Carbohydrates and Nucleic Acids

Carbohydrates

- Synthesized by plants using sunlight to convert CO_2 and H_2O to glucose and O_2.
- Polymers include starch and cellulose.
- Starch is storage unit for solar energy.
- Most sugars have formula $C_n(H_2O)_n$, "hydrate of carbon."

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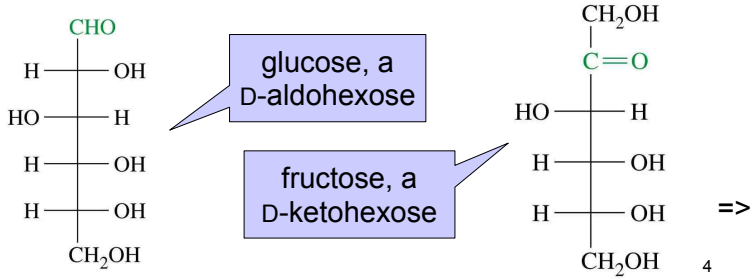
Classification of Carbohydrates

- Monosaccharides or simple sugars
  - ➢polyhydroxyaldehydes or aldoses
  - ➢polyhydroxyketones or ketoses
- Disaccharides can be hydrolyzed to two monosaccharides.
- Polysaccharides hydrolyze to many monosaccharide units. E.g., starch and cellulose have > 1000 glucose units.

=>

Monosaccharides

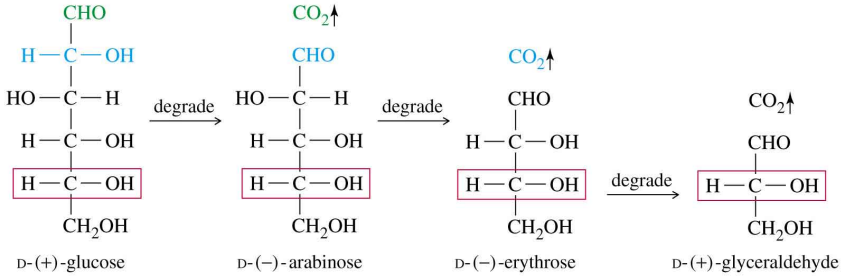
- Classified by:
  - ➢aldose or ketose
  - ➢number of carbons in chain
  - ➢configuration of chiral carbon farthest from the carbonyl group



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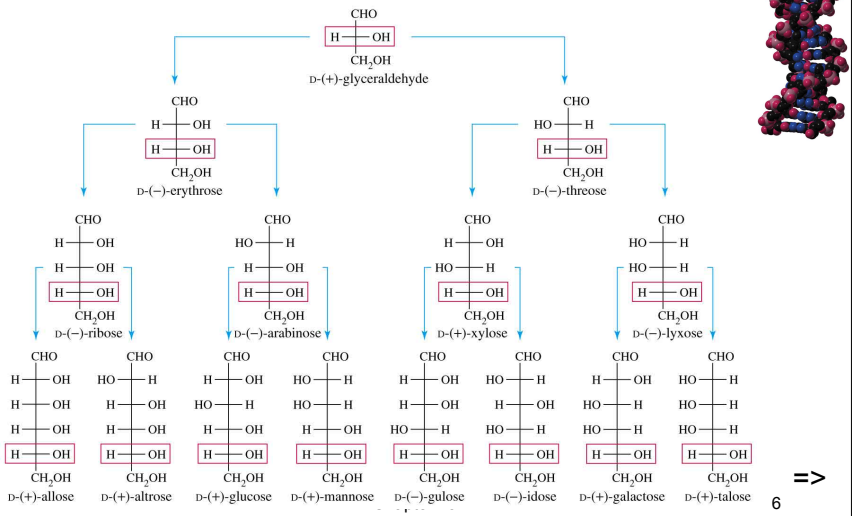
D and L Sugars

- D sugars can be degraded to the dextrorotatory (+) form of glyceraldehyde.
- L sugars can be degraded to the levorotatory (-) form of glyceraldehyde.



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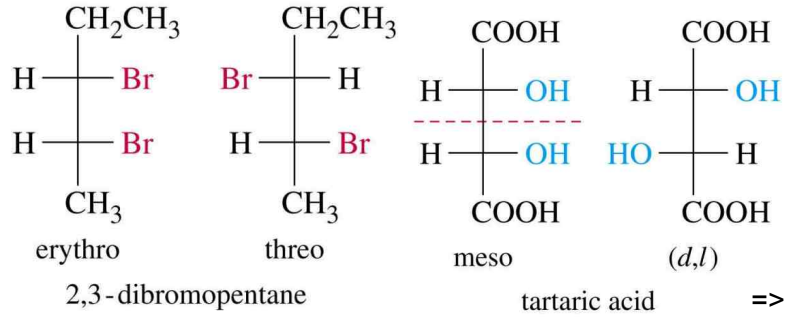
The D Aldose Family



=>

Erythro and Threo

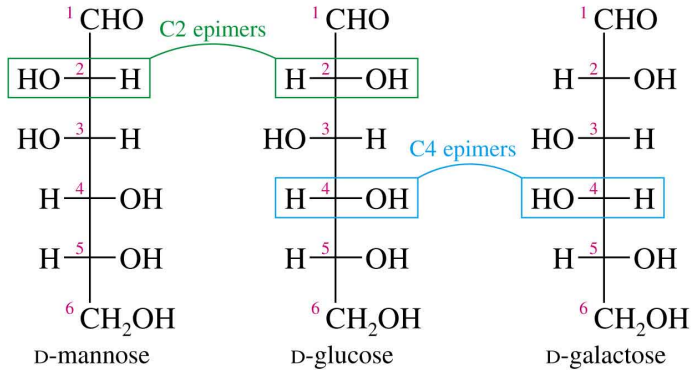
- Terms used for diastereomers with two adjacent chiral C's, without symmetric ends.
- For symmetric molecules, use meso or *d,l*.



=>

Epimers

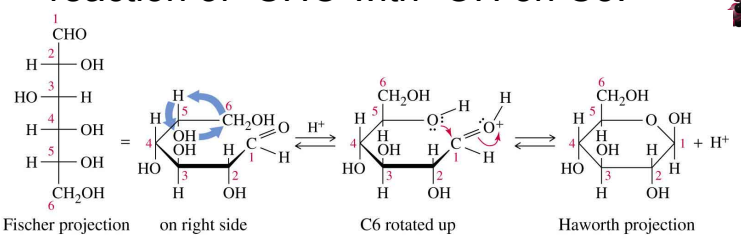
Sugars that differ only in their stereochemistry at a single carbon.



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Cyclic Structure for Glucose

Glucose cyclic hemiacetal formed by reaction of -CHO with -OH on C5.



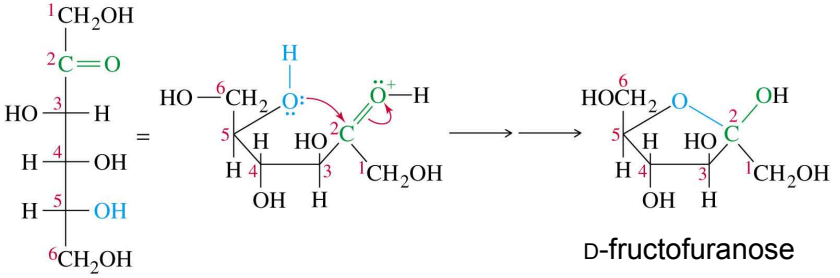


D-glucopyranose

=>

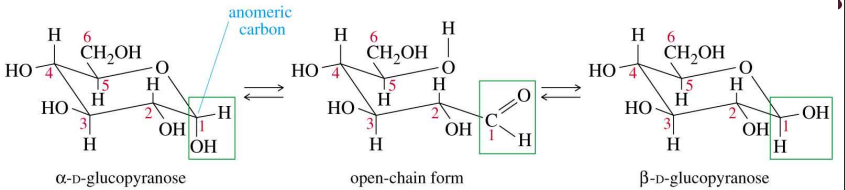
Cyclic Structure for Fructose

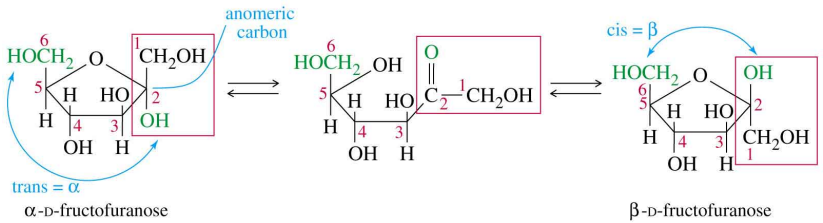
Cyclic hemiacetal formed by reaction of C=O at C2 with -OH at C5.



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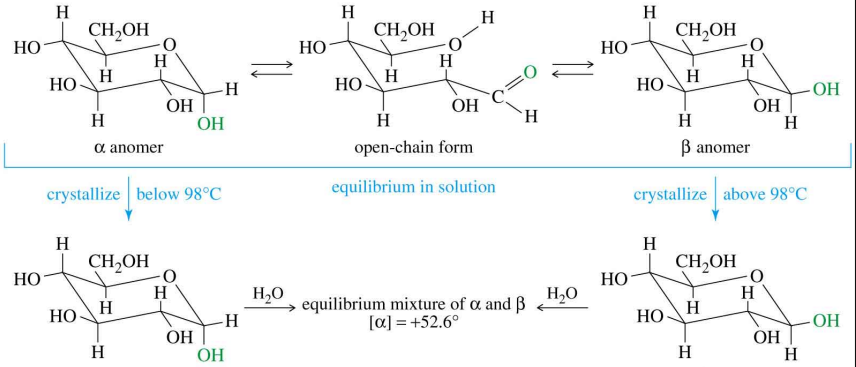
Anomers





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Mutarotation

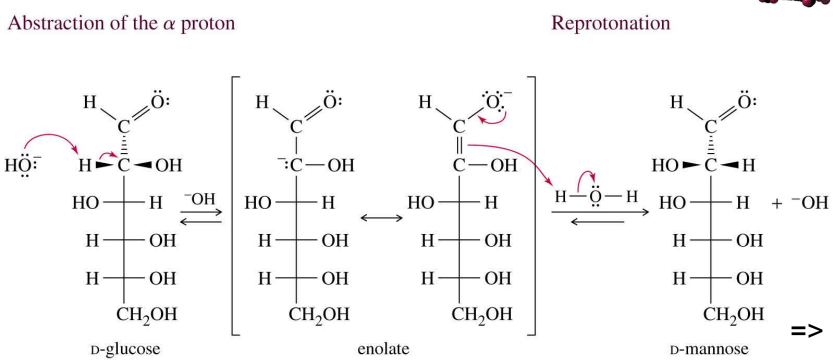


Glucose also called dextrose; dextrorotatory.

=>

Epimerization

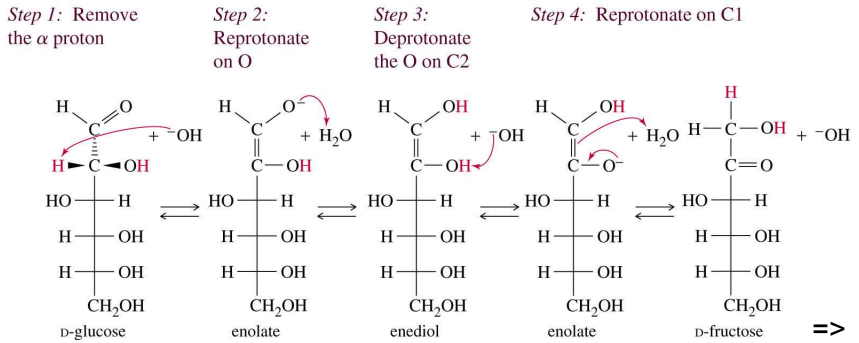
In base, H on C2 may be removed to form enolate ion. Reprotonation may change the stereochemistry of C2.



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Enediol Rearrangement

In base, the position of the C=O can shift. Chemists use acidic or neutral solutions of sugars to preserve their identity.



=>

Reduction of Simple Sugars

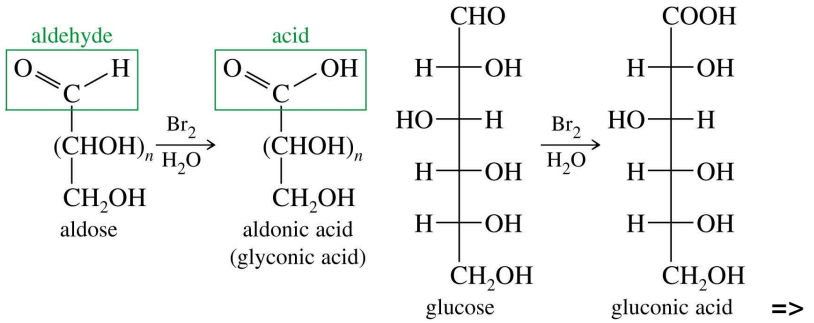
- C=O of aldoses or ketoses can be reduced to C-OH by $NaBH_4$ or H_2/Ni.
- Name the sugar alcohol by adding *-itol* to the root name of the sugar.
- Reduction of D-glucose produces D-glucitol, commonly called D-sorbitol.
- Reduction of D-fructose produces a mixture of D-glucitol and D-mannitol.

=>

Oxidation by Bromine

Bromine water oxidizes aldehyde, but not ketone or alcohol; forms aldonic acid.

Example

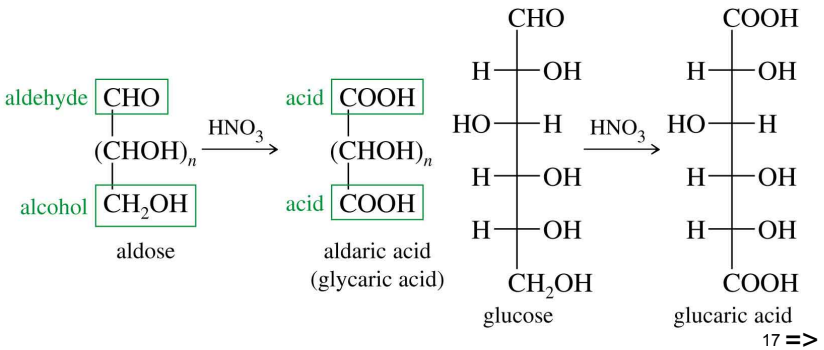


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Oxidation by Nitric Acid

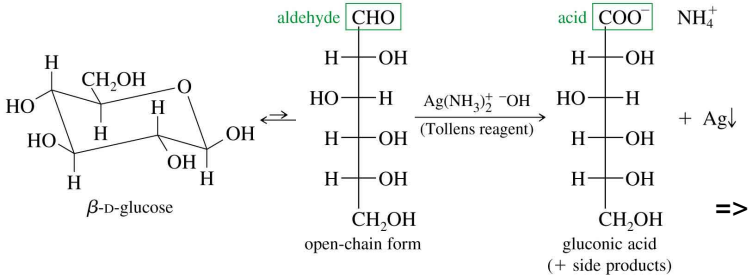
Nitric acid oxidizes the aldehyde and the terminal alcohol; forms aldaric acid.

Example



Oxidation by Tollens Reagent

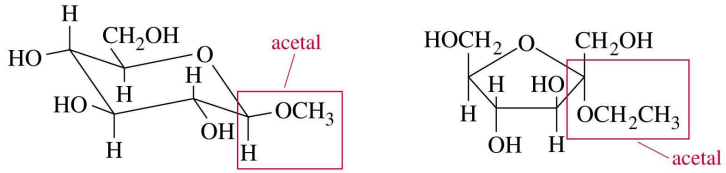
- Tollens reagent reacts with aldehyde, but the base promotes enediol rearrangements, so ketoses react too.
- Sugars that give a silver mirror with Tollens are called reducing sugars.



Nonreducing Sugars

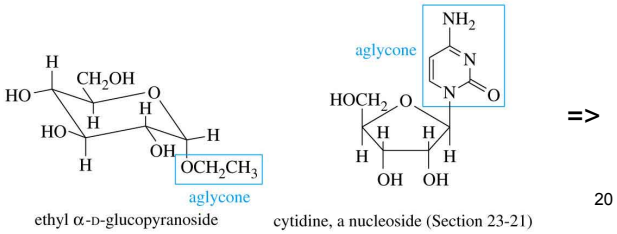
- Glycosides are acetals, stable in base, so they do not react with Tollens reagent.
- Disaccharides and polysaccharides are also acetals, nonreducing sugars.

Examples of nonreducing sugars



Formation of Glycosides

- React the sugar with alcohol in acid.
- Since the open chain sugar is in equilibrium with its α- and β-hemiacetal, both anomers of the acetal are formed.
- Aglycone is the term used for the group bonded to the anomeric carbon.



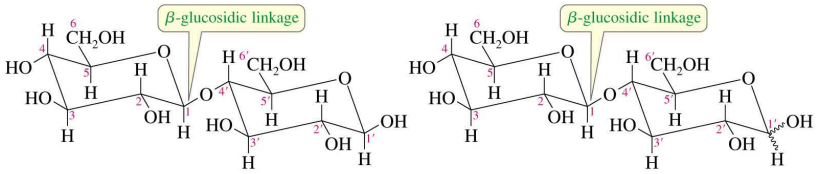
Disaccharides

- Three naturally occurring glycosidic linkages:
- 1-4’ link: The anomeric carbon is bonded to oxygen on C4 of second sugar.
- 1-6’ link: The anomeric carbon is bonded to oxygen on C6 of second sugar.
- 1-1’ link: The anomeric carbons of the two sugars are bonded through an oxygen. =>

Cellobiose

- Two glucose units linked 1-4’.
- Disaccharide of cellulose.
- A mutarotating, reducing sugar.

Cellobiose, 4-O-(β-D-glucopyranosyl)-β-D-glucopyranose or 4-O-(β-D-glucopyranosyl)-D-glucopyranose

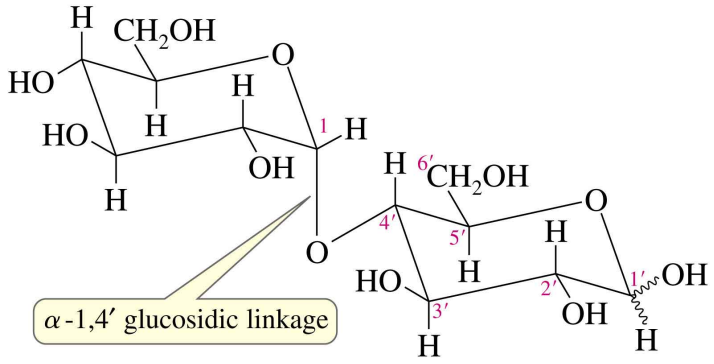


Two alternative ways of drawing and naming cellobiose

Maltose

Two glucose units linked 1-4’.

Maltose, 4-O-(α-D-glucopyranosyl)-D-glucopyranose

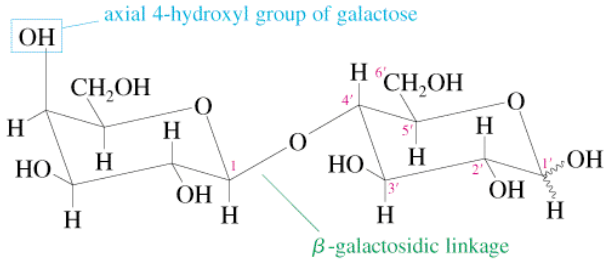


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Lactose

- Galactose + glucose linked 1-4’.
- “Milk sugar.”

Lactose, 4-O-(β-D-galactopyranosyl)-D-glucopyranose

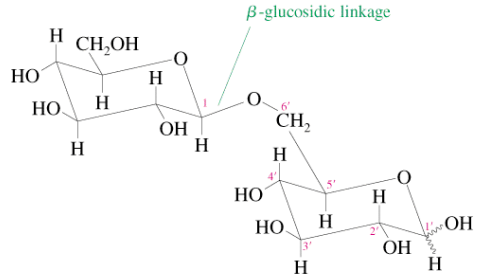


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Gentiobiose

- Two glucose units linked 1-6'.
- Rare for disaccharides, but commonly seen as branch point in carbohydrates.

Gentiobiose, 6-O-(β-D-glucopyranosyl)-D-glucopyranose

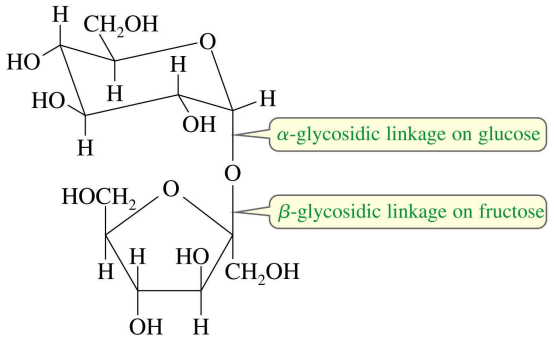


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Sucrose

- Glucose + fructose, linked 1-1'
- Nonreducing sugar

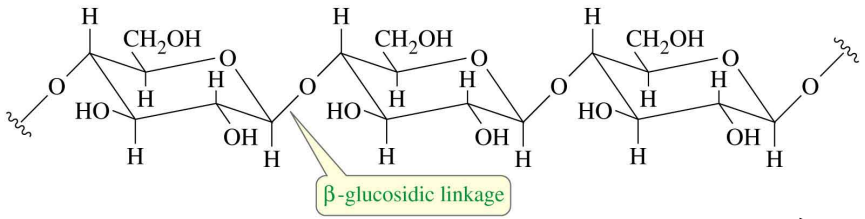
Sucrose, α-D-glucopyranosyl-β-D-fructofuranoside
(or β-D-fructofuranosyl-α-D-glucopyranoside)



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Cellulose

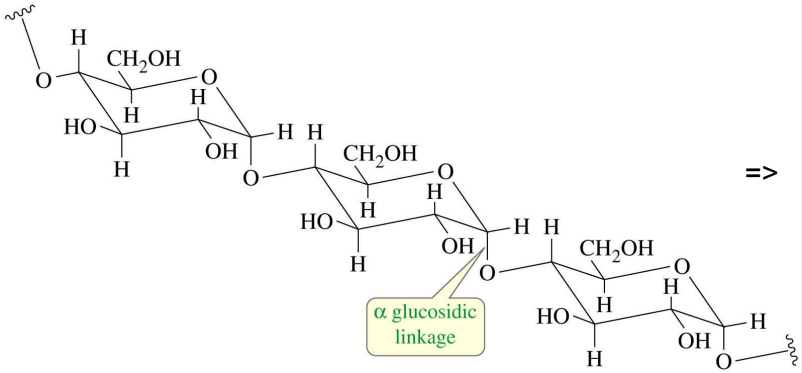
- Polymer of D-glucose, found in plants.
- Mammals lack the β-glycosidase enzyme.



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Amylose

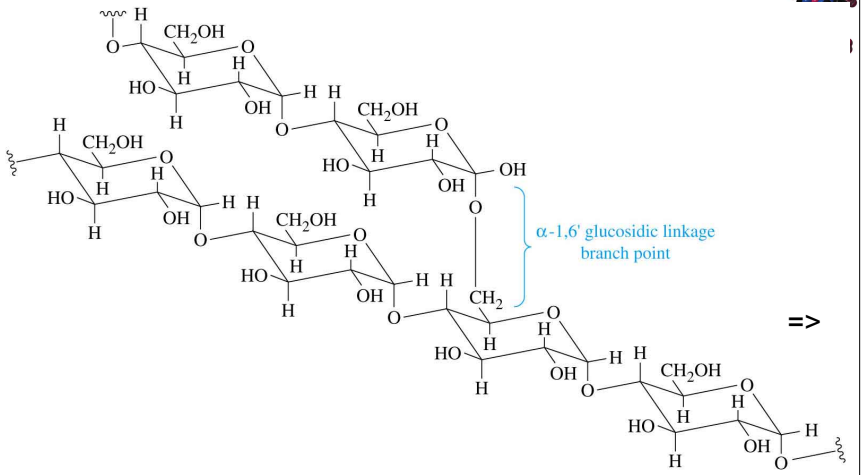
- Soluble starch, polymer of D-glucose.
- Starch-iodide complex, deep blue.



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Amylopectin

Branched, insoluble fraction of starch.



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Glycogen

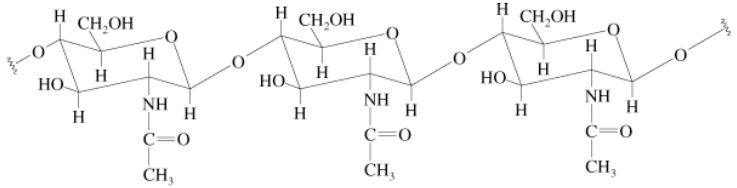
- Glucose polymer, similar to amylopectin, but even more highly branched.
- Energy storage in muscle tissue and liver.
- The many branched ends provide a quick means of putting glucose into the blood.

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Chitin

- Polymer of *N*-acetylglucosamine.
- Exoskeleton of insects.

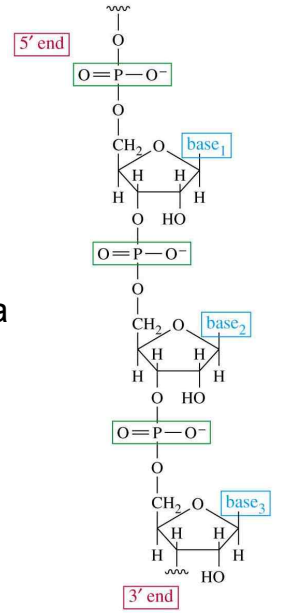
Chitin, or poly(1.4'-O-β-2-acetamido-2-deoxy-D-glucopyranoside), a β-1,4-linked polymer of N-acetylglucosamine



=>

Nucleic Acids

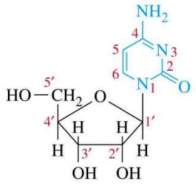
- Polymer of ribofuranoside rings linked by phosphate ester groups.
- Each ribose is bonded to a base.
- Ribonucleic acid (RNA)
- Deoxyribonucleic acid (DNA)

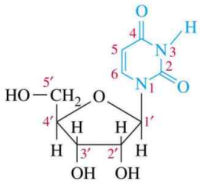


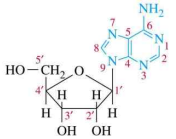
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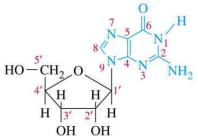
Ribonucleosides

A β-D-ribofuranoside bonded to a heterocyclic base at the anomeric carbon.


cytidine (C)


uridine (U)

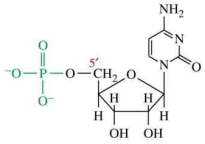

adenosine (A)

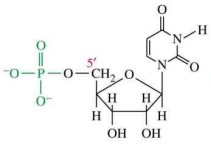

guanosine (G)

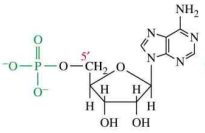
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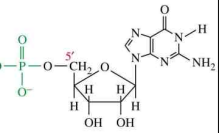
Ribonucleotides

Add phosphate at 5' carbon.

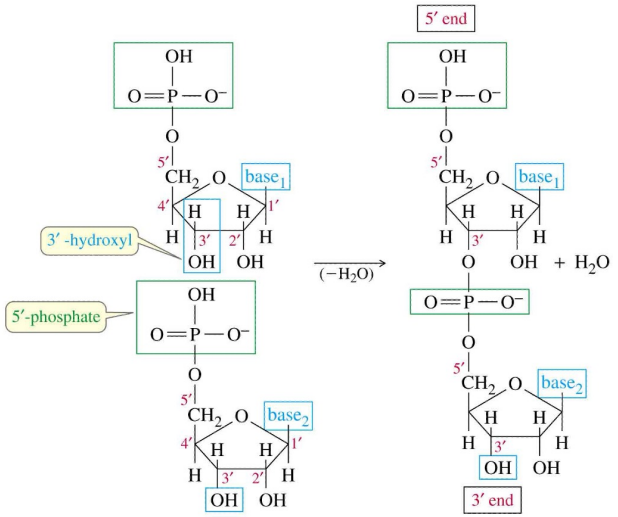

cytidine monophosphate, CMP (cytidylic acid)


uridine monophosphate, UMP (uridylic acid)


adenosine monophosphate, AMP (adenylic acid)


guanosine monophosphate, GMP (guanidylic acid)

Structure of RNA



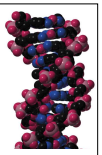
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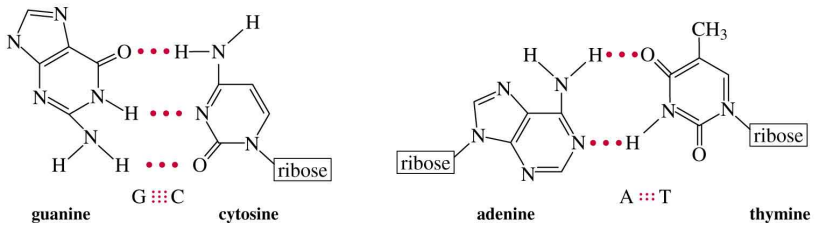
Structure of DNA

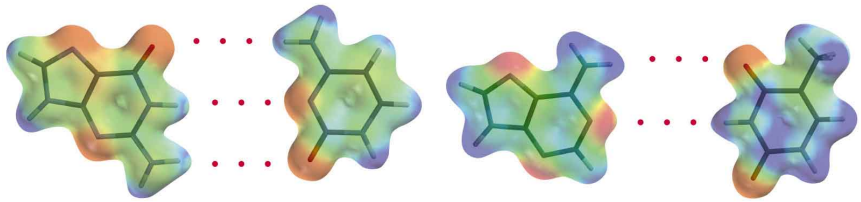
- β-D-2-deoxyribofuranose is the sugar.
- Heterocyclic bases are cytosine, thymine (instead of uracil), adenine, and guanine.
- Linked by phosphate ester groups to form the primary structure.

=>

Base Pairings

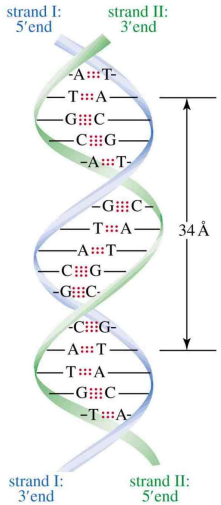


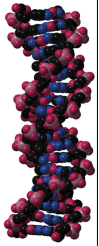




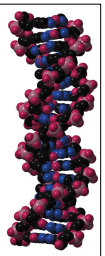
Double Helix of DNA

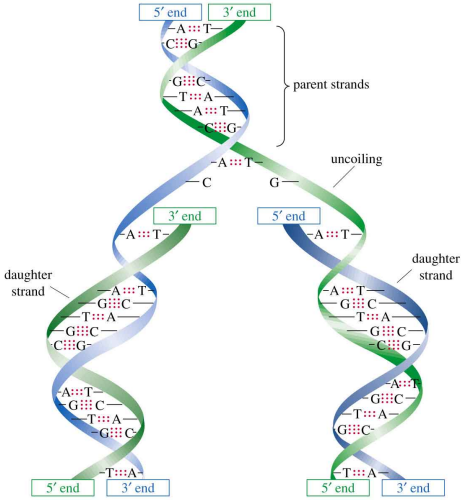
- Two complementary polynucleotide chains are coiled into a helix.
- Described by Watson and Crick, 1953.





DNA Replication





Amino Acids, Peptides, and Proteins



Proteins

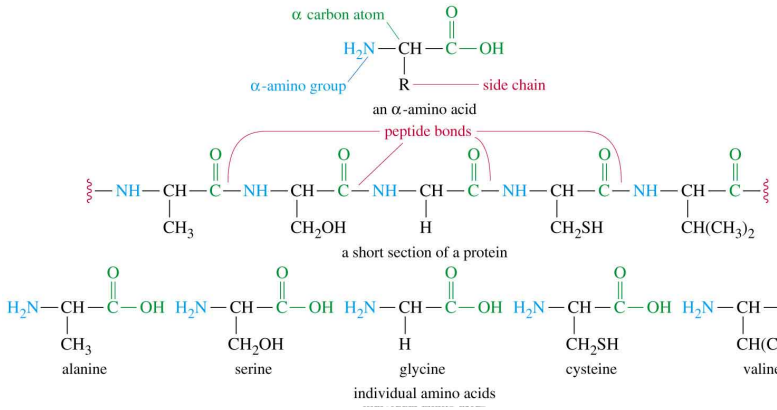


- Biopolymers of α-amino acids.
- Amino acids are joined by peptide bond.
- Variety of functions:
  - ➢structure
  - ➢enzymes
  - ➢transport
  - ➢protection
  - ➢hormones

=>

Structure of Proteins





=>

Amino Acids

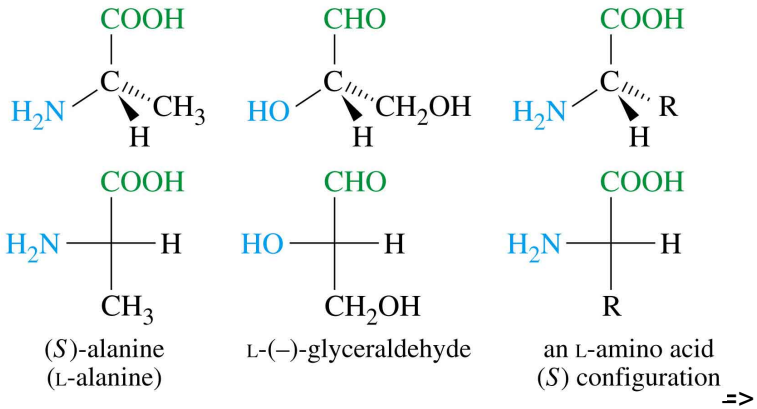


- -NH_2 on the carbon next to -COOH.
- Glycine, NH_2-CH_2-COOH, is simplest.
- With -R side chain, molecule is chiral.
- Most natural amino acids are L-amino acids, related to L-(-)-glyceraldehyde.
- Direction of optical rotation, (+) or (-), must be determined experimentally.

=>

Stereochemistry of α-Amino Acids





=>

Standard Amino Acids



- Twenty standard α-amino acids.
- Differ in side-chain characteristics:
  - ➢ -H or alkyl
  - ➢contains an -OH
  - ➢contains sulfur
  - ➢contains a nonbasic nitrogen
  - ➢has -COOH
  - ➢has a basic nitrogen

=>

Essential Amino Acids



- Arginine (Arg)
- Threonine (Thr)
- Lysine (Lys)
- Valine (Val)
- Phenylalanine (Phe)
- Tryptophan (Trp)
- Methionine (Met)
- Histidine (His)
- Leucine (Leu)
- Isoleucine (Ile)

=>

Complete Proteins



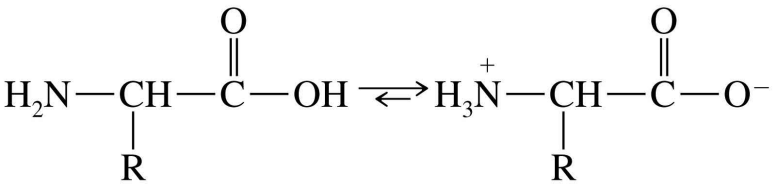
- Provide all the essential amino acids.
- Examples: those in meat, fish, milk, eggs.
- Plant proteins are generally incomplete.
- Vegetarians should eat many different kinds of plants, or supplement diet with milk or eggs.

=>

Zwitterion



- Amino acid exists as a dipolar ion.
- -COOH loses H^+, $-NH_2$ gains H^+.



uncharged structure (minor component)

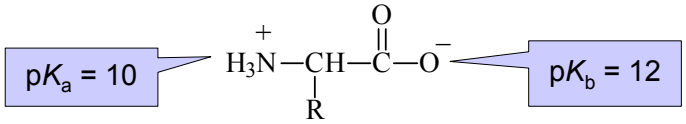
dipolar ion, or zwitterion (major component)

- Actual structure depends on pH.

=>

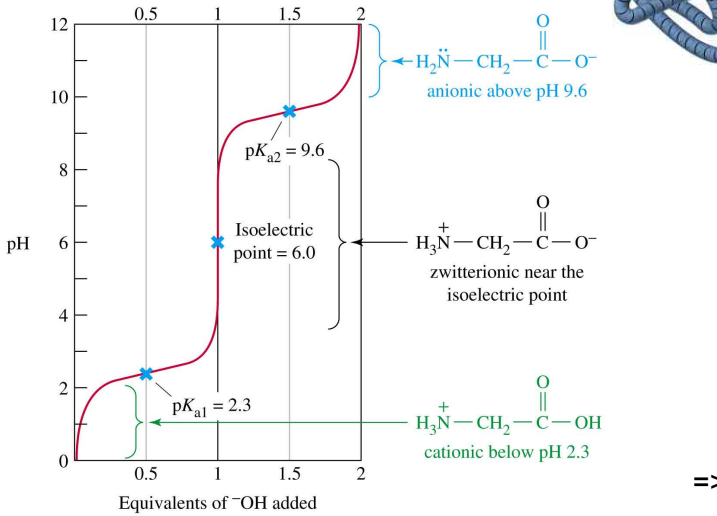
Properties of Amino Acids

- High melting points, over 200°C
- More soluble in water than in ether.
- Larger dipole moments than simple acids or simple amines.
- Less acidic than most carboxylic acids, less basic than most amines.



=>

Structure and pH



=>

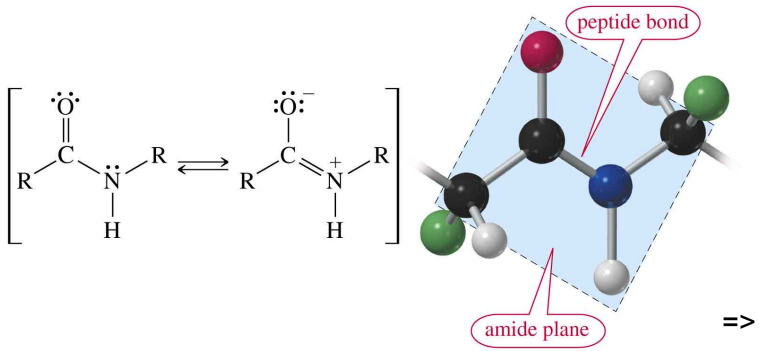
Isoelectric Point

- pH at which amino acids exist as the zwitterion (neutral).
- Depends on structure of the side chain.
- Acidic amino acids, isoelectric pH ~3.
- Basic amino acids, isoelectric pH ~9.
- Neutral amino acids, isoelectric pH is slightly acidic, 5-6.

=>

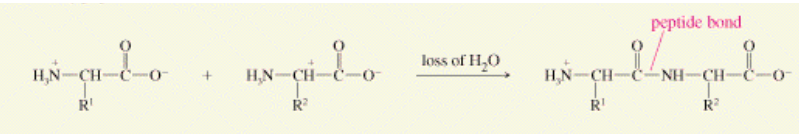
Structure of Peptide

- The peptide bond is an amide bond.
- Amides are very stable and neutral.



=>

Peptide Bond Formation



- The amino group of one molecule condenses with the acid group of another.
- Polypeptides usually have molecular weight less than 5000.
- Protein molecular weight 6000-40,000,000.

=>

Classification of Proteins

- Simple: hydrolyze to amino acids only.
- Conjugated: bonded to a nonprotein group, such as sugar, nucleic acid, or lipid.
- Fibrous: long, stringy filaments, insoluble in water, function as structure.
- Globular: folded into spherical shape, function as enzymes, hormones, or transport proteins.

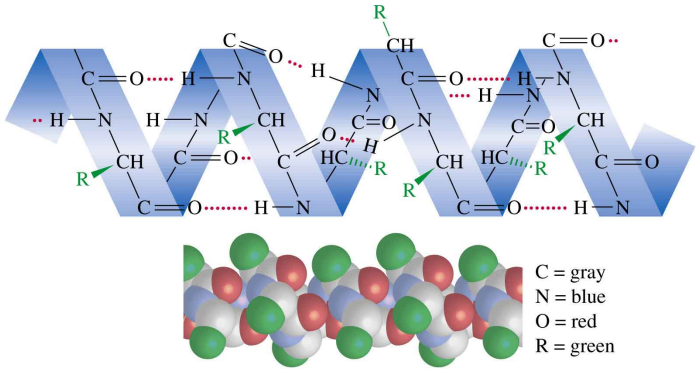
=>

Levels of Protein Structure

- Primary: the sequence of the amino acids in the chain and the disulfide links.
- Secondary: structure formed by hydrogen bonding. Examples are α-helix and pleated sheet.
- Tertiary: complete 3-D conformation.
- Quaternary: association of two or more peptide chains to form protein. =>

Alpha Helix

Each carbonyl oxygen can hydrogen bond with an N-H hydrogen on the next turn of the coil.

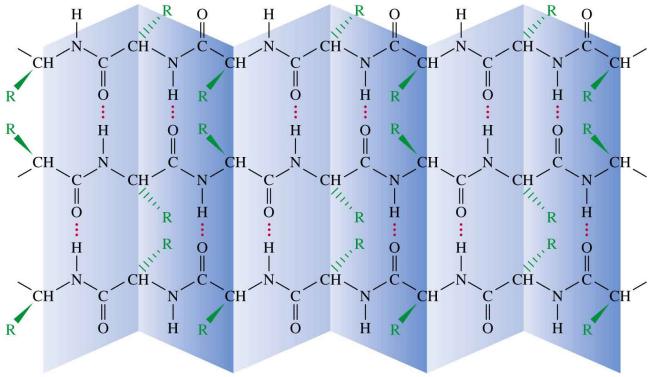


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Pleated Sheet



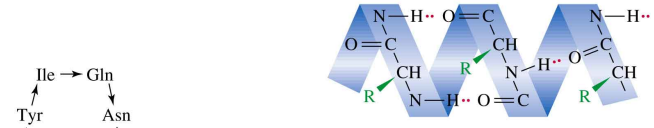
Each carbonyl oxygen hydrogen bonds with an N-H hydrogen on an adjacent peptide chain.



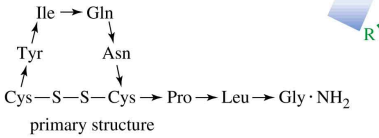
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Summary of Structure

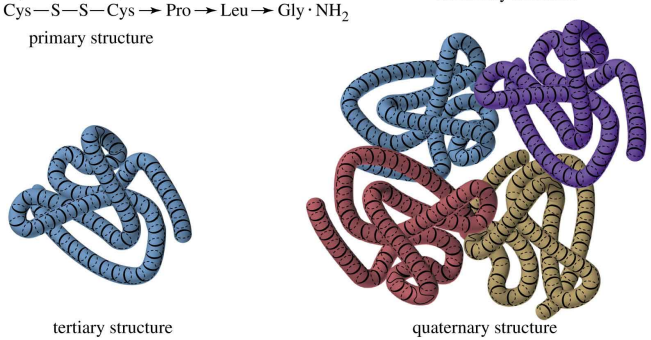




secondary structure



primary structure



tertiary structure

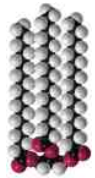
quaternary structure

=>

Lipids



Introduction

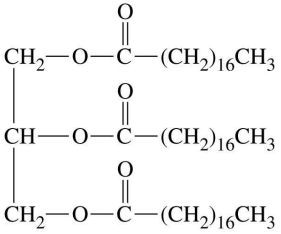


- Classified by solubility, not structure.
- Can be extracted from cells by nonpolar organic solvents.
- Complex lipids are easily hydrolyzed.
  - ➢Waxes
  - ➢Triglycerides
- Simple lipids are not easily hydrolyzed.
  - ➢Steroids
  - ➢Prostaglandins
  - ➢Terpenes

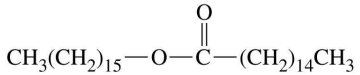
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Examples of Lipids

Examples of complex lipids

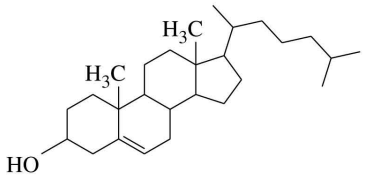


tristearin, a fat



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.
- Spermaceti is found in the head of the sperm whale and is probably used to control buoyancy.
- Most natural waxes are protective coats for plants' leaves, insects' exoskeleton, mammals' fur, and birds' feathers. =>

Triglycerides

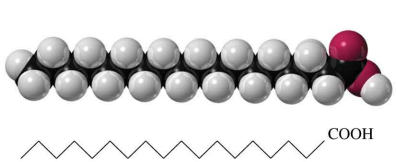
- Fatty acid esters of glycerol.
- Fats
  - ➢Solid at room temperature
  - ➢Most are derived from mammals
- Oils
  - ➢Liquid at room temperature
  - ➢Most are derived from plants or cold-blooded animals. =>

Fatty Acids

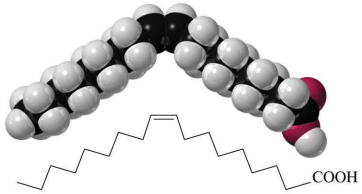
- Unbranched carboxylic acids with 12-20 carbons.
- Most contain an even number of carbons because they are built from acetic acid units.
- Melting points increase with increasing molecular weights.
- Unsaturation greatly lowers the melting point. =>

Melting Points

- A cis double bond bends the molecule so it cannot pack efficiently.
- A trans double bond has less effect.



stearic acid, mp 70°C

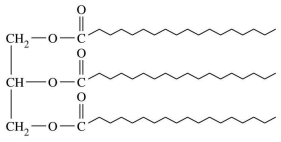


oleic acid, mp 4°C

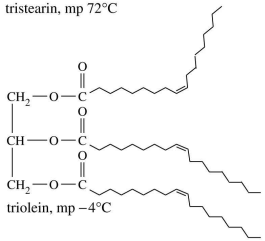
=>

Fats and Oils

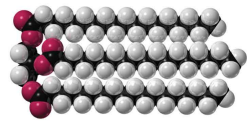
- Most fats have saturated fatty acids.
- Most oils have unsaturated fatty acids.

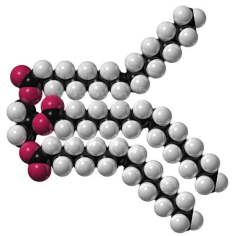


tristearin, mp 72°C



triolein, mp −4°C

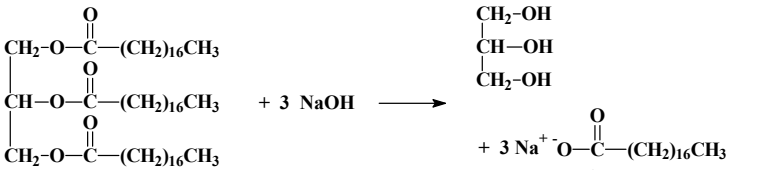




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Saponification

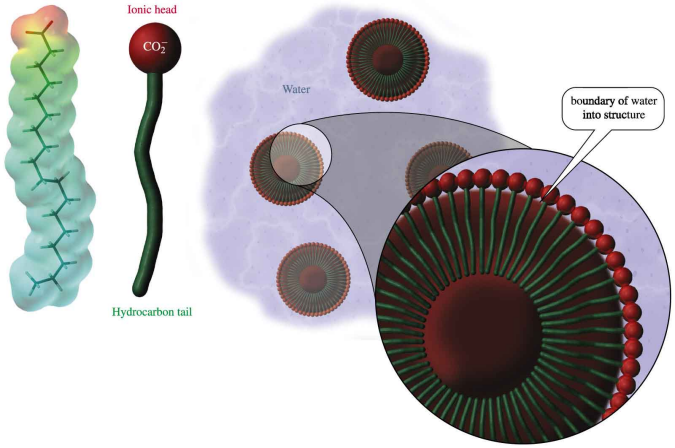
- “Soap-making”
- Base-catalyzed hydrolysis of ester linkages in fats and oils.



A soap

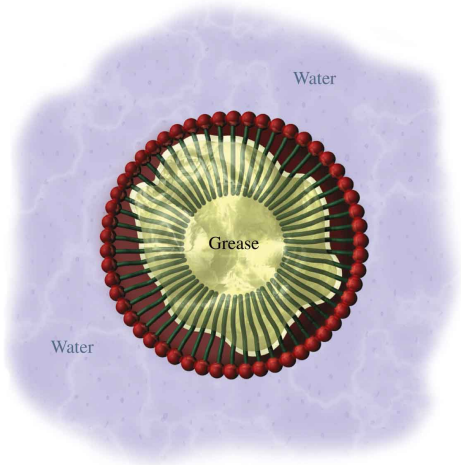
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Soap Structure



=>

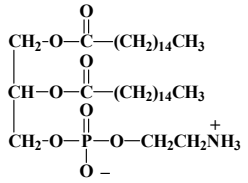
Grease in Soap Solution



=>

Phospholipids

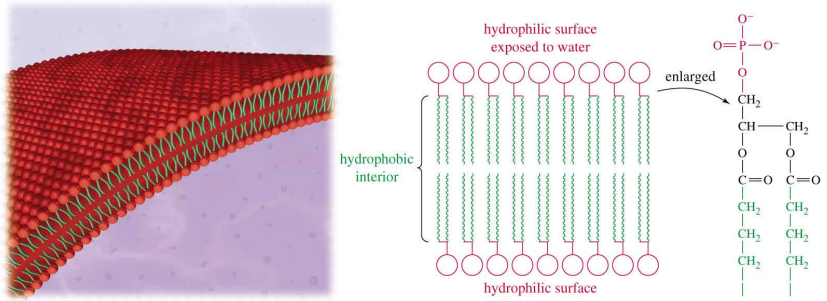
- Contain a phosphate ester bond.
- Phosphoglycerides usually have one phosphoric acid group and two fatty acids.
- The phosphate may have an additional alcohol attached by an ester linkage.



=>

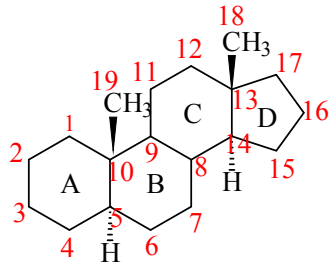
Lipid Bilayer

Cell membranes are a bilayer of phosphoglycerides



 =>

Steroids

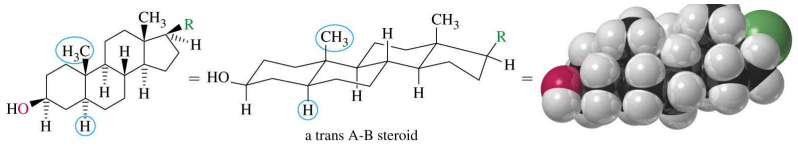


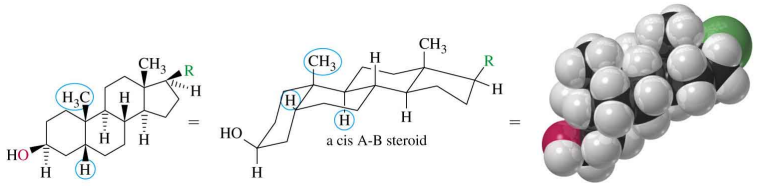
- Polycyclic, usually all *trans*.
- Common structural features:
  - ➢=O or -OH at C3
  - ➢Side chain at C17
  - ➢Double bond from C5 to either C4 or C6.

=>

A-B Ring Junction

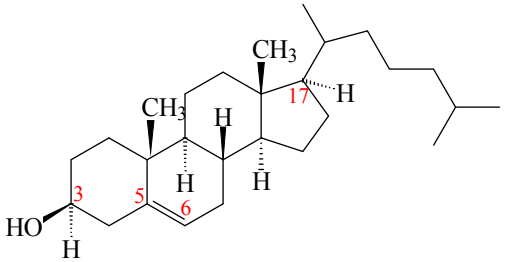
May be cis, but usually is trans.





=>

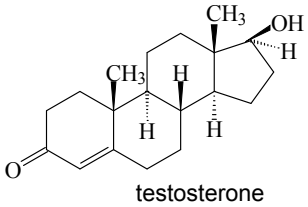
Cholesterol



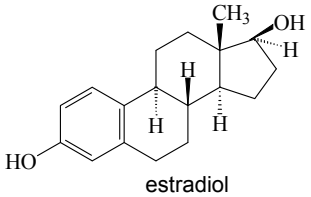
- Common biological intermediate.
- Probably a precursor to other steroids.
- Side chain at C17 and double bond C5-C6.

=>

Sex Hormones



testosterone



estradiol

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

=>

Prostaglandins

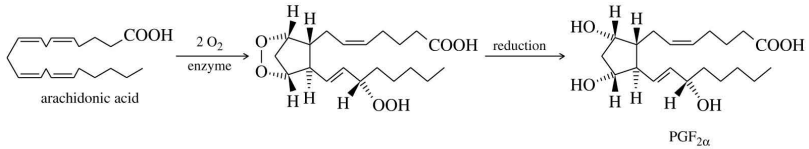
- Biochemical regulators more powerful than steroids.
- Regulate functions such as:
  - ➢Blood pressure
  - ➢Blood clotting
  - ➢Allergic response
  - ➢Digestive activity
  - ➢Labor onset

=>

Structure of Prostaglandins



- Cyclopentane ring with two long side chains trans to each other.
- Most have 20 carbon atoms.
- Derived from arachidonic acid.



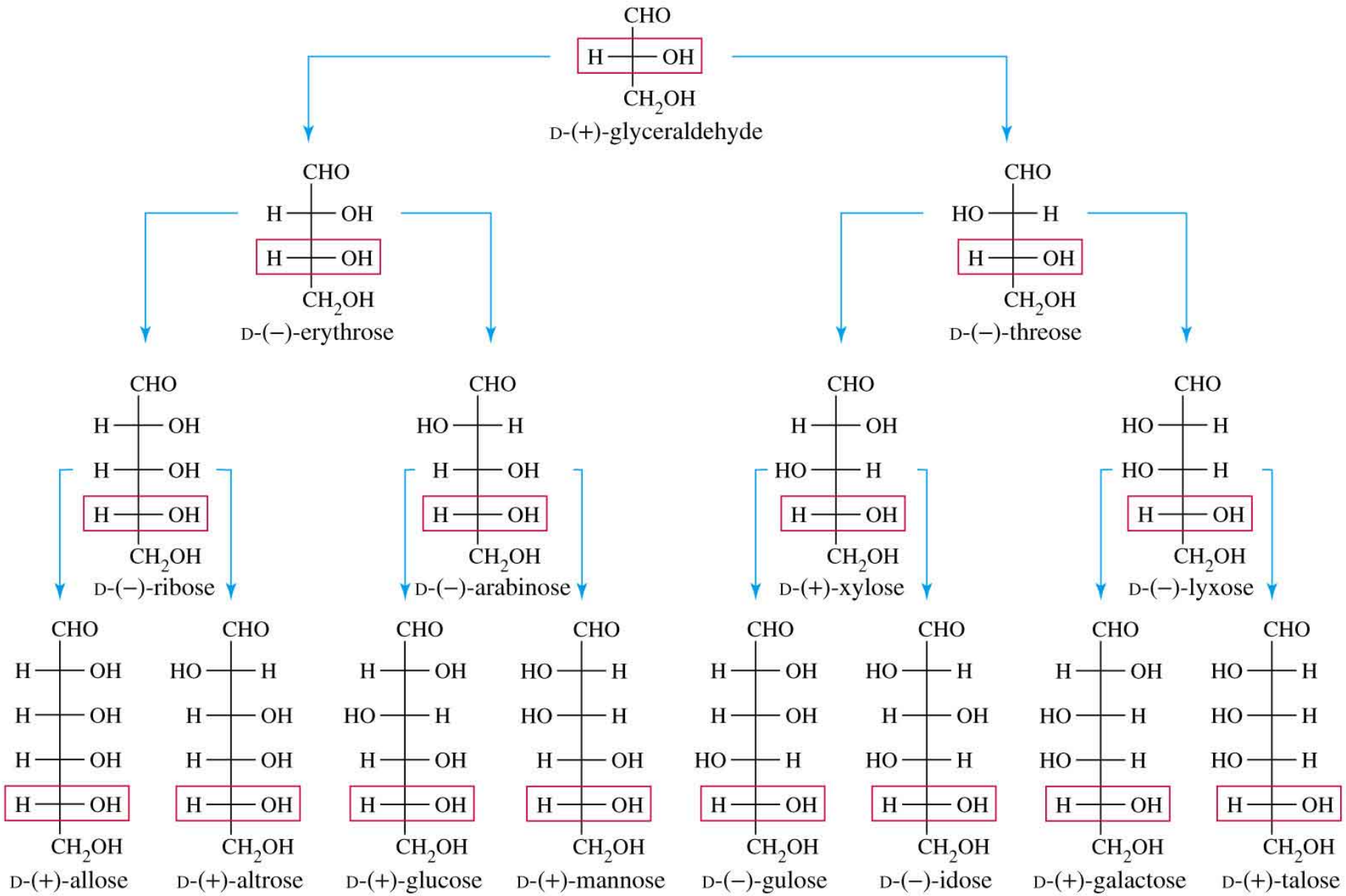
arachidonic acid

$PGF_{2\alpha}$

=>

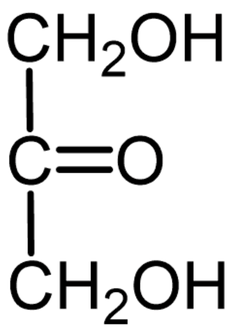
The D Aldose Family



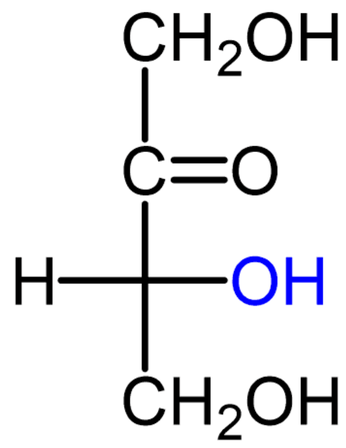


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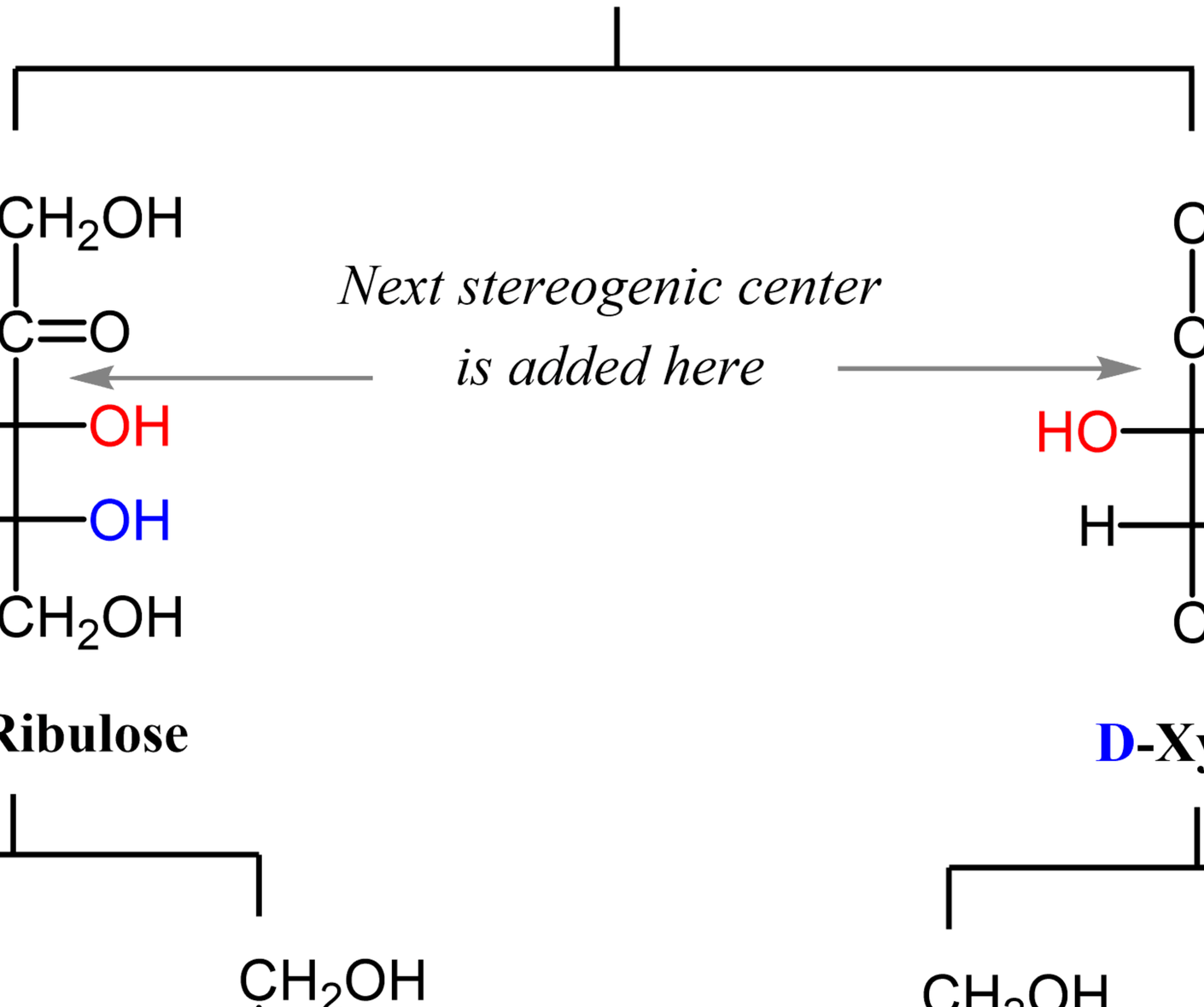
The family of D-ketoses



Dihydroxyacetone

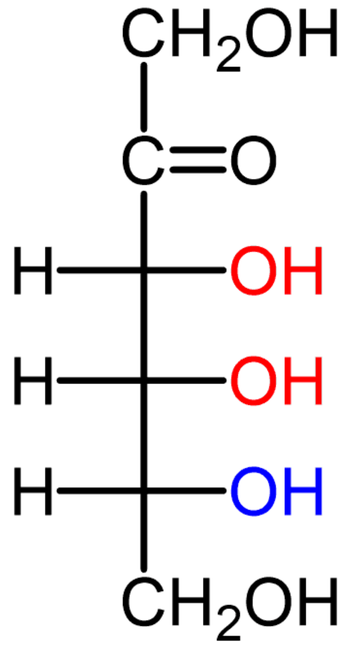


D-Erythrulose

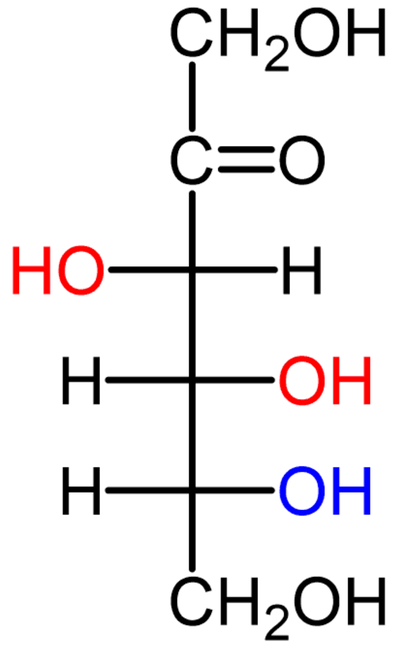


D-Ribulose

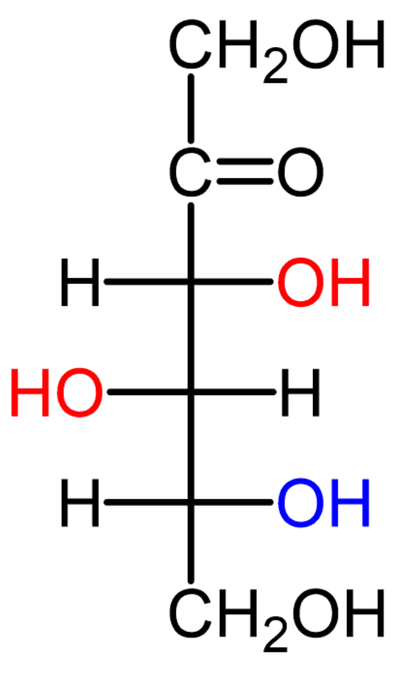
D-Xylulose



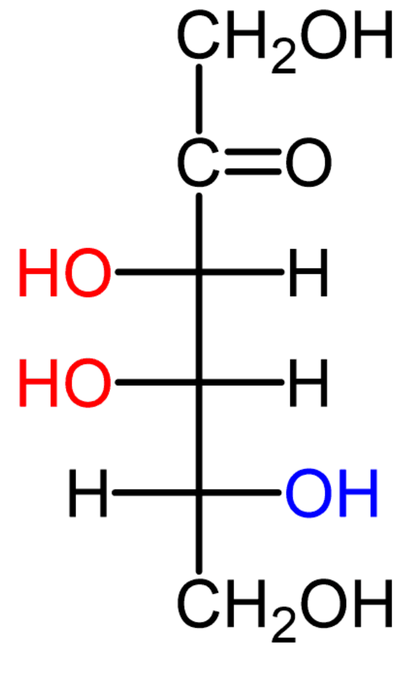
D-Psicose



D-Fructose



D-Sorbose



D-Tagatose

Each chiral center is added below the carbonyl group generating two additional stereoisomers.