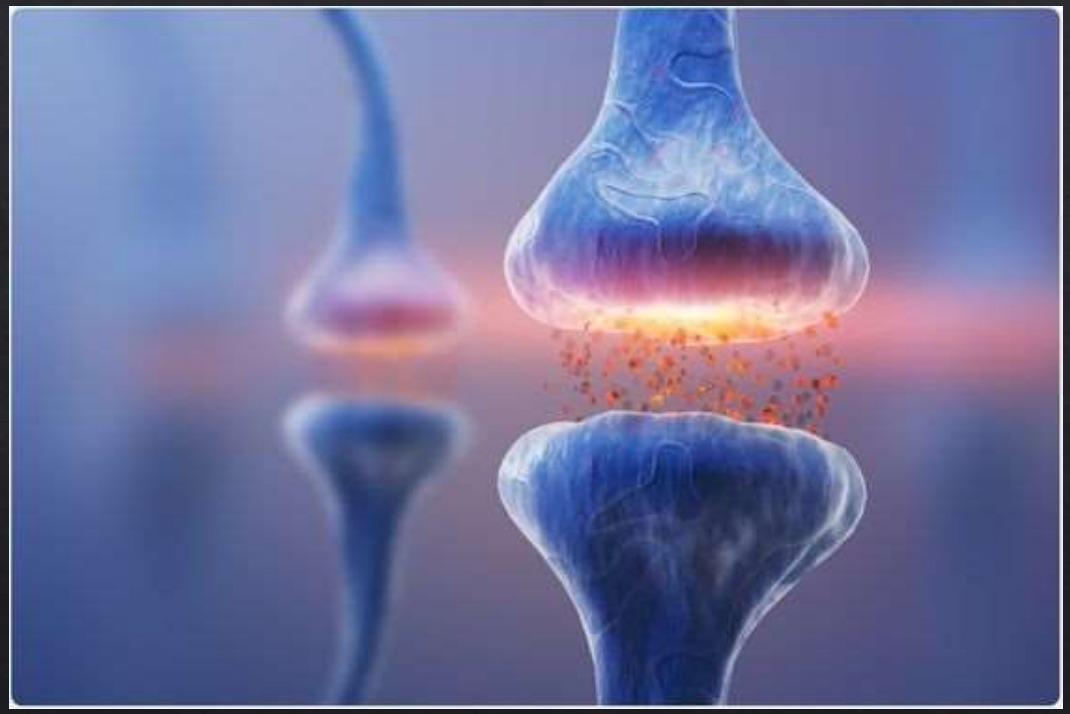
- Steroids are oxidized derivatives of sterols.
- Steroids have the sterol nucleus but lack the alkyl chain found in cholesterol.
- They are more polar than cholesterol.
- Steroid hormones are synthesized from cholesterol in gonads and adrenal glands.
- They are carried through the body in the bloodstream, usually attached to carrier proteins.
- Many of the steroid hormones are male and female sex hormones.



Picture from Nelson&Cox

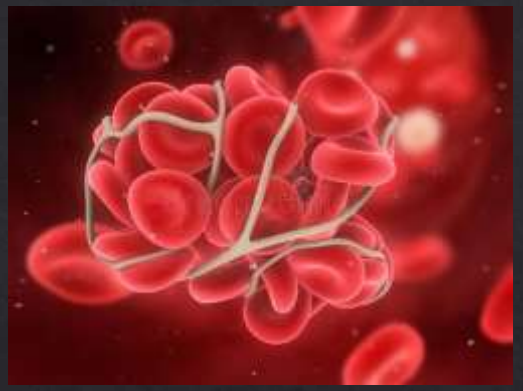
Biologically active lipids

- Are present in much smaller amounts than storage or structural lipids
- Play vital roles as signaling molecules between nearby cells
- Lipid-soluble vitamins (A, D, E, and K)



Eicosanoids

- Enzymatic oxidation of arachidonic acid yields:
  - Prostaglandins (inflammation and fever)
  - Thromboxanes (formation of blood clots)
  - Leukotrienes (smooth muscle contraction in lungs)
  - Lipoxins (powerful antiinflammatory)



Plant lipophilic compounds

- Volatile compounds:
  - Attract pollinators
  - Repel herbivores/parasites
  - Communication
  - Widely used in cosmetics and medical

Vitamins

- Essential, need to be assumed with the diet. Two classes:
  - Fat-soluble
  - Water soluble

Picture from pngall

Vitamin D is synthesized from cholesterol and regulates calcium metabolism

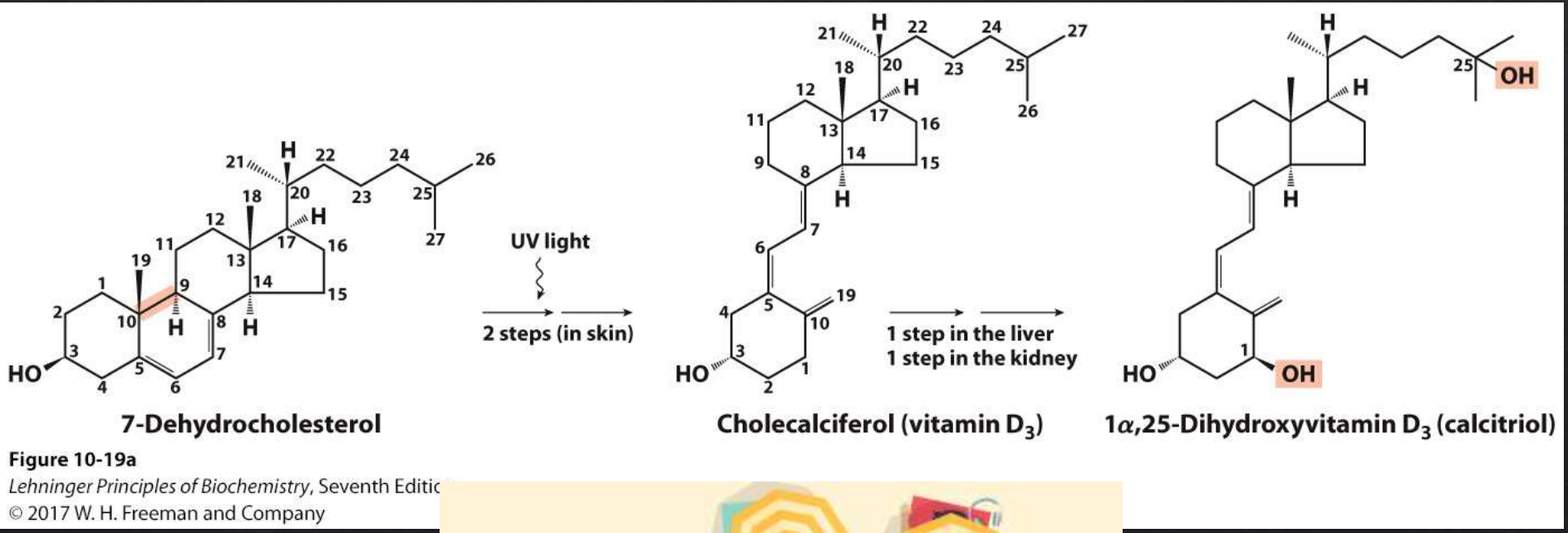


Figure 10-19a

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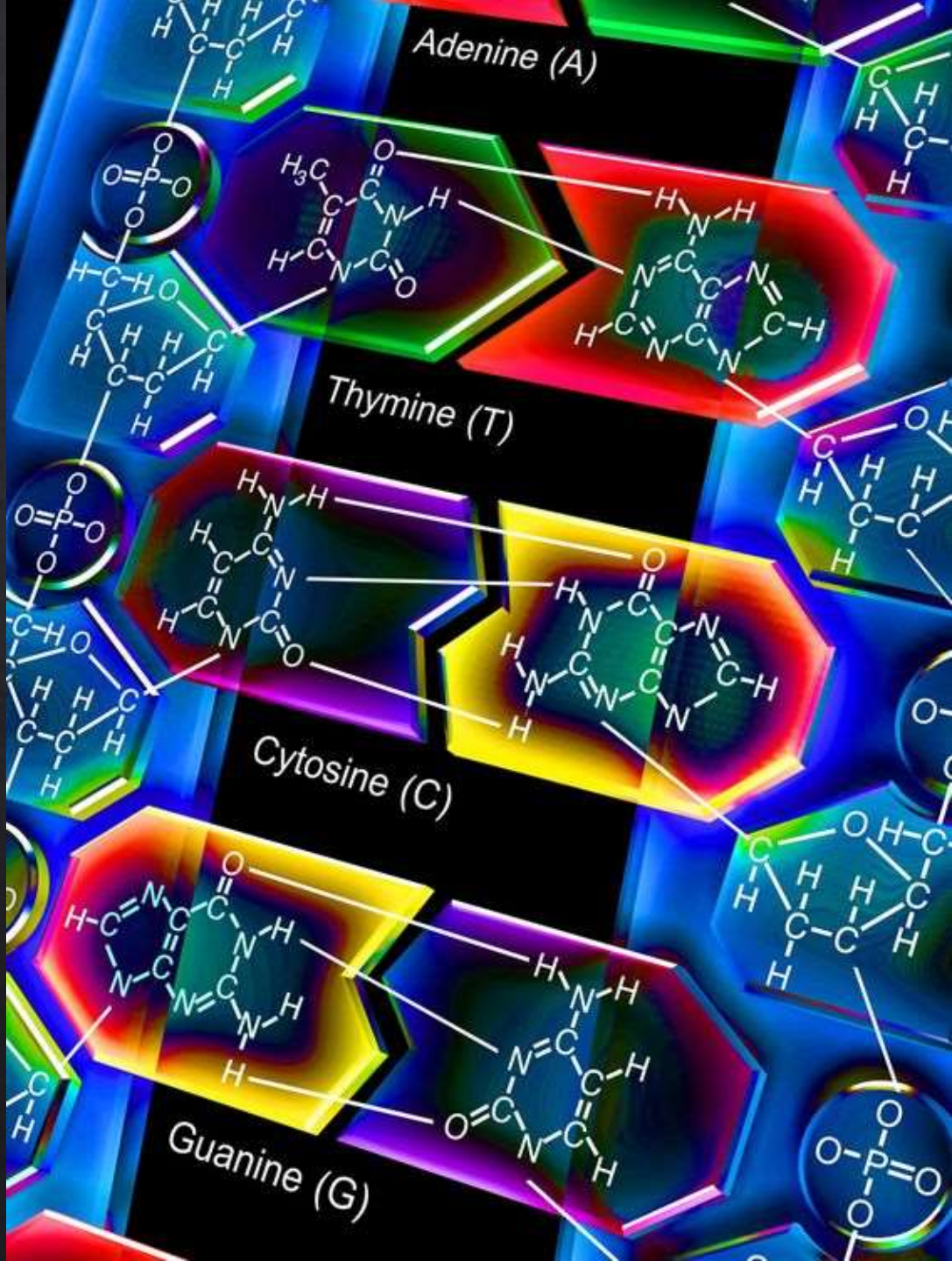
Nucleotides

Mostly known as building block of **DNA** and **RNA**.

Involved also in:

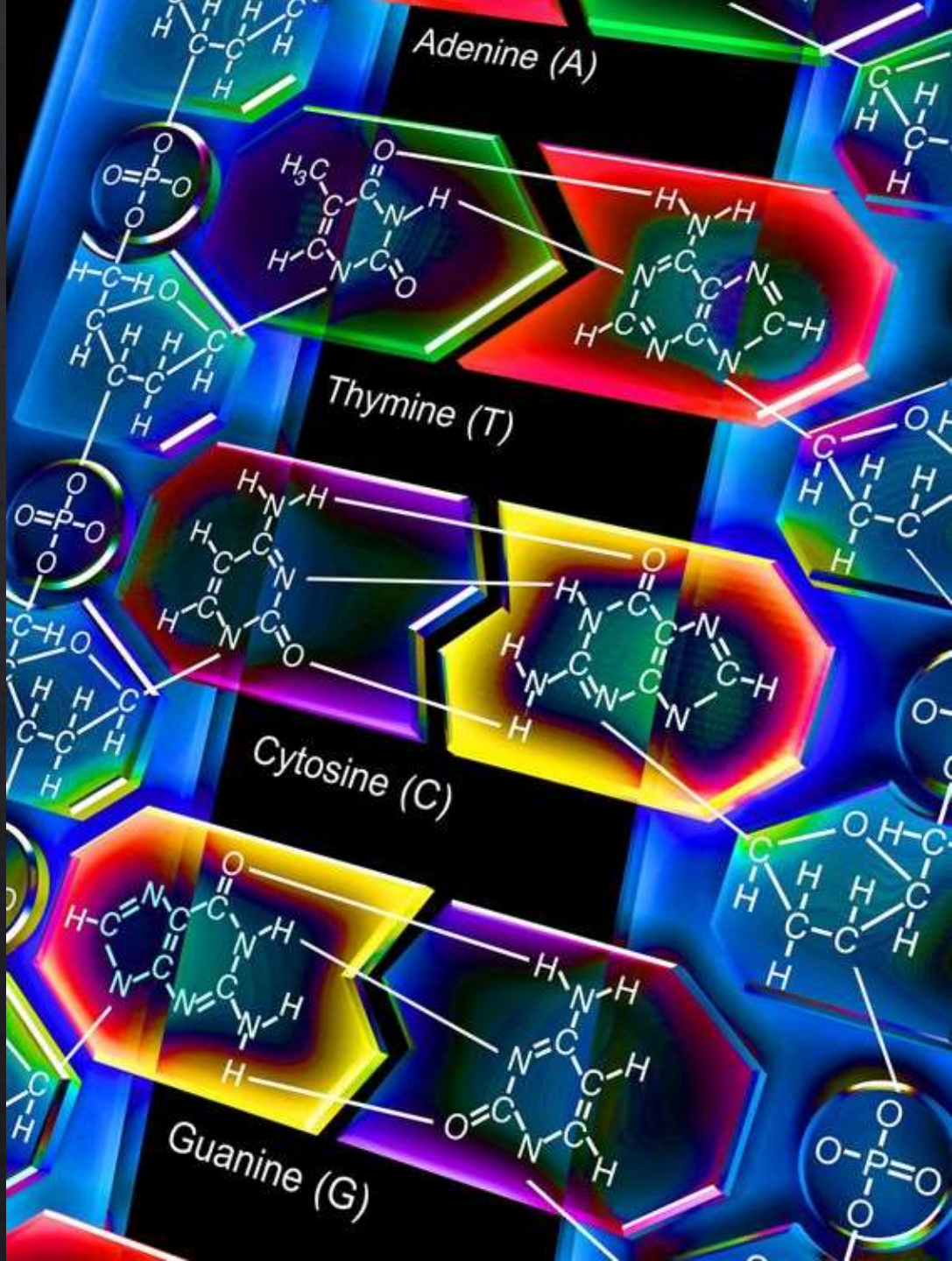
- Metabolic transaction
- Response to hormones & stimuli
- Enzyme cofactors



Nucleic acids

Nucleotides are also used in the monomer form for cellular functions:

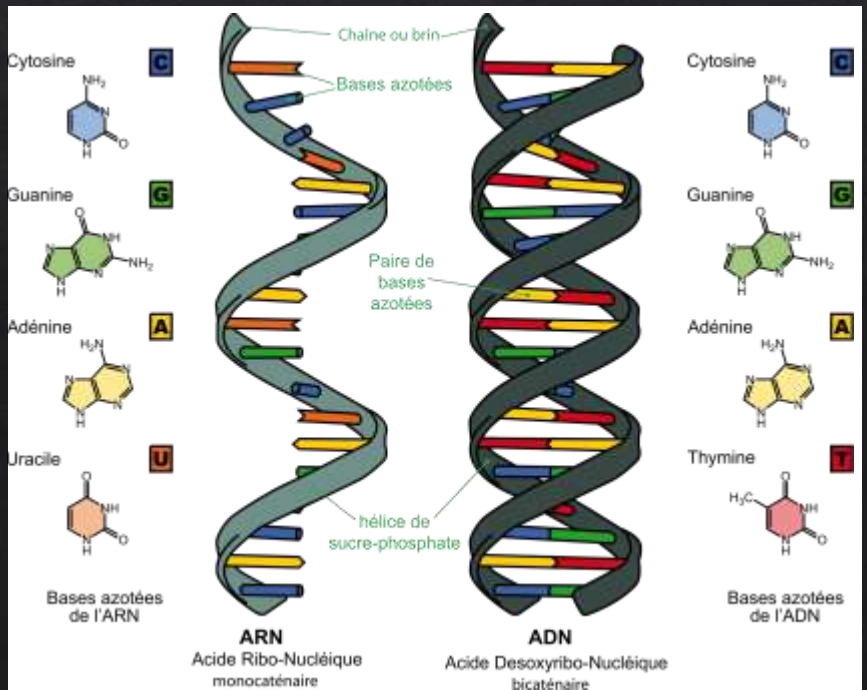
- energy for metabolism (ATP)
- enzyme cofactors (NAD^+)
- signal transduction (cAMP)



Nucleic acids

Nucleic acids are polymers of nucleotides used for:

- storage of genetic info (DNA)
- transmission of genetic info (mRNA)
- processing of genetic information (ribozymes)
- protein synthesis (tRNA and rRNA)



Picture by Sponk

Nucleotides – what are they?

Nucleotide =

- nitrogeneous base
- pentose
- phosphate

Nucleoside =

- nitrogeneous base
- pentose

Carbon AND nitrogen atoms on the nitrogenous base are numbered in cyclic format. Carbons of the pentose are designated N' to alleviate confusion.

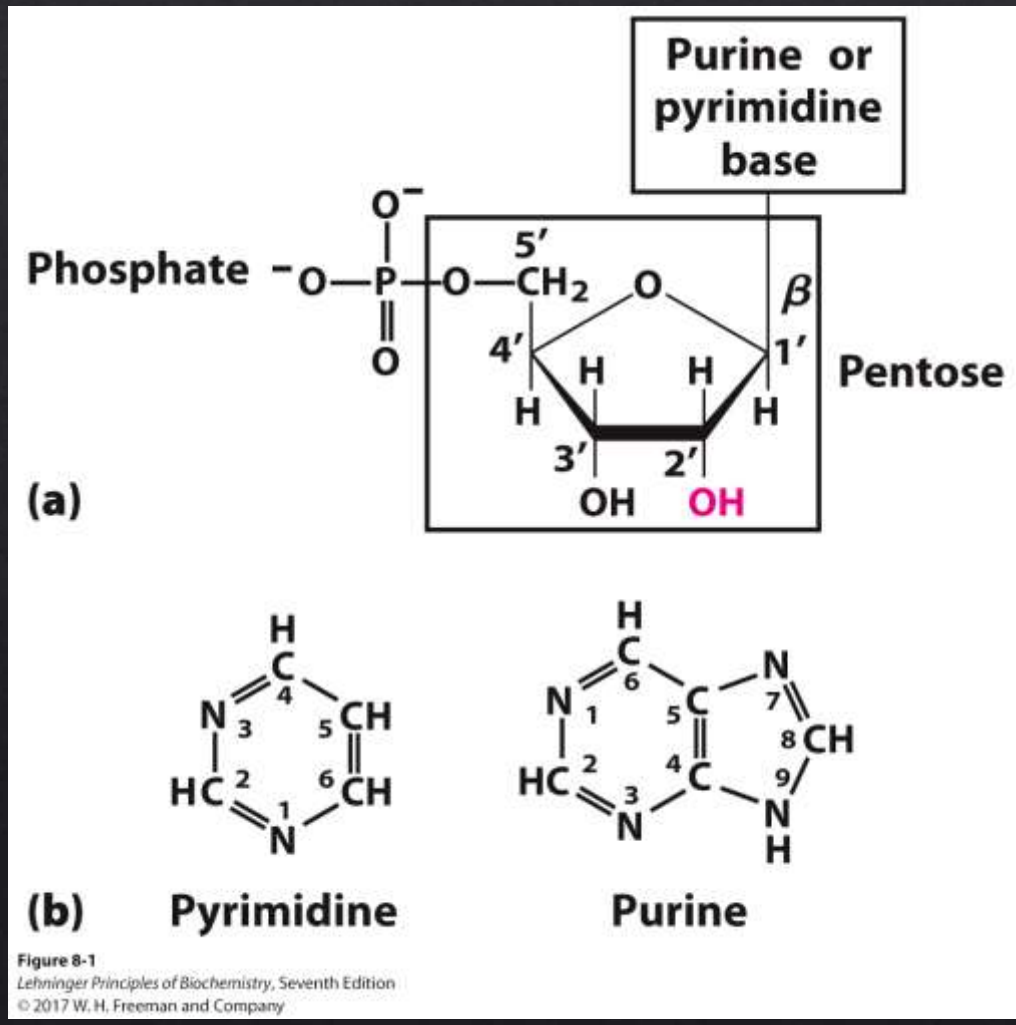
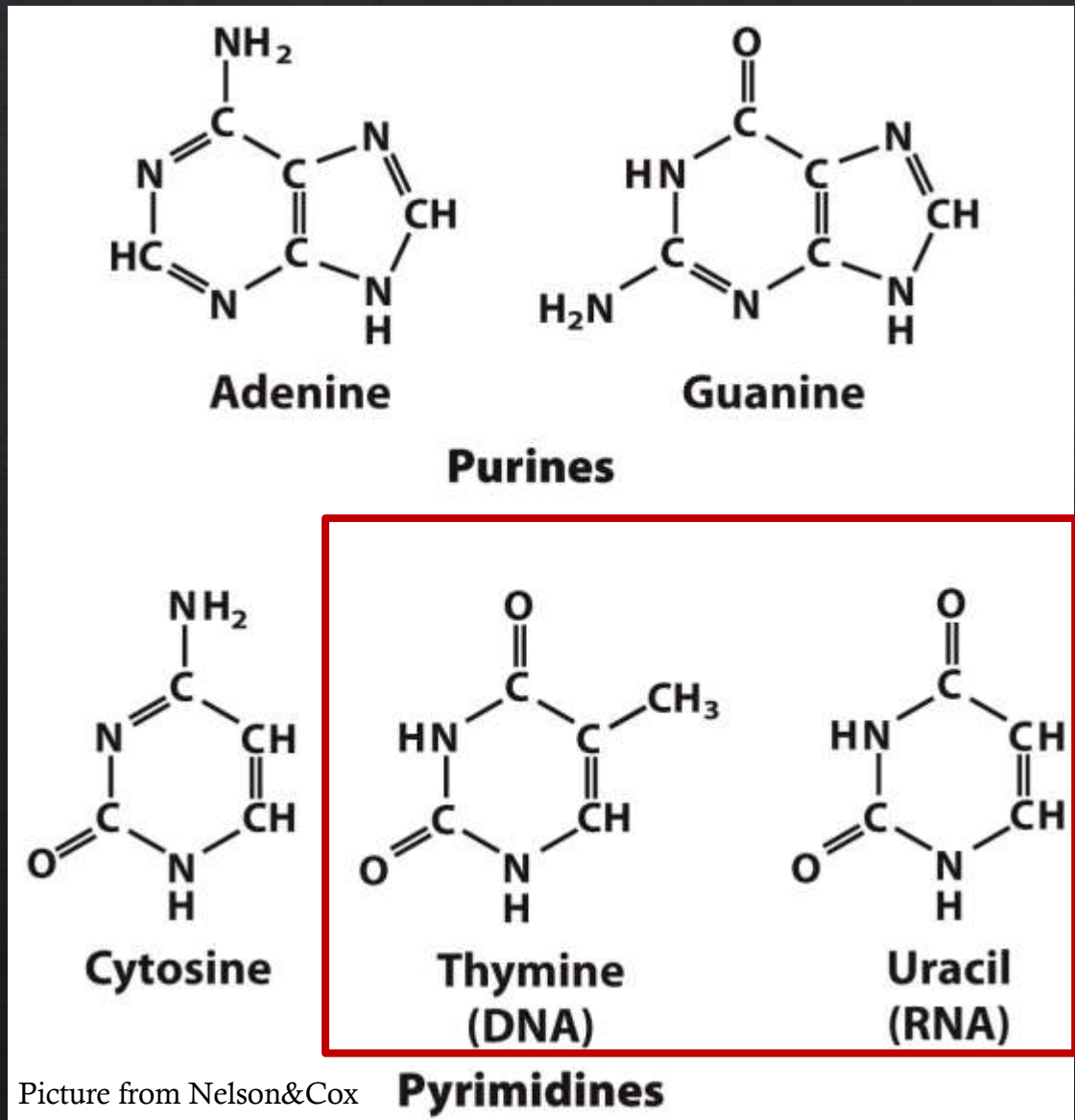


Figure 8-1
Lehninger Principles of Biochemistry, Seventh Edition

Nucleotides

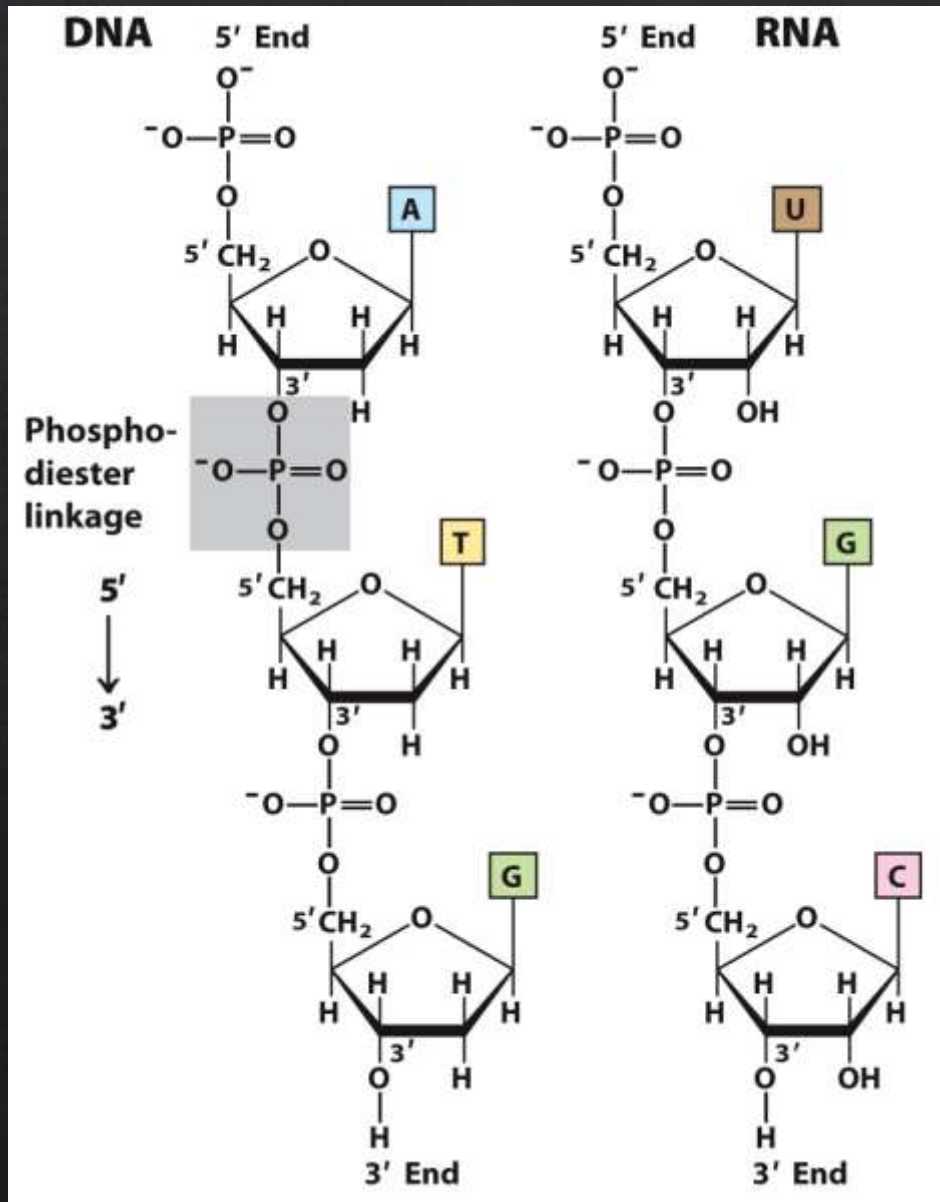
- Cytosine, adenine, and guanine are found in both DNA and RNA.
- Thymine is found only in DNA.
- Uracil is found only in RNA.
- All are good H-bond donors and acceptors.
- Neutral molecules at pH 7



Picture from Nelson&Cox

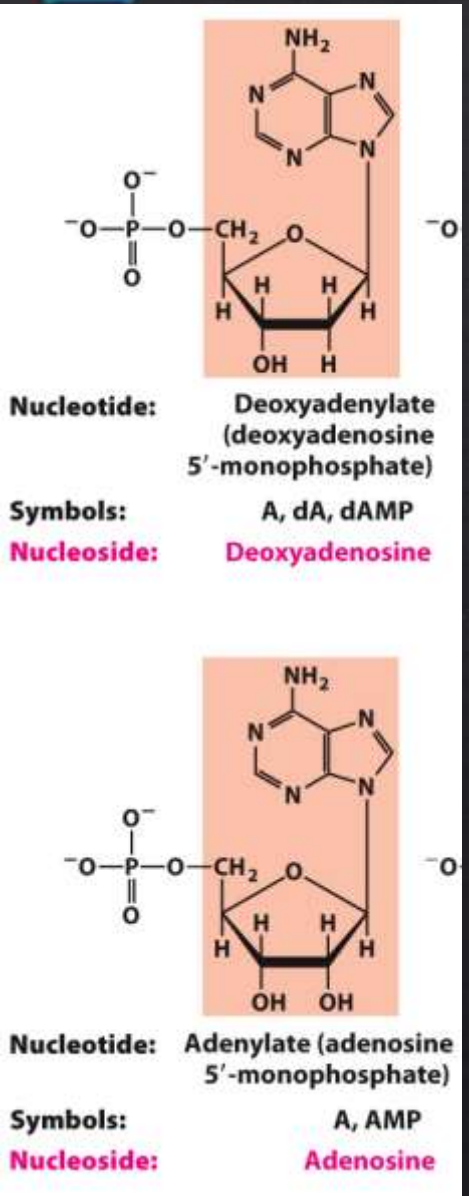
Phosphodiester linkage

- the 5′-phosphate group of one nucleotide is joined to the 3′-hydroxyl group of the next in a **phosphodiester linkage**
- covalent backbones of nucleic acids consist of alternating phosphate and pentose residues
- RNA and DNA backbones are hydrophilic
- Sugars form H-bonds with water



Picture from Nelson&Cox

DNA & RNA

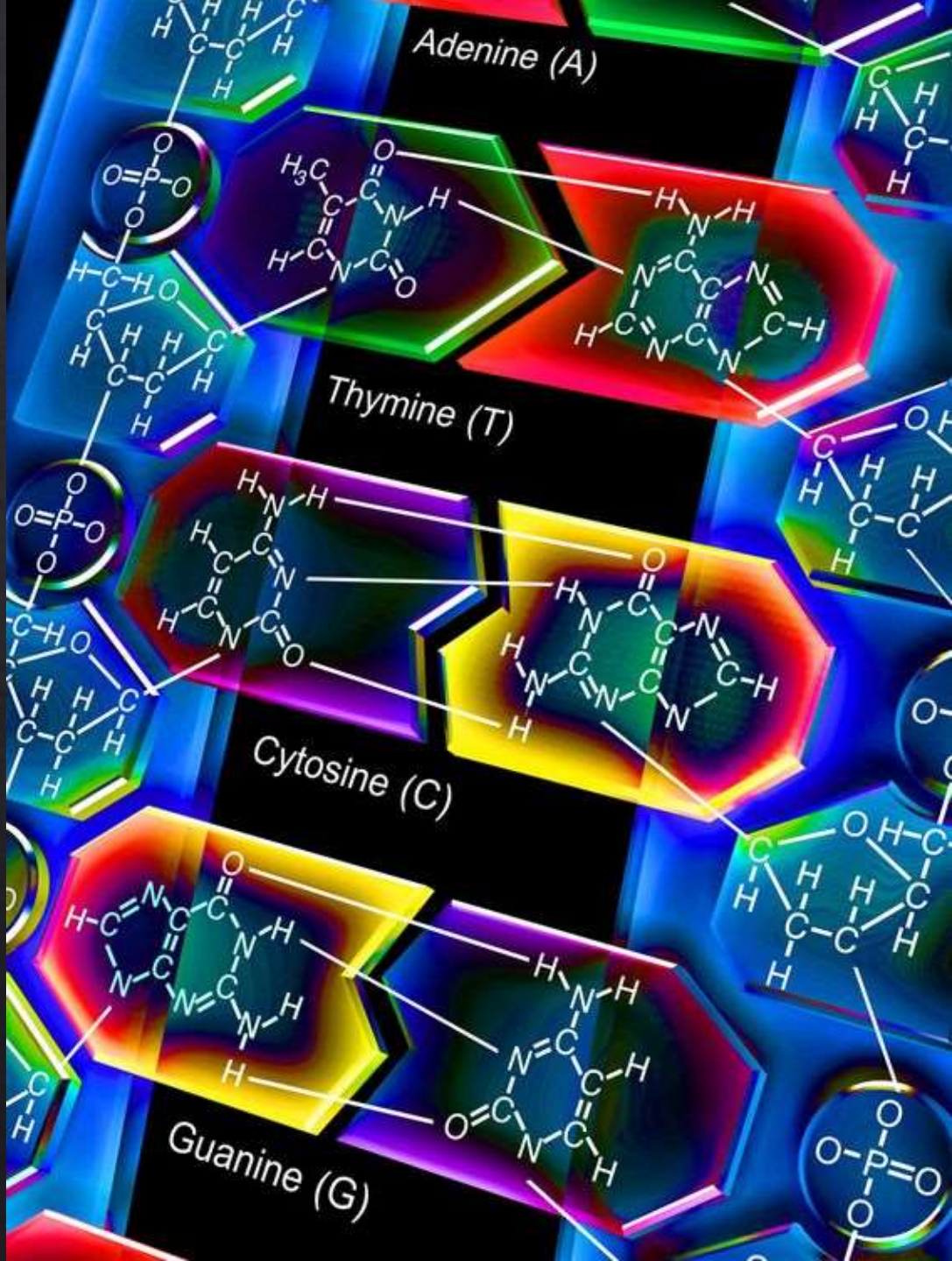


- Main difference: the sugar! (D-ribose in RNA, 2'-deoxy-D-ribose in DNA)
- Uracil/Thymine
- RNA single strand, DNA double strand
- DNA storage of information, RNA multiple functions

Picture from Nelson&Cox

DNA structure

- Right-handed double helix
- DNA strands are complementary and antiparallel
- Nucleotides form H-bonds purine-pyrimidine (C-G, A-T)
- The core of structure is given by “base stacking” and metal cations



DNA structure

- B-form is the one we're more familiar with but A and Z forms are also possible
- We can also have triple strand DNA, or even four strands DNA

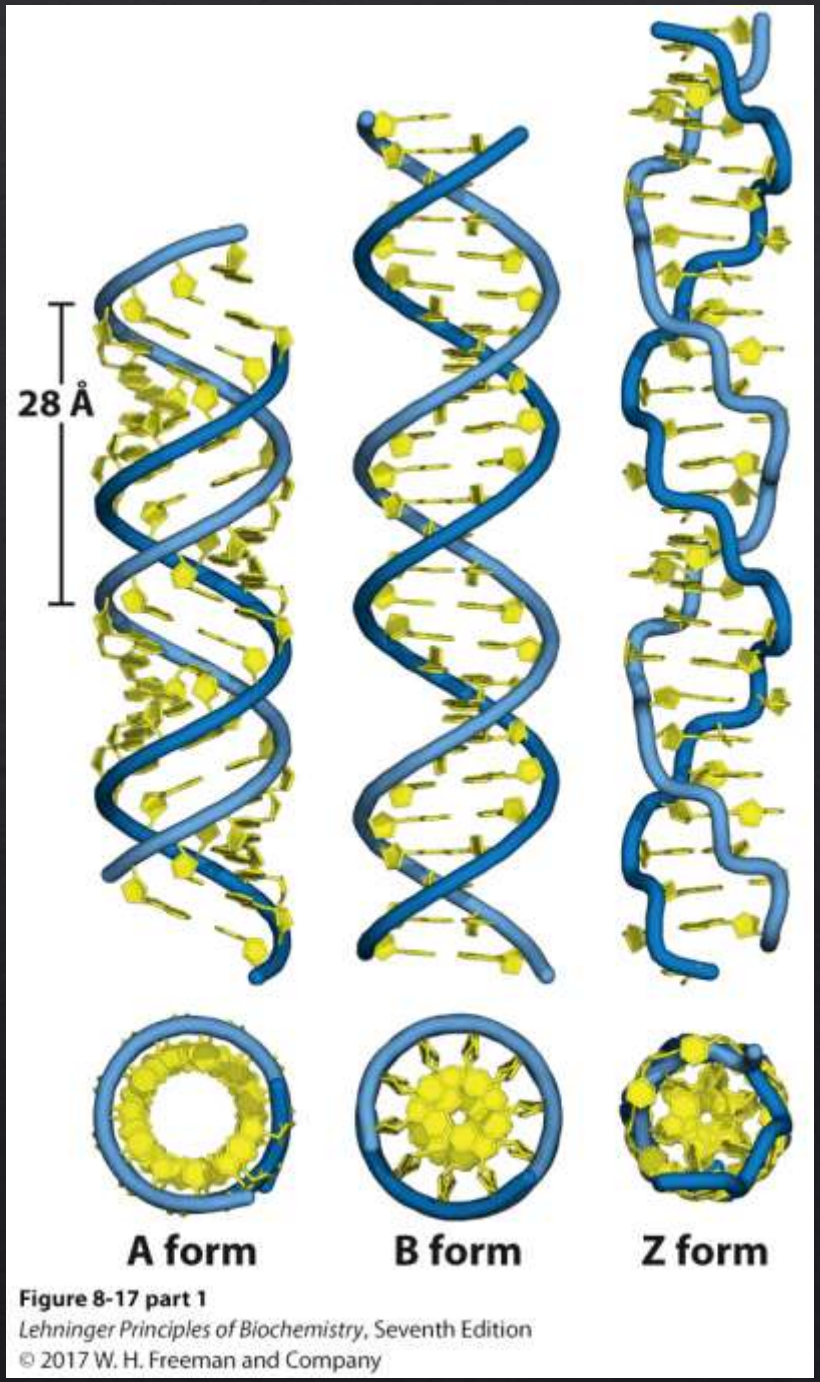


Figure 8-17 part 1
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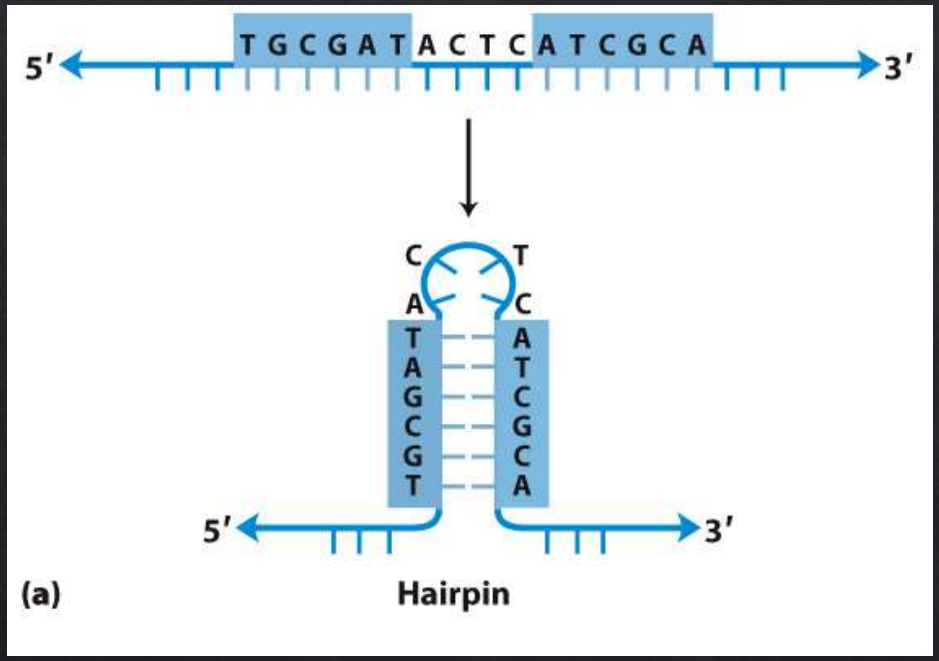
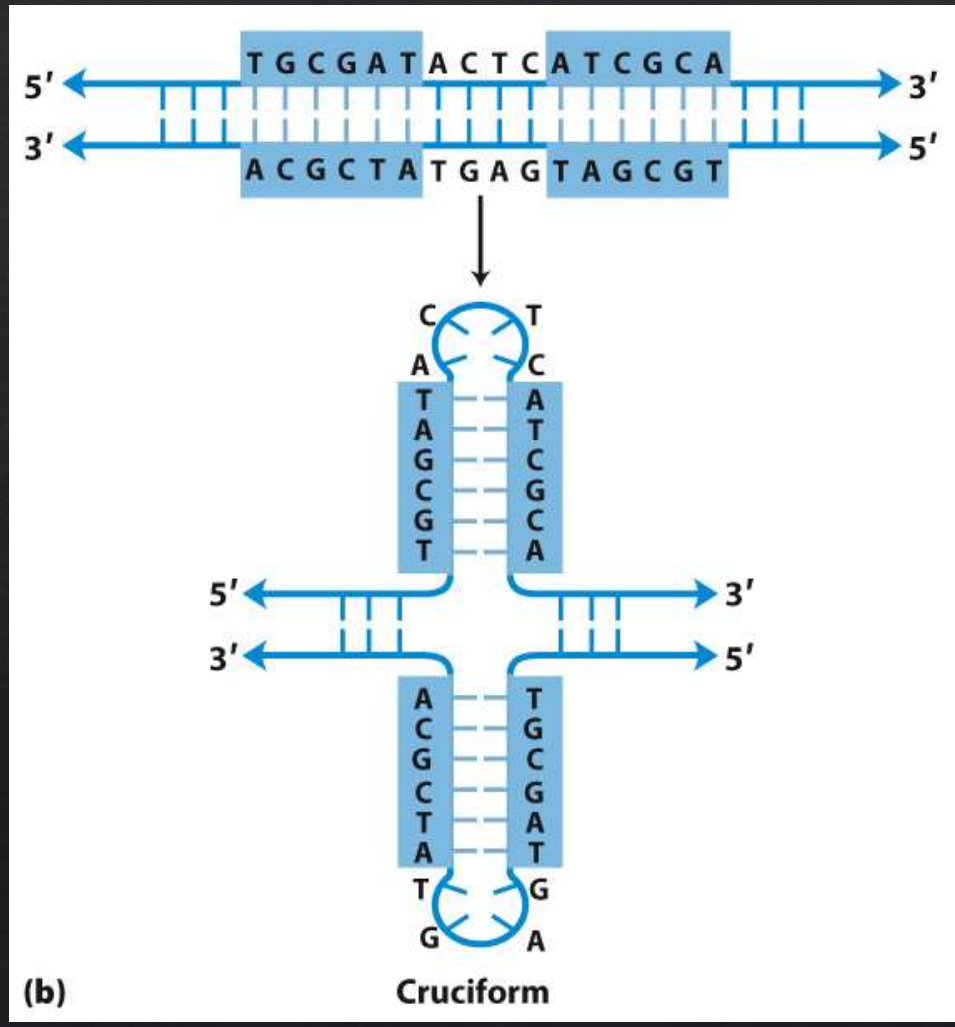
DNA structure





DNA sequences can influence the structure (e.g. palindrome sequences or mirror repeats)

Pictures from Nelson&Cox

DNA replication

- Each strand can work as template (always 5’-3’)
- Extreme pH and temperature can denature DNA
- DNA can anneal again after denaturation

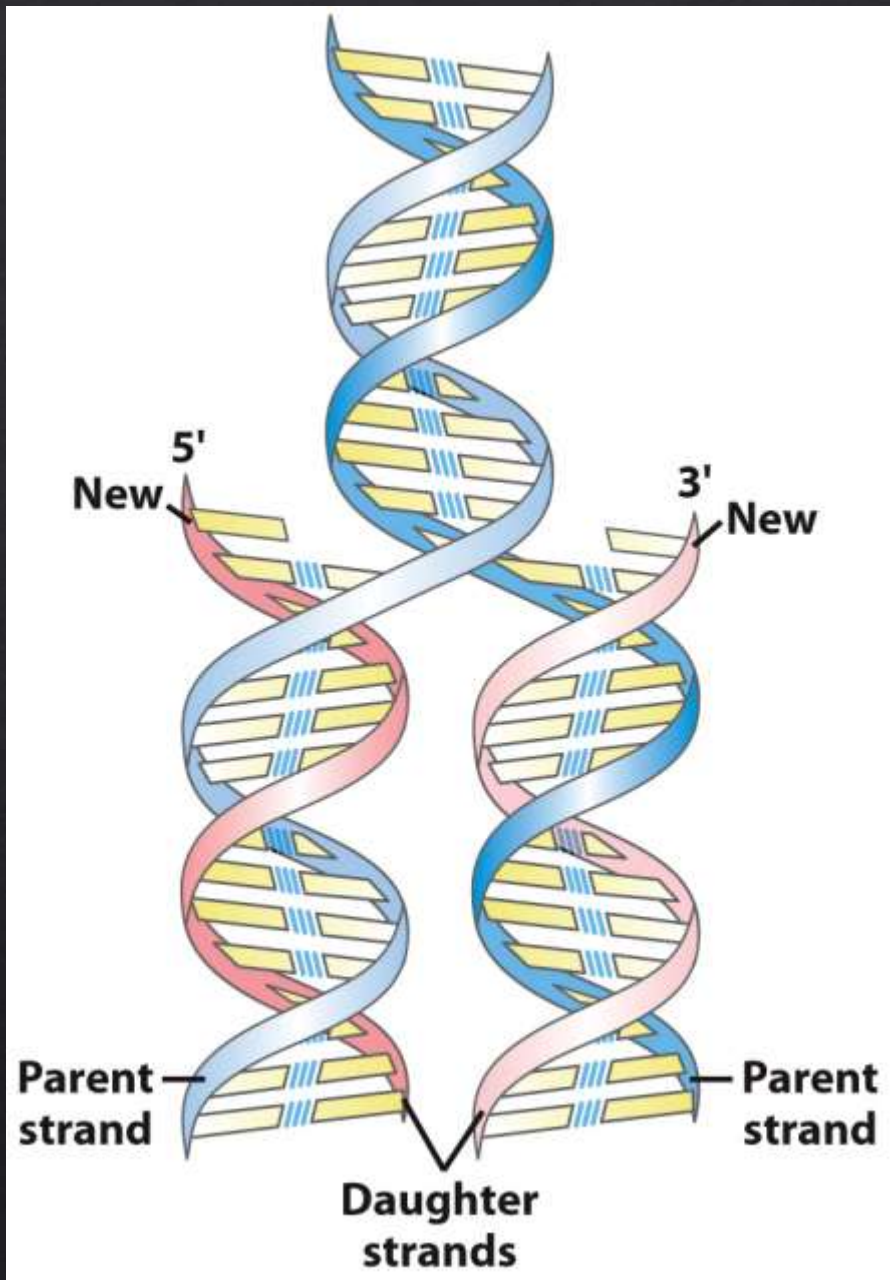


Figure 8-15
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RNA

RNA structure can be more complex

- mRNA
- tRNA
- rRNA
- And more

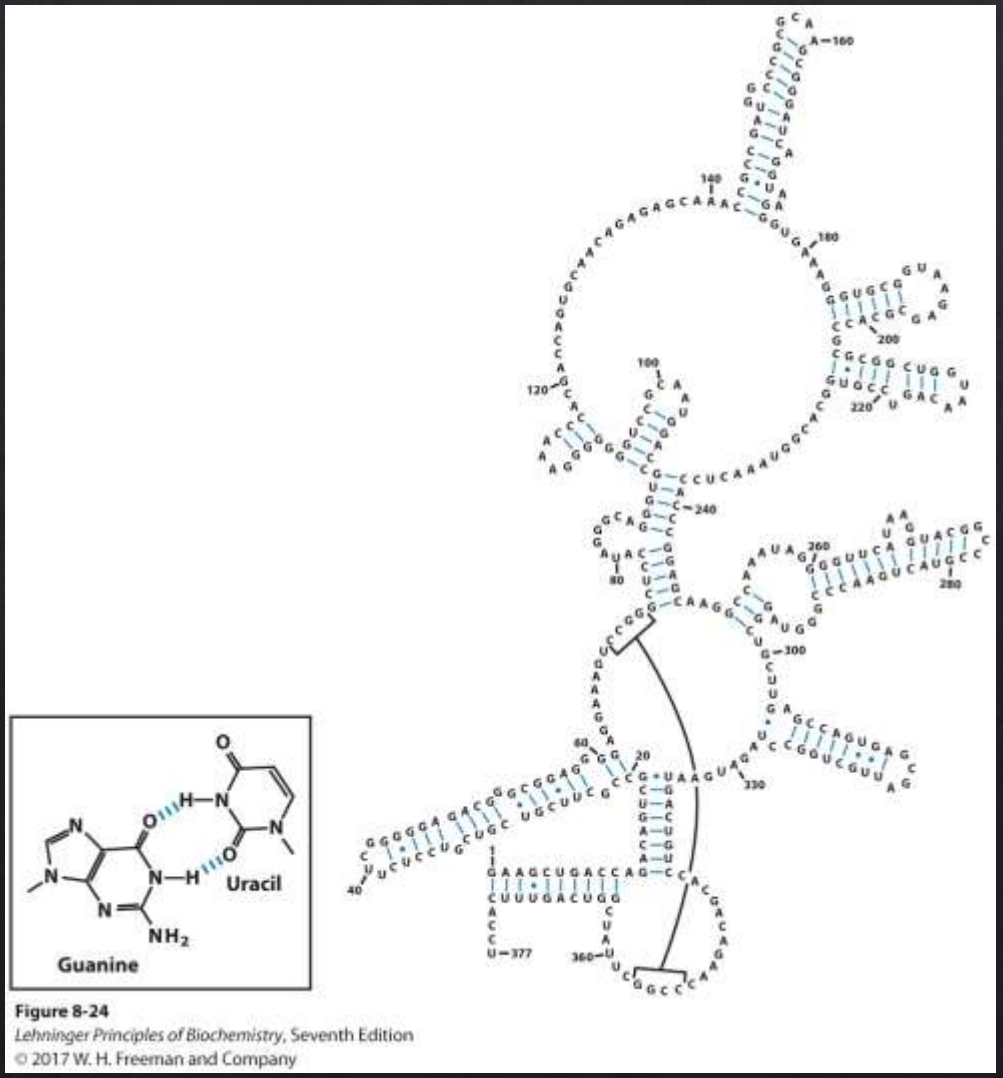

Figure 8-24
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