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Biopolymers

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biopolymers

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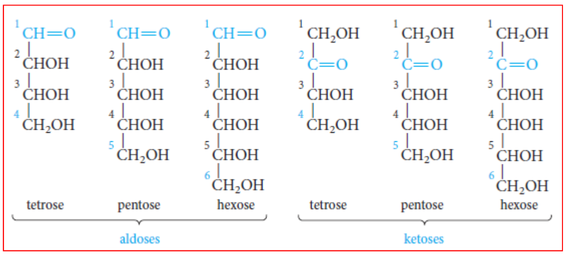
POLYSACCHARIDES

- The word ***carbohydrate*** can be expressed as *hydrates of carbon* because molecular formulas of these compounds.
  Example; Glucose has the molecular formula $C_6H_{12}O_6$, which might be written as $C_6(H_2O)_6$.
- ***Carbohydrates*** are polyhydroxyaldehydes, polyhydroxyketones, or substances that give such compounds on hydrolysis.
- The chemistry of ***carbohydrates*** is mainly the combined chemistry of two functional groups: the hydroxyl group and the carbonyl group.
- ***Carbohydrates*** are usually classified according to their structure as monosaccharides, oligosaccharides, or polysaccharides.
- The term ***saccharide*** comes from Latin (*saccharum,* sugar) and refers to the sweet taste of some simple carbohydrates.
- The three classes of carbohydrates are related to each other through hydrolysis.

$$\text{polysaccharide} \xrightarrow[H^+]{H_2O} \text{oligosaccharides} \xrightarrow[H^+]{H_2O} \text{monosaccharides}$$

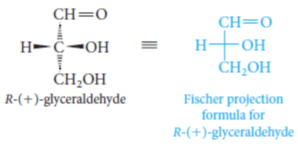
$$\underset{\substack{\text{starch} \\ \text{(a polysaccharide)}}}{[C_{12}H_{20}O_{10}]_n} \xrightarrow[H^+]{n\,H_2O} \underset{\substack{\text{maltose} \\ \text{(a disaccharide)}}}{n\,C_{12}H_{22}O_{11}} \xrightarrow[H^+]{n\,H_2O} \underset{\substack{\text{glucose} \\ \text{(a monosaccharide)}}}{2n\,C_6H_{12}O_6}$$

- ***Monosaccharides*** (or simple sugars, as they are sometimes called) are carbohydrates that cannot be hydrolyzed to simpler compounds.

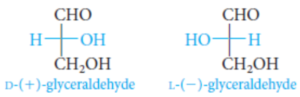


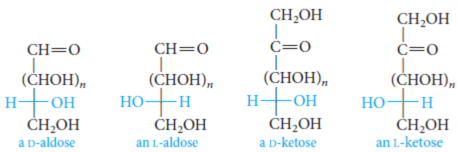
- ***Polysaccharides*** contain many monosaccharide units—sometimes hundreds or even thousands. Usually, but not always, the units are identical.
  Example; starch and cellulose, contain linked units of the same monosaccharide, glucose.
- ***Oligosaccharides*** (from the Greek *oligos,* few) contain at least two and generally no more than a few linked monosaccharide units. They may be called **disaccharides**, **trisaccharides**, and so on, depending on the number of units, which may be the same or different.
  Example; Maltose is a disaccharide made of two glucose units.
  Sucrose is made of two different monosaccharide units: glucose and fructose.

Chirality in Monosaccharides; Fischer Projection Formulas and D,L-Sugars



- He used a small capital d to represent the configuration of (+)-glyceraldehyde, with the hydroxyl group on the *right;* its enantiomer, with the hydroxyl group on the *left,* was designated L-(2)-glyceraldehyde.
  The most oxidized carbon (CHO) was placed at the top.





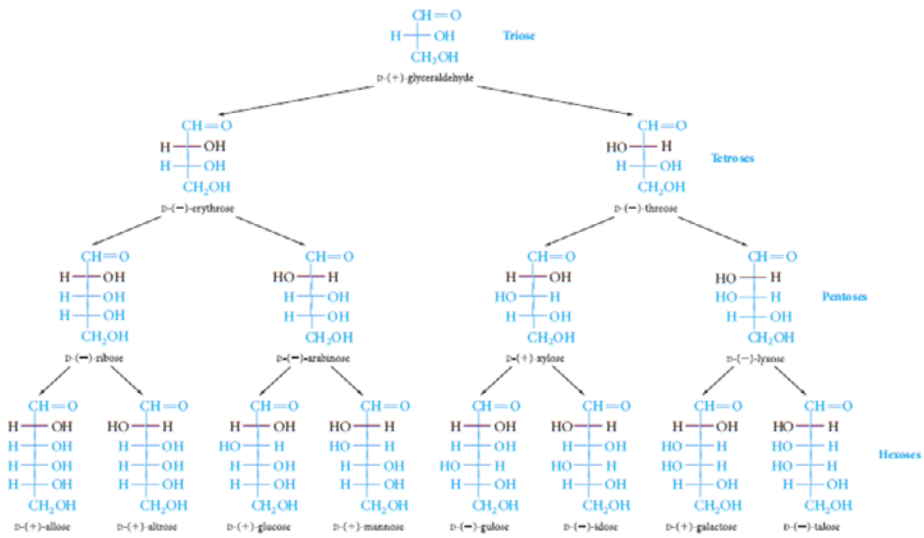


Figure 16.1
Fischer projection formulas and genealogy chart for the D-aldoses with up to six carbon atoms.

- *Diastereomers;* when two or more stereoisomers of a compound have different configurations at one or more (but not all) of the equivalent (related) stereocenters and are not mirror images of each other.

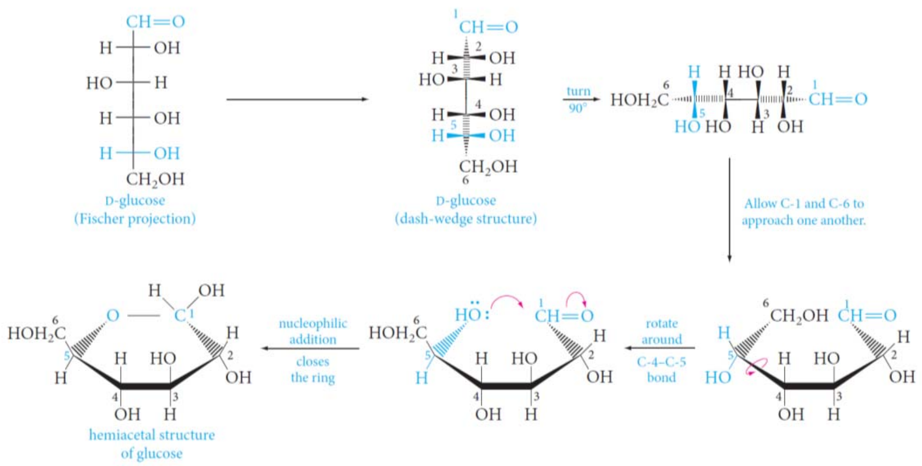
- *Epimers*; A special name is given to diastereomers that differ in configuration *at only one stereogenic center.*
- Each pair has the same configurations at all stereogenic centers except one.

- *Examples;*
  - D-(-)-Erythrose and D-(-)-threose are not only diastereomers, they are epimers.
  - D-glucose and D-mannose are epimers (at C-2)
  - D-glucose and D-galactose are epimers (at C-4).

- **Dextrorotation (+)** and **levorotation** (-) are terms describing circular direction of rotating plane-polarized light.
  - *Dextrorotatory (+);* If the light rotates clockwise, (rotation to the right).
  - *Levorotatory (-);* if it rotates counterclockwise, (rotation to the left).

The Cyclic Hemiacetal Structures of Monosaccharides

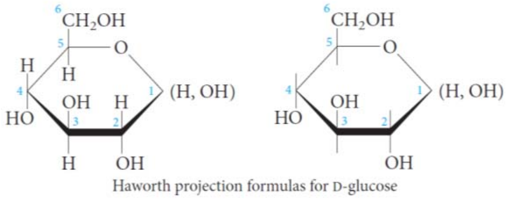
- ***Monosaccharides** exist mainly in cyclic, hemiacetal forms* and not in the acyclic aldo- or keto-forms.



Manipulation of the Fischer projection formula of D-glucose to bring the C-5 hydroxyl group in position for cyclization to the hemiacetal form.

Haworth projection

- o The carbons are arranged clockwise numerically, with C-1 at the right.
- o Substituents attached to the ring lie above or below the plane.

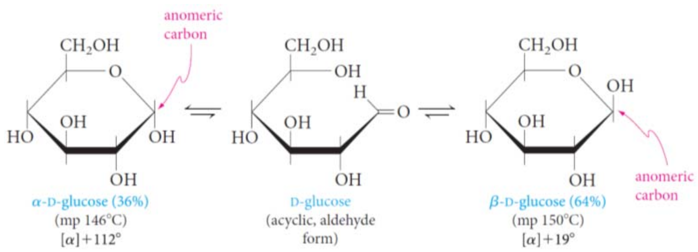


Haworth projection formulas for D-glucose

- **Carbons 1** through 5 are part of the ring structure, but carbon 6 (the -CH_2OH group) is a substituent on the ring.
- **C-1** is special. *C-1 is the hemiacetal carbon* (it carries a hydroxyl group, and it is also connected to C-5 by an ether linkage).
- **C-2**, **C-3**, and **C-4** are secondary alcohol carbons.
- **C-6** is a primary alcohol carbon;
- **C-5** is an ether carbon.
- Hydroxyl groups on the *right* in the Fischer projection are *down* in the Haworth projection (and conversely, hydroxyl groups on the *left* in the Fischer projection are *up* in the Haworth projection).
- For **D-sugars**, the terminal -CH_2OH group is *up* in the Haworth projection; for **L-sugars**, it is down.

Anomeric Carbons; Mutarotation

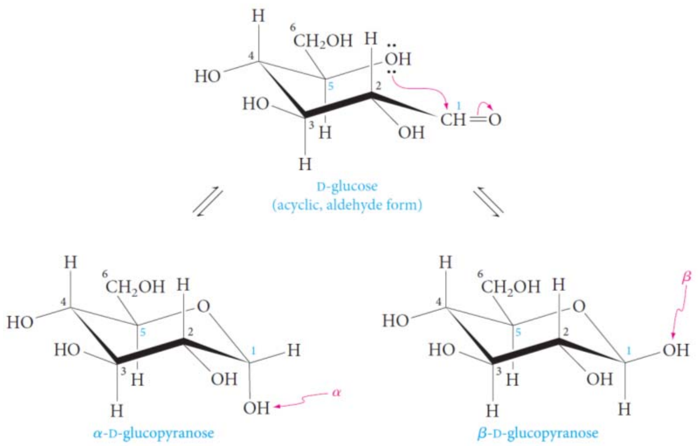
- o ***Anomeric carbon;*** The hemiacetal carbon, the carbon that forms the new stereogenic center.
- o ***Anomers;*** Two monosaccharides that differ only in configuration at the anomeric center are (a special kind of epimers).
- o ***Anomers*** are called α or β, depending on the position of the hydroxyl group.
- o For monosaccharides in the D-series, the hydroxyl group is "down" in the α anomer and "up" in the β anomer.



- If D-glucose is crystallized from methanol, the pure α form is obtained.
- Crystallization from acetic acid gives the β form.
- The α and β forms of D-glucose are *diastereomers.*

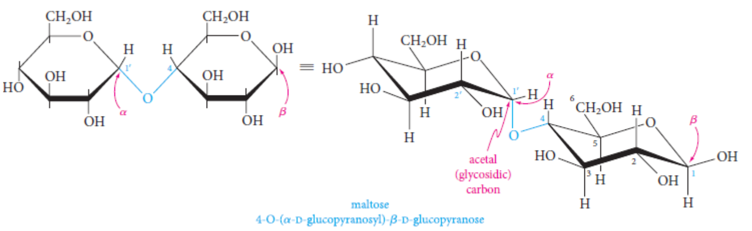
Conformations of Pyranoses; chair conformation

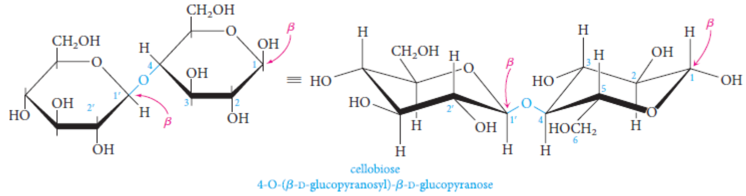
- At the anomeric carbon (C-1), where the hydroxyl group may be axial (in the α anomer) or equatorial (in the β anomer).



Disaccharides

- The most common oligosaccharides are disaccharides.
- In a disaccharide, two monosaccharides are linked by a glycosidic bond between the anomeric carbon of one monosaccharide unit and a hydroxyl group on the other unit.





- ***Carbohydrates*** are the most abundant organic compounds, constituting three-fourths of the dry weight of the plant world.
- They represent a great storehouse of energy as a food for humans and animals.
- About 400 billion tons of sugars is produced annually through natural photosynthesis.
- While these sugars differ in specific biological activity, their gross chemical reactivity are almost identical, permitting one to often employ mixtures within chemical reactions without regard to actual structure with respect to most physical properties of the resulting product.
- ***Carbohydrates*** are diverse with respect to both occurrence and size.
- ***Examples;*** Familiar mono and disaccharides include glucose, fructose, sucrose (table sugar), cellobiose, and mannose .

Familiar polysaccharides along with their natural sources, purity, molecular weight, amount, and location of source.

Polysaccharide	Source	Monomeric sugar unit(s)	Structure	Mol. wt.
Amylopectin	Corn, potatoes	D-Glucose	Branched	10^6–10^7
Amylose	Plants	D-Glucose	Linear	10^4–10^6
Chitin	Animals	2-Acetamidoglucose		
Glycogen	Animals (muscles)	D-Glucose	Branched	$>10^8$
Inulin	Artichokes	D-Fructose	Linear (largely)	10^3–10^6
Mannan	Yeast	D-Mannose	Linear	—
Cellulose	Plants	D-Glucose	Linear (2D)	10^6
Xylan	Plants	D-Xylose	Linear (largely)	—
Lichenan	Iceland moss	D-Glucose	Linear	10^5
Galactan	Plants	D-Galactose	Branched	10^4
Arabinoxylan	Cereal grains	L-Arabinofuranose linked to xylose chain	Branched	$>10^4$
Galactomannans	Seed mucilages	D-Mannopyranose chains with D-galactose side chains	Linear (largely)	10^5
Arabinogalactan	Lupin, soybean, coffee beans	D-Galactopyranose chain, side chain galactose and arabinose	Branched	10^5
Carrageenan	Seaweeds	Complex—contains β-galactopyranose linked to 3,6-anhydro-D-galactopyranose	Linear	10^5–10^6
Agar	Red seaweeds	Same as above except for L-galactopyranose	Linear	—
Alginic	Brown seaweeds	β-D-Mannuronic acid and α-L-guluronic acid	Linear	—

- The most important polysaccharides are ***cellulose*** and ***starch***.
- These may be hydrolyzed by acids or enzymes to lower molecular weight carbohydrates (oligosaccharides) and finally to D-glucose.

Hydrolysis by acids or enzymes

Polysaccharides (***cellulose*** and ***starch)***

↓

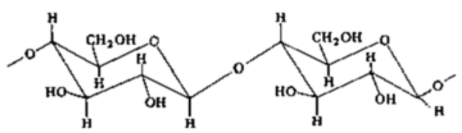
Lower molecular weight carbohydrates (***oligosaccharides***)

↓

Monomers (***D-glucose***)

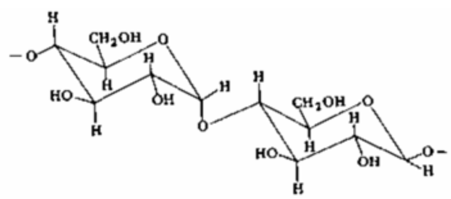
- The latter (***D-glucose***) is the building block, or mer, for carbohydrate polymers, and since it cannot be hydrolyzed further, it is called a *monosaccharide*.

- ***Cellobiose*** and ***maltose***, which are the repeat units in cellulose and starch, are disaccharides, consisting of molecules of D-glucose joined together through carbon atoms 1 and 4.



Chair form of <u>cellobiose</u> repeat unit in cellulose

- The D-glucose units in cellobiose are joined by a β -acetal linkage



Chair of <u>maltose</u> repeat unit in amylose.

- The D-glucose units in maltose are joined by an α-acetal linkage.

- The hydroxyl groups in the β form of D-glucose are present in the equatorial positions, and the hydroxyl on carbon 1 (the anomeric carbon atom) in the α form is in the axial position.

- The hydroxyl groups in the β form of D-glucose are present in the equatorial positions, and the hydroxyl on carbon 1 (the anomeric carbon atom) in the α form is in the axial position.

- While the chair forms shown for D-glucose, cellobiose, and maltose exist in all disaccharides and polysaccharides, simple Boeseken-Haworth perspective planar hexagonal rings will be used for simplicity in showing polymeric structures of most carbohydrates.