Chemistry 110

Bettelheim, Brown, Campbell & Farrell

Eighth Edition

Introduction to General,

Organic and Biochemistry

Chapter 20

Carbohydrates

Polyhydroxy Aldehydes & Ketones

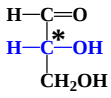
Carbohydrates

- **A Carbohydrate is a polyhydroxyaldehyde, a polyhydroxyketone, or a substance that gives these compounds on hydrolysis.**
- **A Monosaccharide is a carbohydrate that cannot be hydrolyzed to a simpler carbohydrate. Monosaccharides have the general formula $C_nH_{2n}O_n$, where n varies from 3 to 8.**
- **Aldose is a monosaccharide containing an aldehyde group.**
- **Ketose is a monosaccharide containing a ketone group.**
- **Monosaccharides are classified by their number of carbon atoms.**

Name	Formula
Triose	$C_3H_6O_3$
Tetrose	$C_4H_8O_4$
Pentose	$C_5H_{10}O_5$
Hexose	$C_6H_{12}O_6$
Heptose	$C_7H_{14}O_7$
Octose	$C_8H_{16}O_8$

Monosaccharides

- **There are only two Trioses: One aldotriose; One ketotriose**



D-Glyceraldehyde

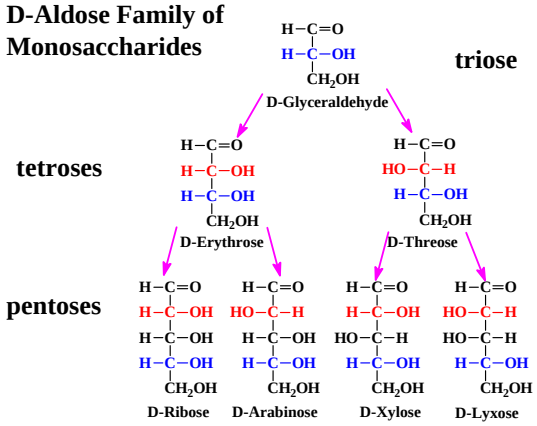
Dihydroxyacetone

- **Glyceraldehyde has a tetrahedral stereocenter and exists as two enantiomers. Only D-glyceraldehyde occurs naturally.**
- **The D- and L- nomenclature proposed by Emil Fischer in 1891 is well entrenched in carbohydrate chemistry. The enantiomer shown, with the *-OH on the right with +13.5° rotation is assigned the D- (*dextro*, on the right) prefix.**
- **All natural sugars have the penultimate –OH on the right.**

Rules for Fischer Projections

- **Visualize the molecule with its main carbon chain vertical and with the bonds that hold the chain together projecting to the rear at each stereocenter. Carbon 1 is at the top, at or nearest the carbonyl group. You will find that in 3D space the molecule will roll up into a ring.**
- **Mentally flatten the structure, stereocenter by stereocenter, onto a plane surface. Represent each stereocenter either as the intersection of two lines or conventionally as a carbon atom.**
- **The horizontal lines at a stereocenter actually represent bonds that project forward, out of the plane of the paper, or outward from ring.**
- **The vertical lines at a stereocenter actually represent bonds that project rearward, behind the plane. In 3D space the carbons make a ring and the H & OH groups project outward.**

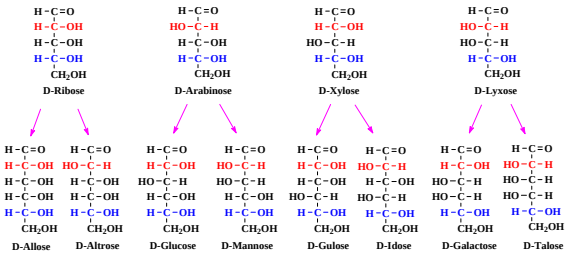
D-Aldose Family of Monosaccharides



D-Aldose Family of Monosaccharides

All D-aldose sugars are built up from glyceraldehyde.

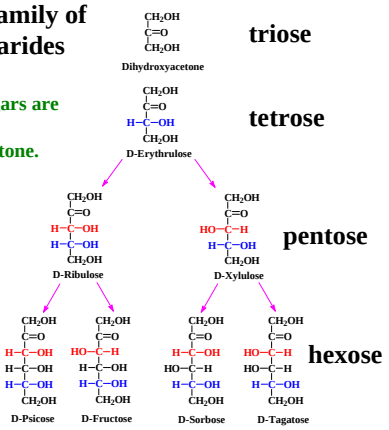
pentoses



hexoses

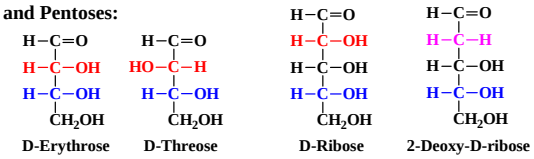
D-Ketose Family of Monosaccharides

All ketose sugars are built up from dihydroxyacetone.

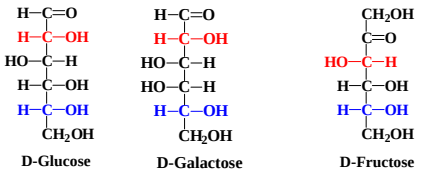


Monosaccharides

- The most common Tetroses and Pentoses:

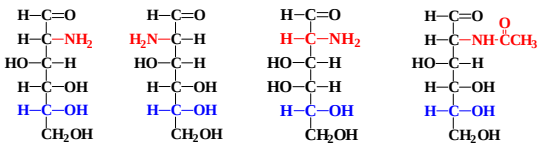


- The most common Hexoses:



Amino Sugars

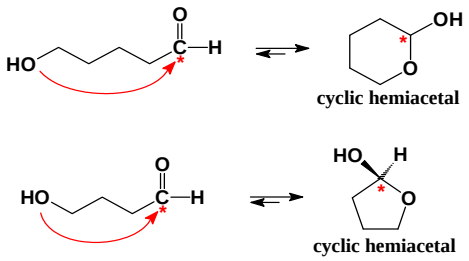
- Amino sugars contain an -NH_2 group in place of an -OH group.
- Only three amino sugars are common in nature:
  D-glucosamine, D-mannosamine, and D-galactosamine



- The last is an amido derivative of D-glucosamine.

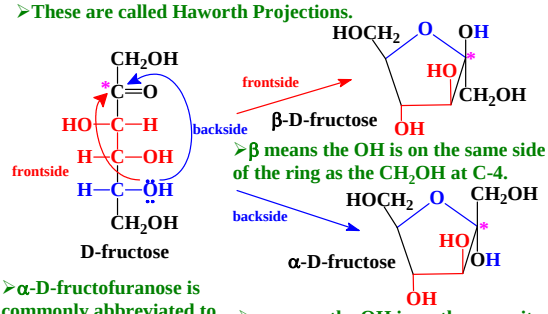
Addition Reactions to the Carbonyl Group

➢When an alcohol and aldehyde (ketone) functionality are present in the same molecule and a 5- or 6-membered ring can form, the cyclic hemiacetal form is predominate.



Cyclic Forms of Monosaccharides Hemiacetals

➢These are called Haworth Projections.

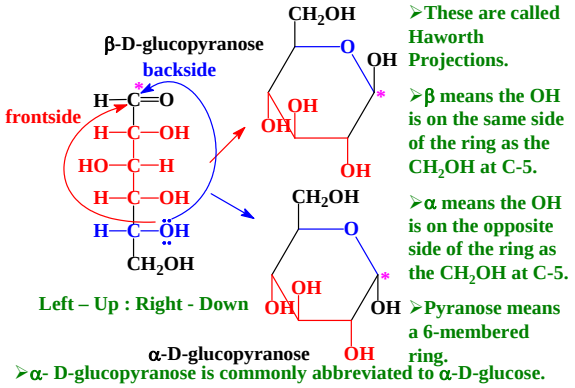


➢β means the OH is on the same side of the ring as the CH_2OH at C-4.

➢α-D-fructofuranose is commonly abbreviated to α-D-fructose.

➢α means the OH is on the opposite side of the ring as the CH_2OH at C-4.

Cyclic Forms of D-Glucose - Hemiacetals



➢These are called Haworth Projections.

➢β means the OH is on the same side of the ring as the CH_2OH at C-5.

➢α means the OH is on the opposite side of the ring as the CH_2OH at C-5.

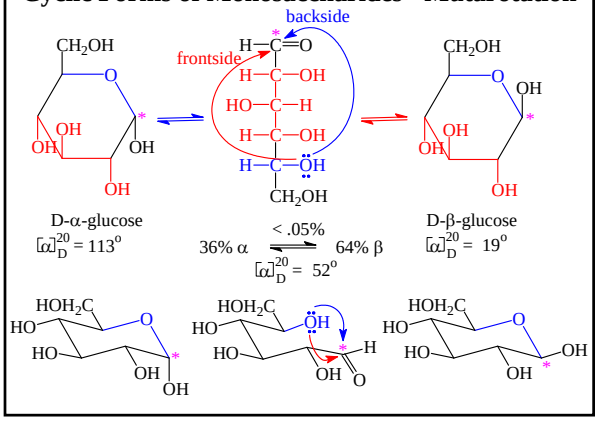
➢Pyranose means a 6-membered ring.

➢α- D-glucopyranose is commonly abbreviated to α-D-glucose.

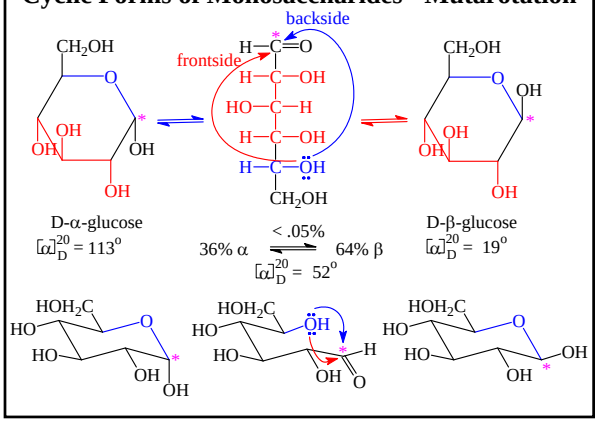
Understanding Haworth Projections

- **A five- or six-membered cyclic hemiacetal is represented as a planar ring, lying nearly horizontally, i.e. roughly perpendicular to the plane of the paper.**
- **Groups bonded to the carbons of the ring then lie either above or below the plane of the ring.**
- **The new carbon stereocenter created in forming the cyclic hemiacetal structure is called an anomeric carbon.**
- **Stereoisomers that differ in configuration only at the anomeric carbon are called anomers.**
- **The anomeric carbon of an aldose is C-1; that of the most common ketoses is C-2.**
- **aldopentoses also form cyclic hemiacetals.**
- **the most prevalent forms of D-ribose and other pentoses in the biological world are furanoses.**

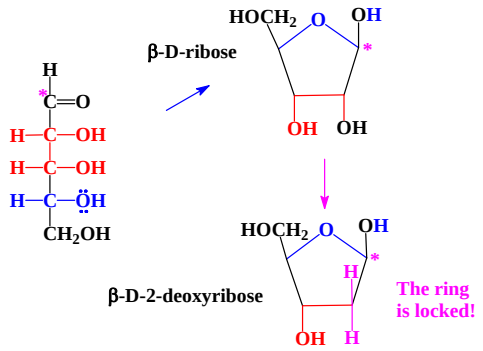
Cyclic Forms of Monosaccharides - Mutarotation



Cyclic Forms of Monosaccharides - Mutarotation

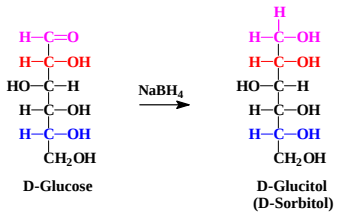


Cyclic Forms of Ribose & Deoxyribose



Reduction of Monosaccharides - Alditols

- The carbonyl group of a monosaccharide can be reduced to an hydroxyl group by a variety of reducing agents, including $NaBH_4$ and H_2 in the presence of a transition metal catalyst.
- the reduction product is called an alditol.

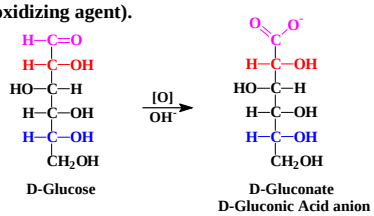


- D-Sorbitol is found in berries, plums, apples, seaweed, & algae.
- It is used to make candies and as a sugar substitute for diabetics.
- It is 60% as sweet as sucrose.

- Other common alditols are erythritol, mannitol and xylitol.

Oxidation of Monosaccharides – Aldonic Acids

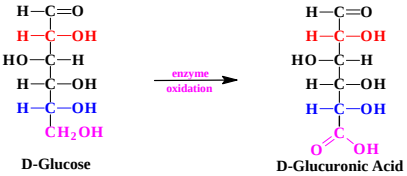
- The aldehyde group of an aldose is oxidized under basic conditions to a carboxylate anion.
- The oxidation product is called an aldonic acid.
- Any carbohydrate that reacts with an oxidizing agent to form an aldonic acid is classified as a reducing sugar (it reduces the oxidizing agent).



- Any sugar which mutarotates will be a reducing sugar because the cyclic hemiacetal will open to the chain form during the interconversion.

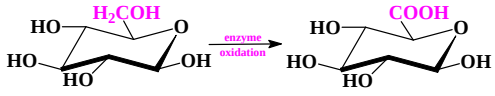
- Even 2-ketoses can form an aldehyde by tautomerism! See text!

Oxidation of Monosaccharides – Uronic Acids



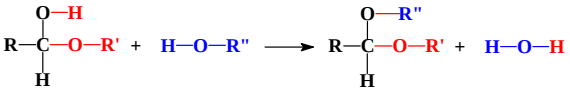
D-Glucose D-Glucuronic Acid

➢D-Glucuronic Acid is formed by enzyme oxidation of D-glucose. It is widely distributed in the plant and animal world. In humans it is found in connective tissues and is used by the liver to detoxify foreign phenols so they can be excreted in the urine.



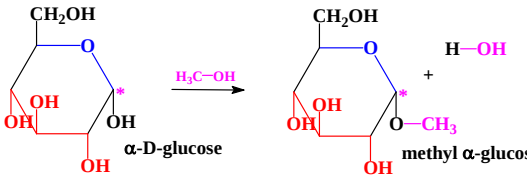
β-D-Glucose β-D-Glucuronic Acid

Monosaccharide Hemiacetals Form Acetals



hemiacetal alcohol acetal water

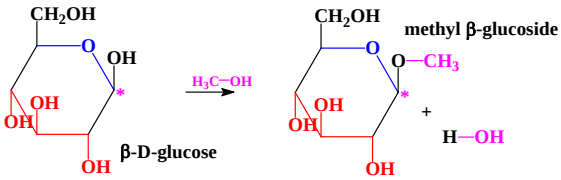
Acetals of Sugars are called Glycosides



α-D-glucose methyl α-glucoside

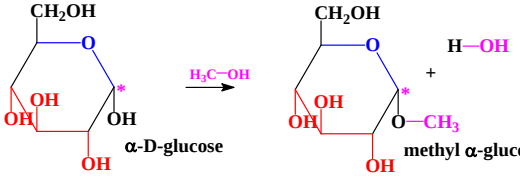
The acetal bond at the anomeric carbon is called a glycosidic bond.

Both *alpha* and *beta* Glycosides Form



β-D-glucose methyl β-glucoside

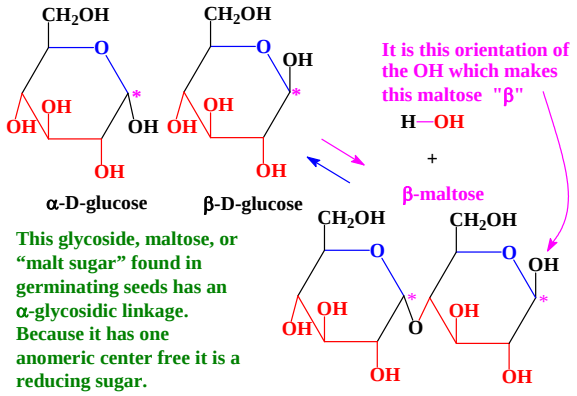
Both reactions require an acid catalyst or an enzyme.



α-D-glucose methyl α-glucoside

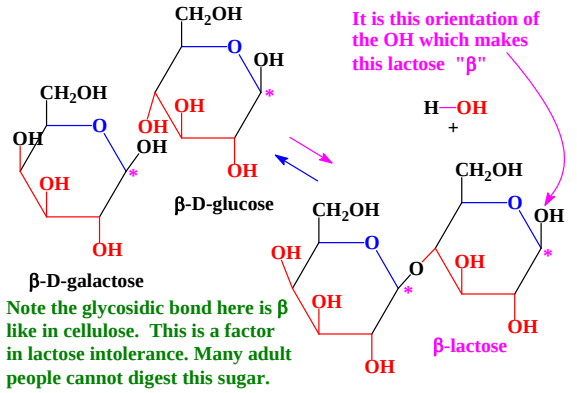
Mutarotation is not possible here; the α & β are not in equilbrium.

Disaccharides are Acetals - Maltose



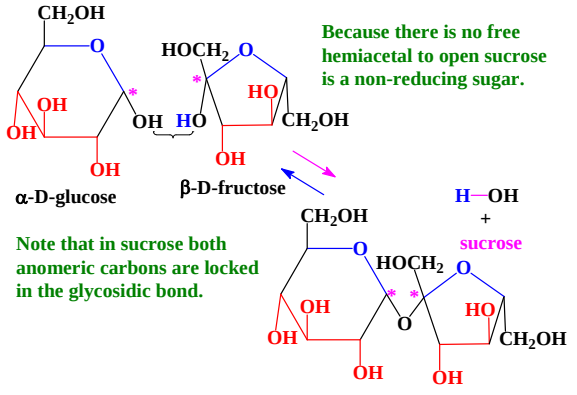
This glycoside, maltose, or "malt sugar" found in germinating seeds has an α-glycosidic linkage. Because it has one anomeric center free it is a reducing sugar.

Disaccharides are Acetals - Lactose



Note the glycosidic bond here is β like in cellulose. This is a factor in lactose intolerance. Many adult people cannot digest this sugar.

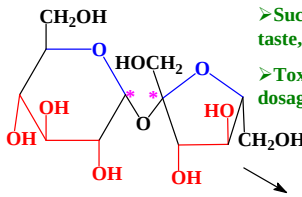
Disaccharides are Acetals - Sucrose



Because there is no free hemiacetal to open sucrose is a non-reducing sugar.

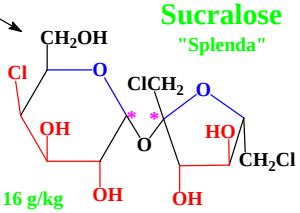
Note that in sucrose both anomeric carbons are locked in the glycosidic bond.

A Non-nutritive Sweetener Derived from Sucrose



Sucrose

- Sucralose has an intensely sweet taste, much greater than sucrose.
- Toxicity is quite low compared to dosage.



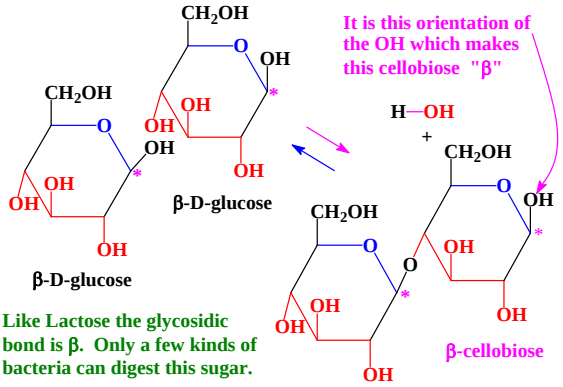
Sucralose

"Splenda"

IUPAC: 1,6-Dichloro-1,6-dideoxy-β-D-fructofuranosyl-4-chloro-4-deoxy-α-D-galactopyranoside

LD_{50} = 16 g/kg

This Disaccharide is Not Digestible



β-D-glucose

β-D-glucose

It is this orientation of the OH which makes this cellobiose "β"

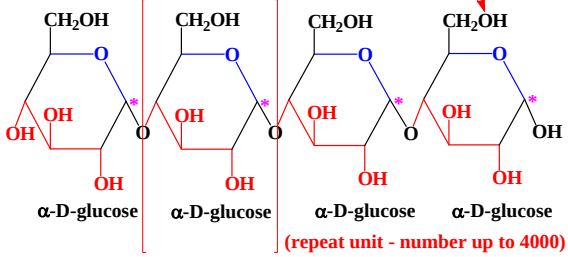
β-cellobiose

Like Lactose the glycosidic bond is β. Only a few kinds of bacteria can digest this sugar.

Polysaccharides - Starch

- **Polysaccharide:** a carbohydrate consisting of large numbers of monosaccharide units joined by glycosidic bonds.
- **Starch:** a polymer of D-glucose is edible/digestible.

Starch consists of two components:
- amylose - unbranched chains having up to 4000 glucose units.
- amylopectin has branches of 24-30 glucose units at these points.

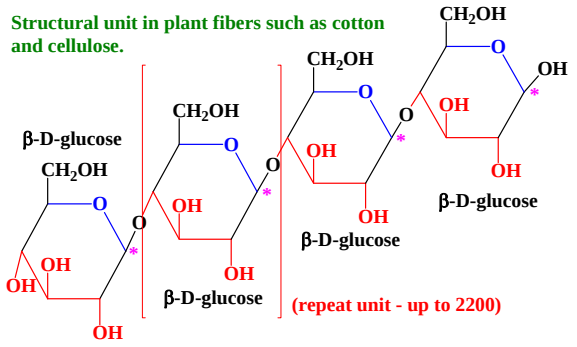


α-D-glucose α-D-glucose α-D-glucose α-D-glucose

(repeat unit - number up to 4000)

Polysaccharides - Cellulose

Structural unit in plant fibers such as cotton and cellulose.



The β 1-4 glycosidic bond is digestible by only a few organisms.