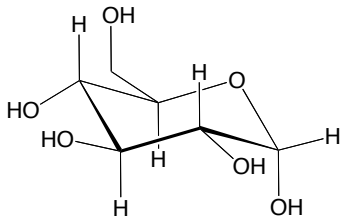
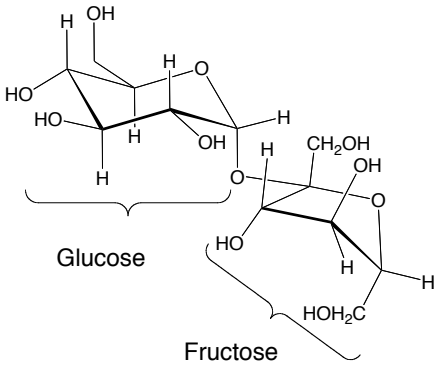
What are Carbohydrates?

- Polyhydroxylated aldehydes and ketones
- Commonly called sugars
- General formula of common sugars
  - Glucose: $C_6(H_2O)_6$
  - Glyceraldehyde: $C_3(H_2O)_3$



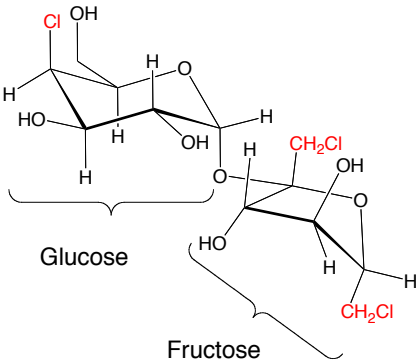
Glucose



Glucose

Fructose

Sucrose

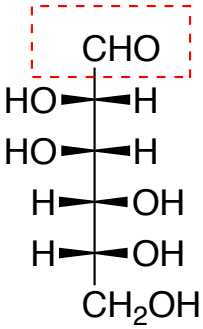


Glucose

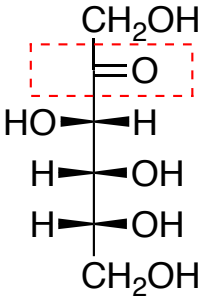
Fructose

Sucralose (Splenda)

Aldoses and Ketoses



D-mannose



D-mannoketose

triose: 3 carbons
tetrose: 4 carbons
pentose: 5 carbons
hexose: 6 carbons

Glyceraldehyde

1 **2** **3** **4**

(*R*)-2,3-dihydroxypropanal

D-(+)-glyceraldehyde

(*S*)-2,3-dihydroxypropanal

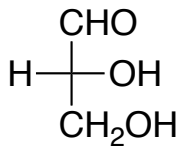
L-(–)-glyceraldehyde

- Structures **2** and **3** are drawn in the original Fisher projection
- Structures **1** and **4** are drawn in the Victor-Meyer modification

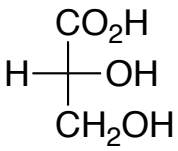
--Now commonly called the Fisher Projection

The D and L designations

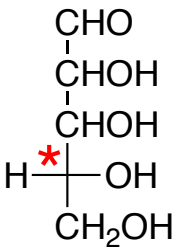
- The D and L signify the relationship of a particular sugar to glyceraldehyde
- They **<u>do not</u>** designate the optical rotation of the sugar
- Optical Rotation is designated by the lowercase letters. i.e.
  - ➢ *d* or (+) for dextrorotary
  - ➢ *l* or (–) for levorotary



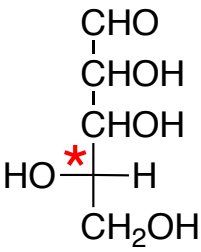
D-(+)-glyceraldehyde



D-(–)-lactic acid



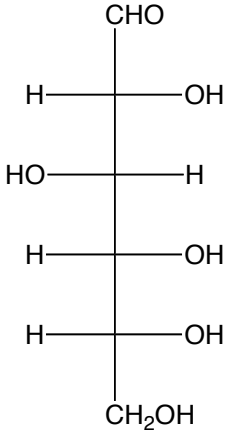
A D-pentose



An L-pentose

Drawing Fisher Projections of Monosaccharides

1. Draw aldehyde or ketone carbon at the top
2. Number from top to bottom
3. The asymmetric carbon of highest number is used to designate D or L



D-glucose

Some Terms

Methylol-

Absolute configuration-

Number of stereoisomers-

Enantiomers-

Diastereomers-

Epimers-

Anomers-

Types of Saccharides

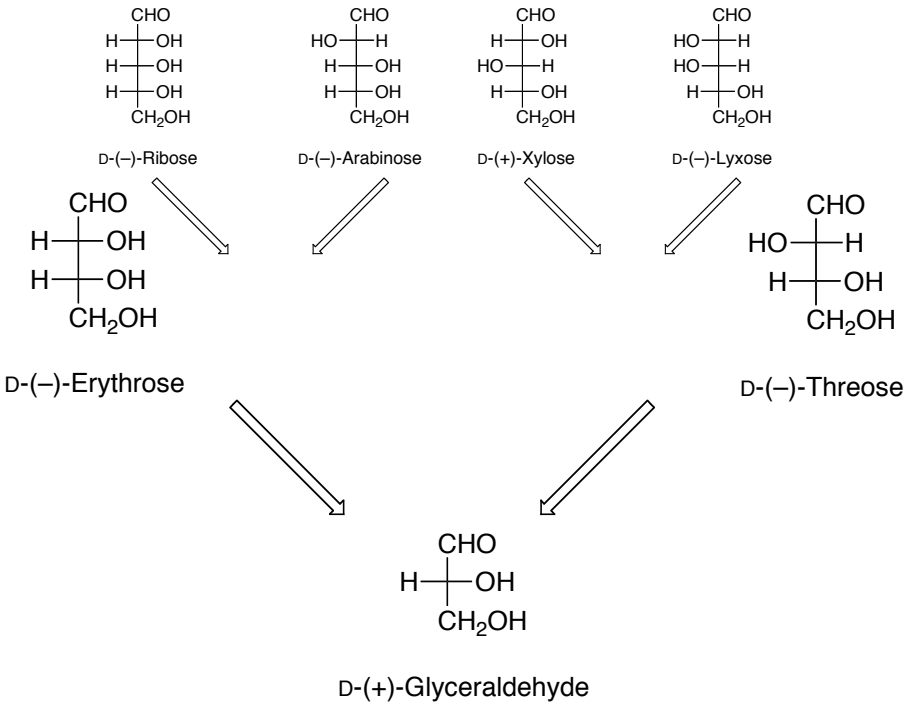
Monosaccharides-

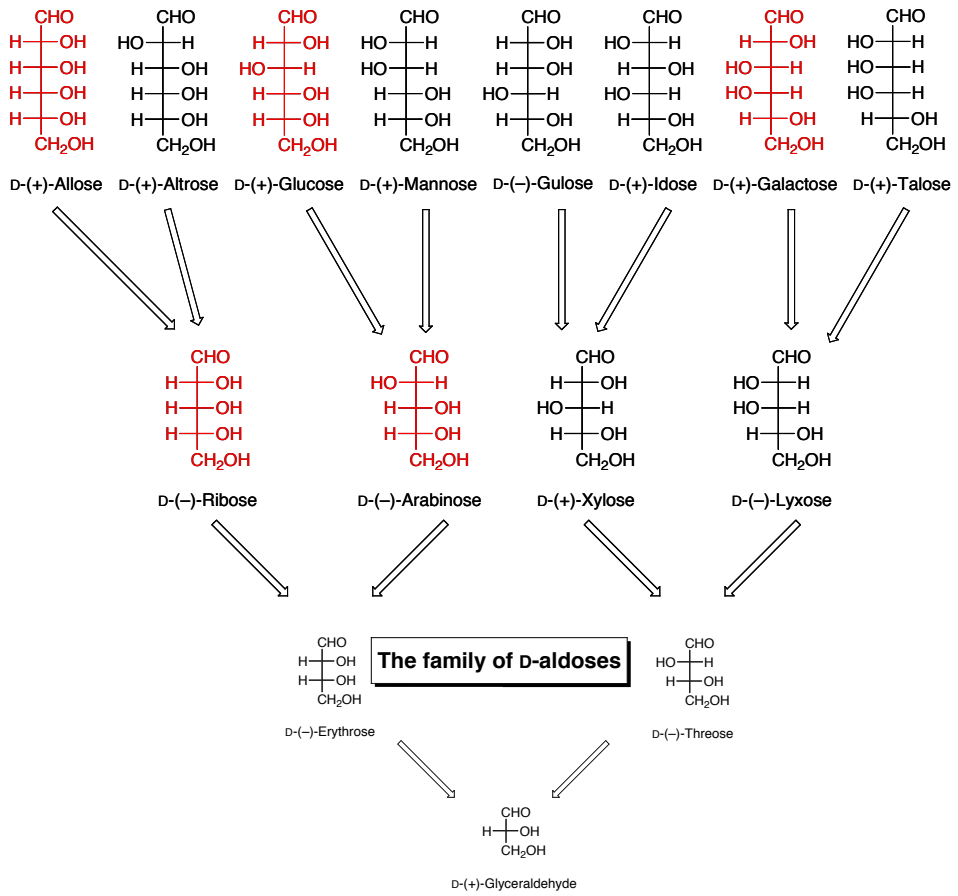
Disaccharides-

Oligosaccharides-

Polysaccharides-

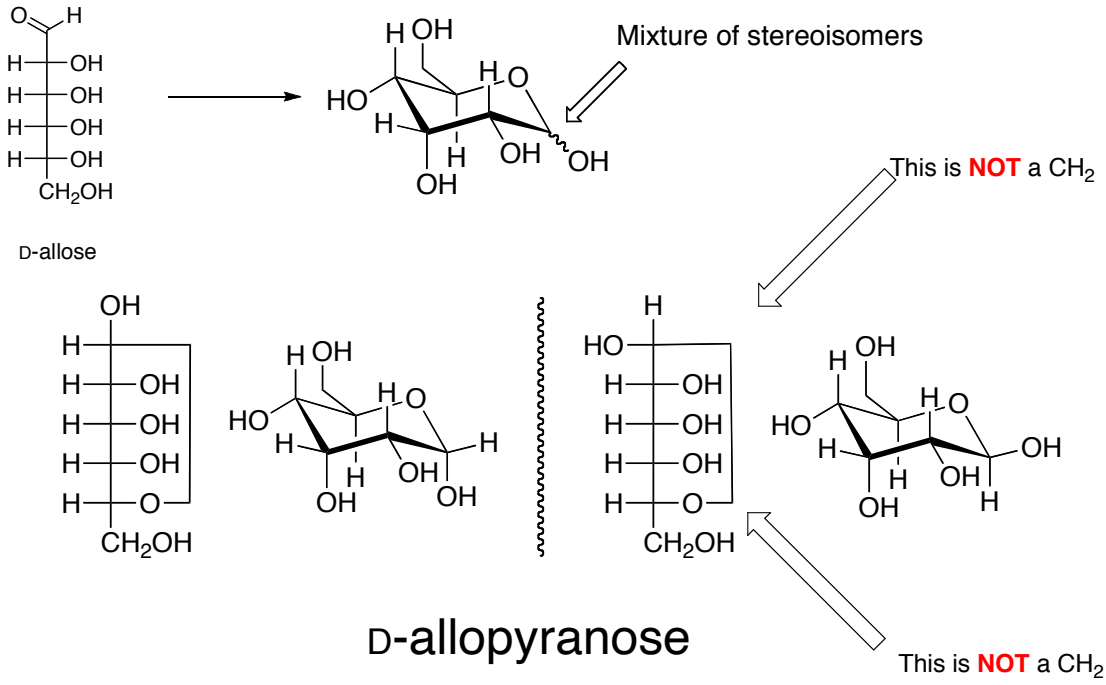
The Family of D-Aldoses





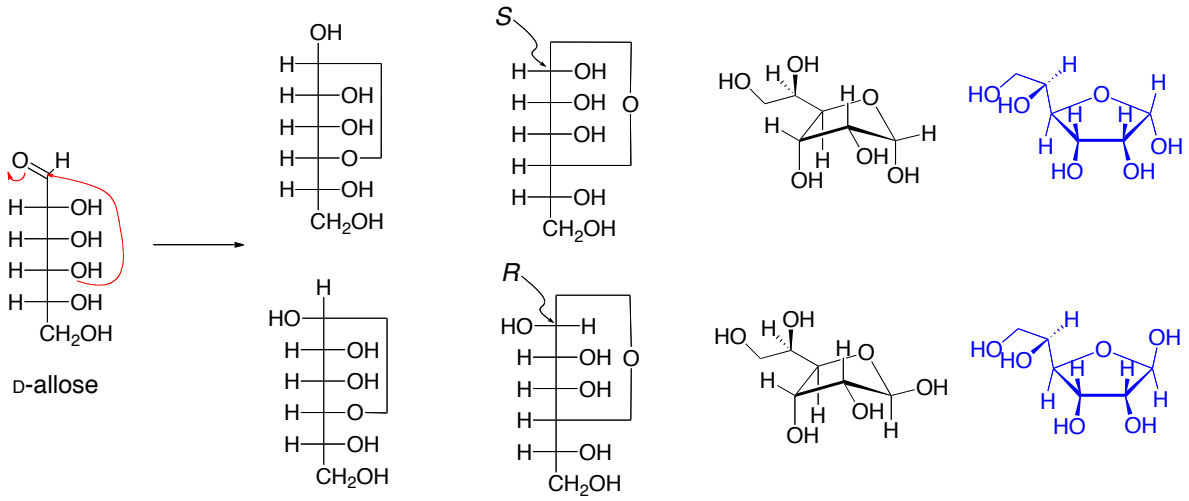
Cyclic Forms of Carbohydrates

pyranoses



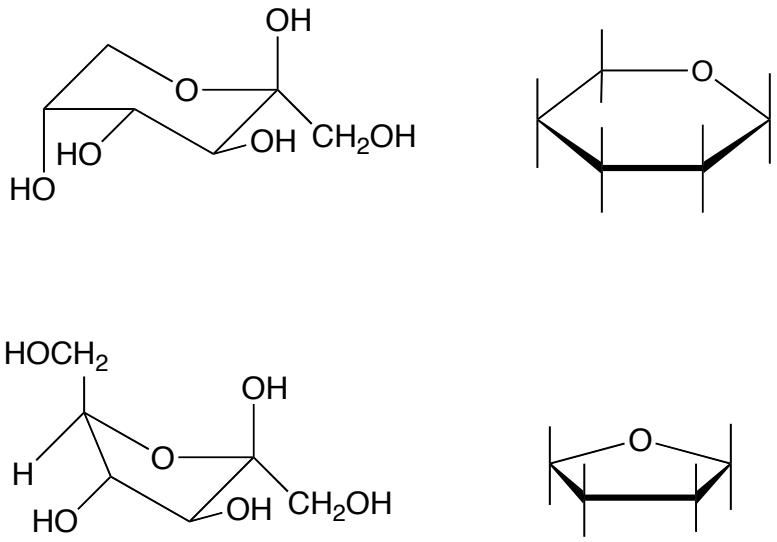
Cyclic Forms of Carbohydrates

furanoses and “special” Fisher projections

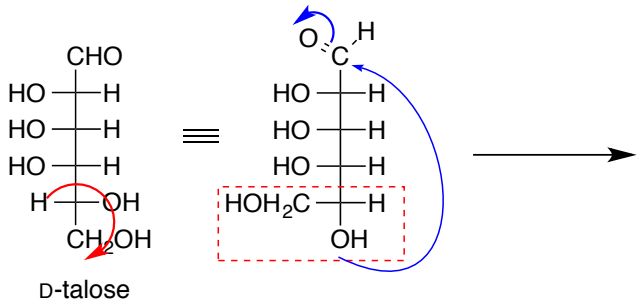


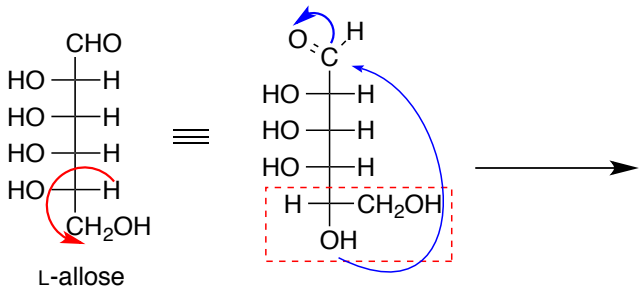
D-allofuranose

Haworth Formulas

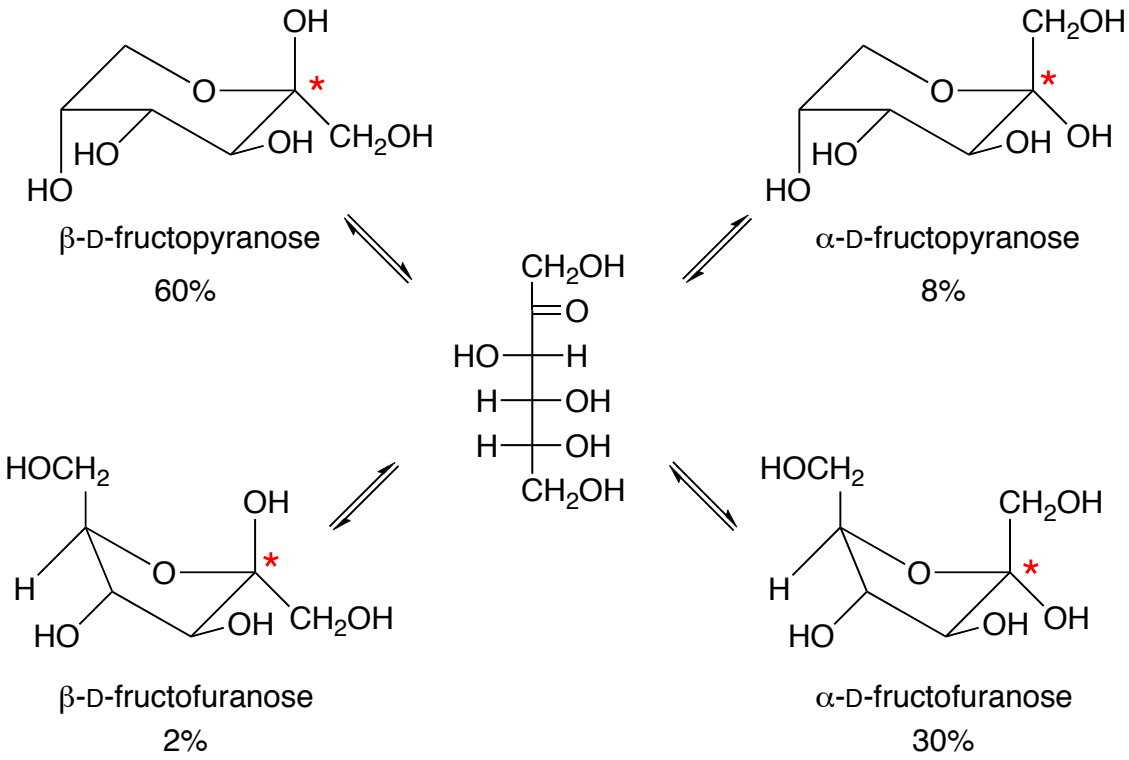


Fisher–>pyranose form



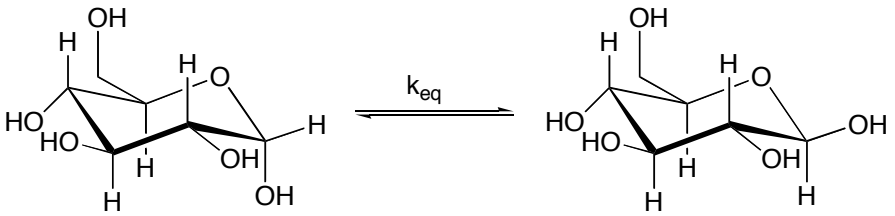


D-Fructose Cyclic Isomers



Mutarotation

A change in specific rotation that accompanies the equilibrium of α- and β-anomers.



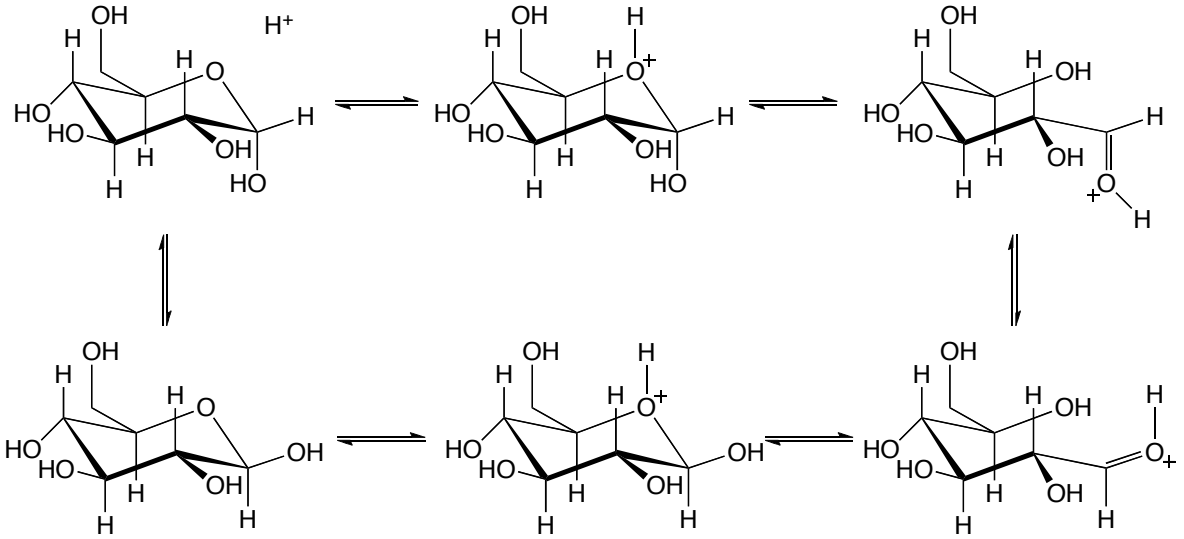
α-D-(+)-Glucose
$[\alpha]_D$ +112

β-D-(+)-Glucose
$[\alpha]_D$ +18.7

At equilibrium $[\alpha]_D$ +52.7

64% of β, 36% of α and 0.003% of the open chain form

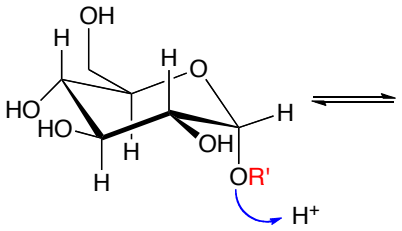
Mechanism of Mutarotation



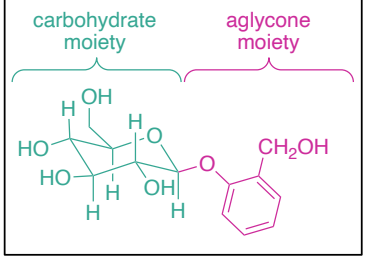
Reactions of Carbohydrates

- Glycoside formation/hydrolysis
- Ether formation (Ag_2O/CH_3I)
- Acetonide formation
- Ester formation (Ac_2O, AcCl & pyridine)
- Reduction ($NaBH_4$)
- Reducing/non-reducing sugers
- Methods of oxidation
  - Silver oxide/ammonia (Tollens)
  - Bromine/water
  - Copper sulfate (Benedicts & Fehlings rgts)
  - HNO_3
  - Periodic Acid/oxidative cleavage
- Kilani-Fisher Synthesis

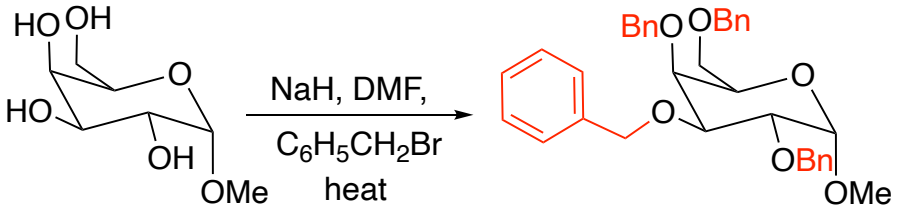
Glycoside Formation/Hydrolysis

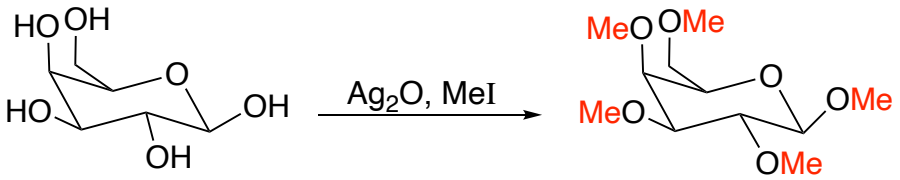


Glycoside Parts

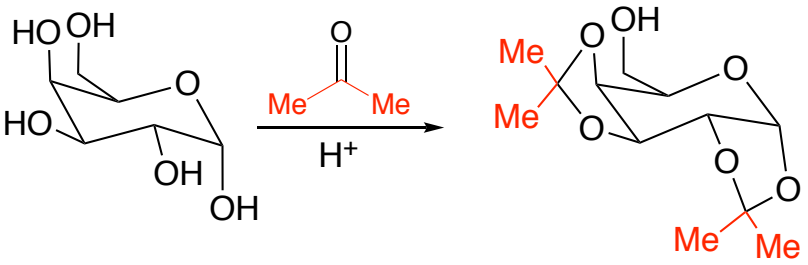


Ether Formation



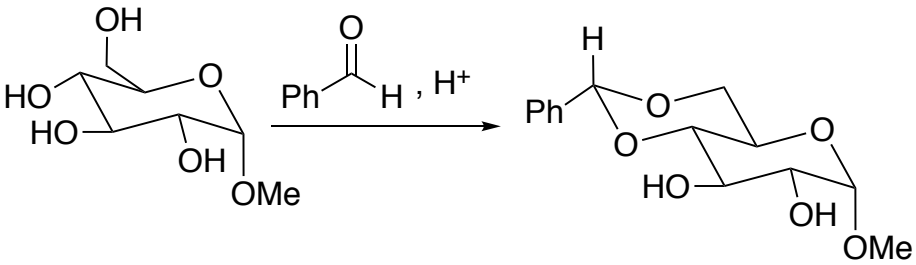


Acetonide Formation



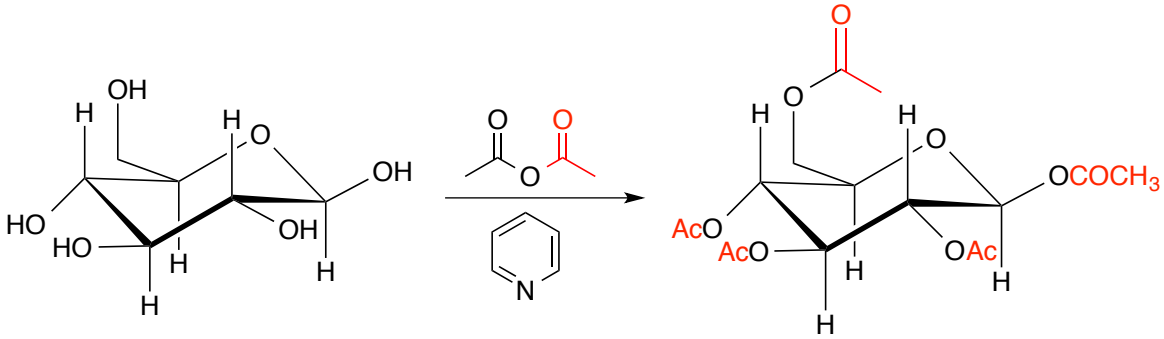
cis hydroxyls protected as a dimethyl acetal

Employing Chairs for Diol-Protection



Selectively protect 2 OH groups if they make a 6-membered ring in a chair conformation

Ester Formation

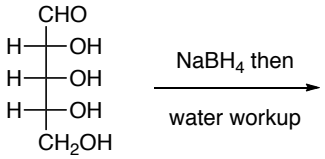


β-D-glucopyranose

penta-*O*-acetyl-β-D-glucopyranose

A reaction with an acid anhydride or acid chloride in the presence of a weak base leads to ester formation

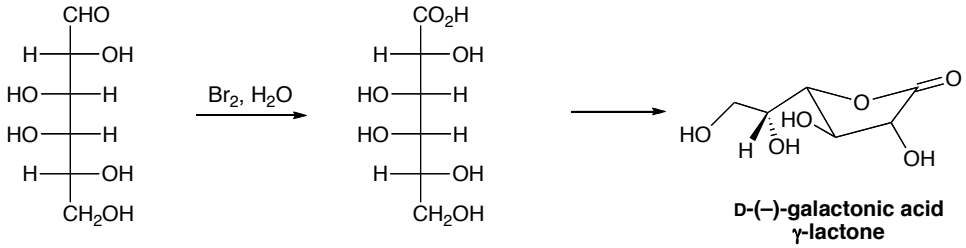
Reduction



D-ribose

ribitol/adonitol ($4/gram)

Oxidation



galactose

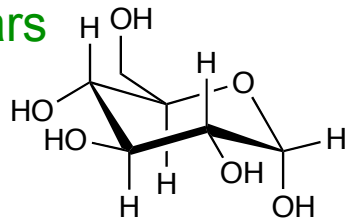
galactonic acid

D-(–)-galactonic acid γ-lactone

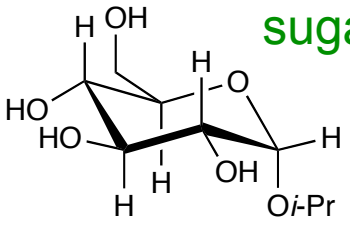
Reducing & Nonreducing sugars

Only reducing sugars can be oxidized

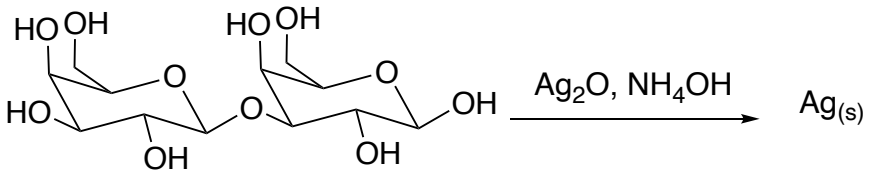
Reducing sugars



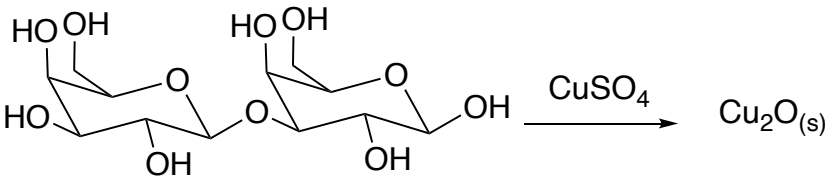
Nonreducing sugars



Oxidation Tests



Tollen's Test

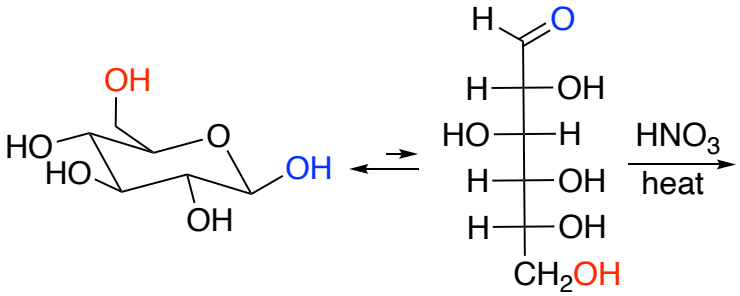


Fehling's or Benedict's Reagent

Fehling's solution is prepared from solutions of copper(II) sulfate, Rochelle salt (potassium sodium tartrate tetrahydrate), and NaOH

Benedict's reagent is prepared from sodium carbonate, sodium citrate and copper(II) sulfate.

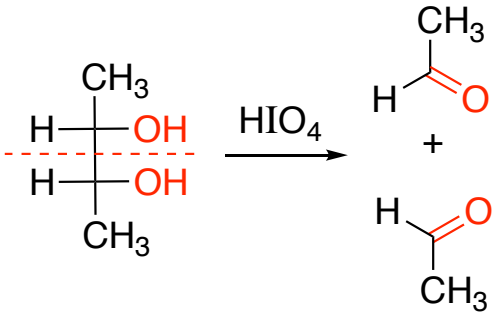
HNO_3 Oxidation (Aldaric Acids)

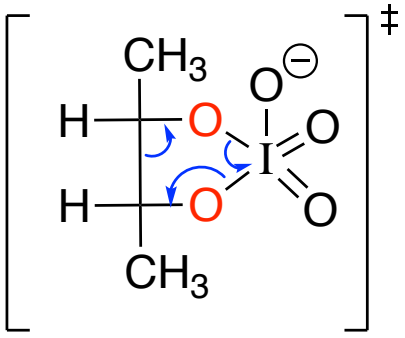


β-D-glucose

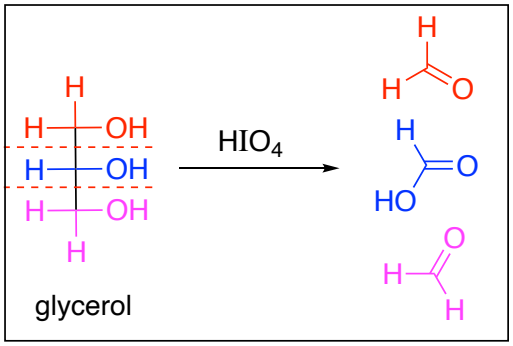
Under vigorous conditions a dicarboxylic acid called an **aldaric acid** is formed

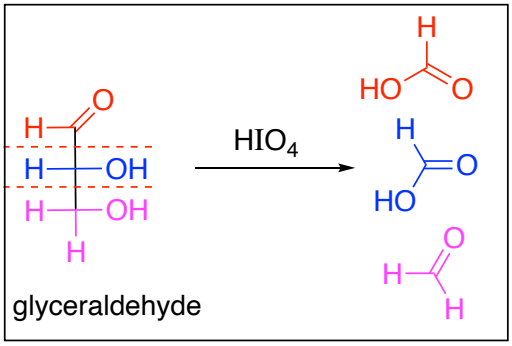
Periodic Acid

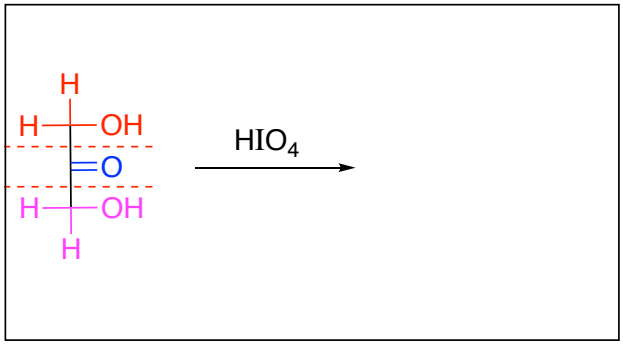




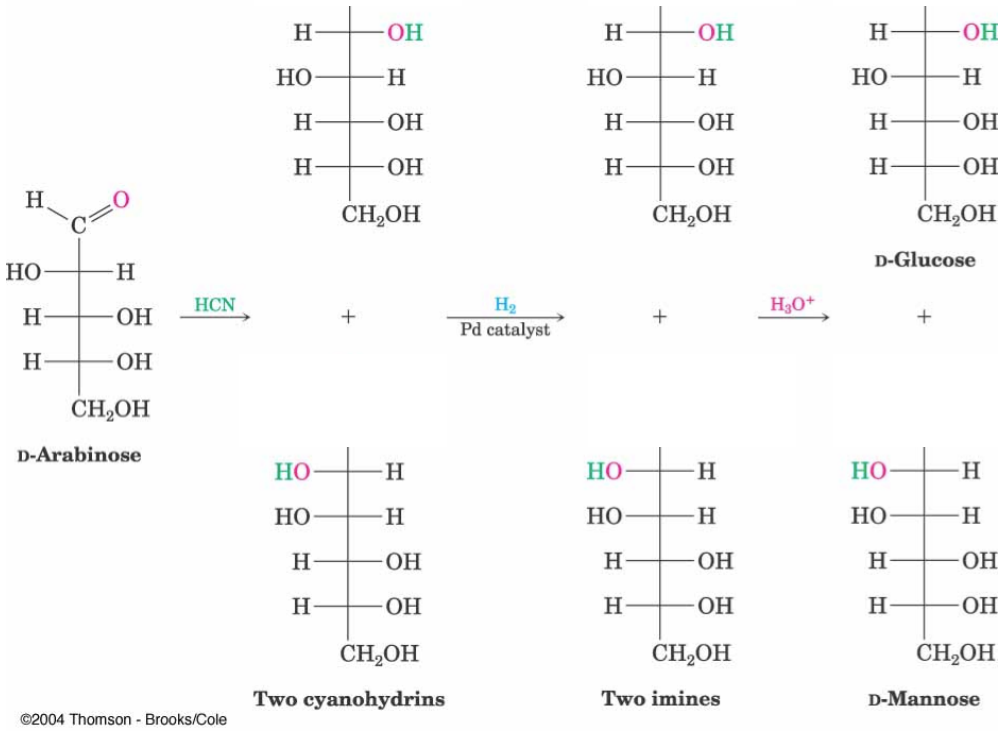
Oxidative Cleavage



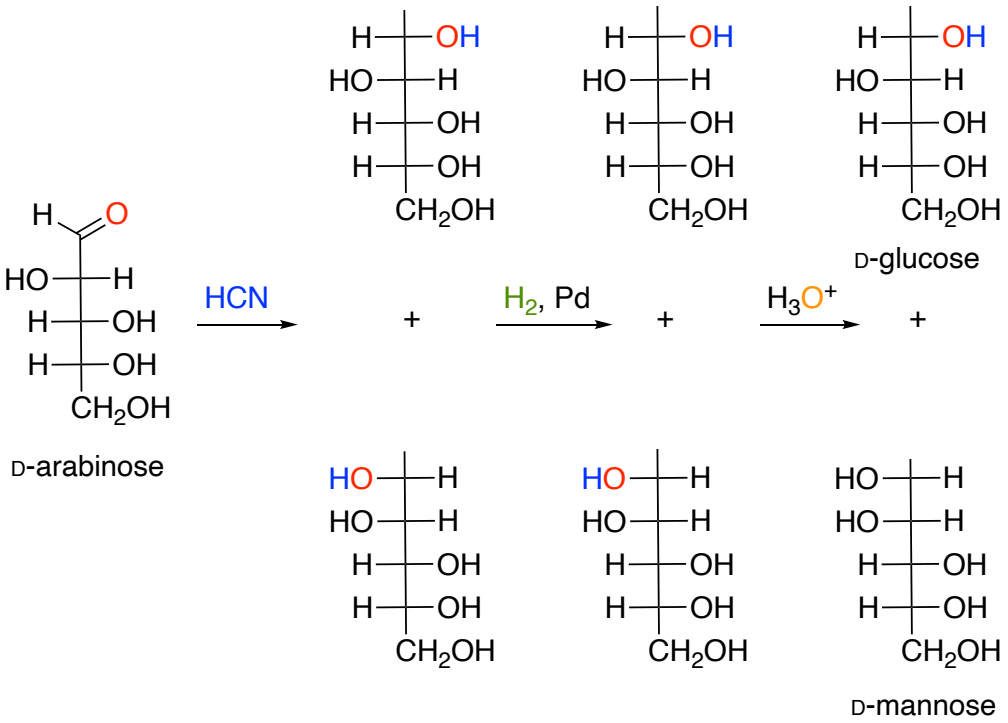




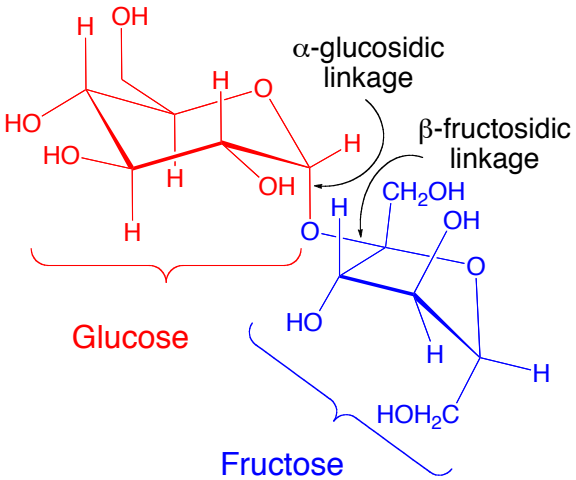
Kilani-Fisher Synthesis



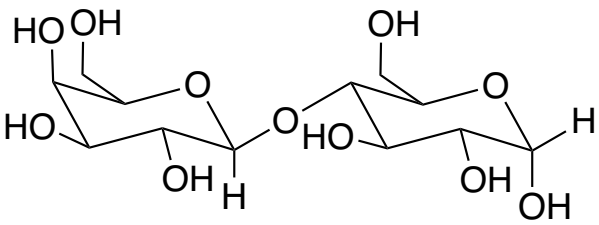
Kilani-Fisher Synthesis



Sucrose: A Disaccharide

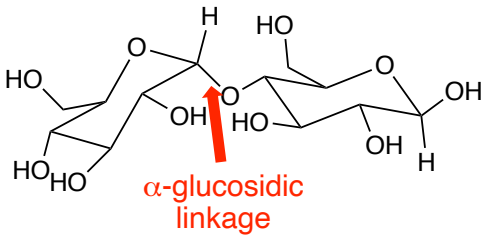


Lactose

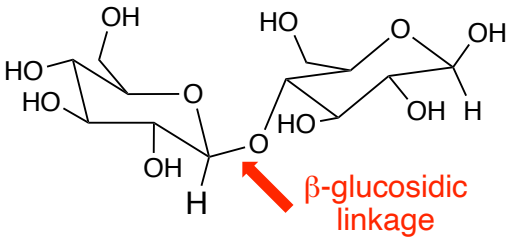


Disaccharides (of Glucose)

- Maltose
  - » Maltose is the disaccharide of D-glucose having an α-linkage
  - » Maltose results from hydrolysis of starch by the enzyme diastase
    - The two glucose units of maltose are joined by an α-glucosidic linkage

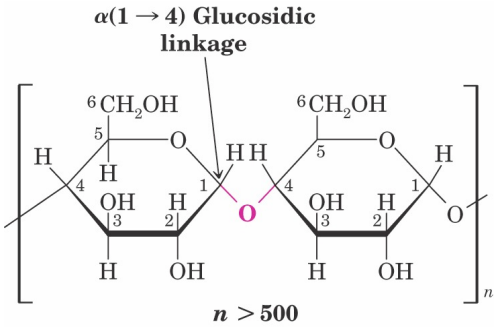


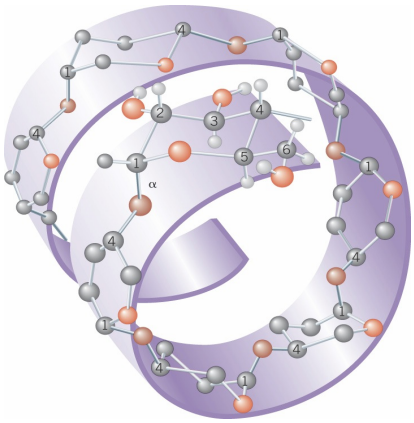
- Cellobiose
  - » Cellobiose is the disaccharide of D-glucose having a β-linkage



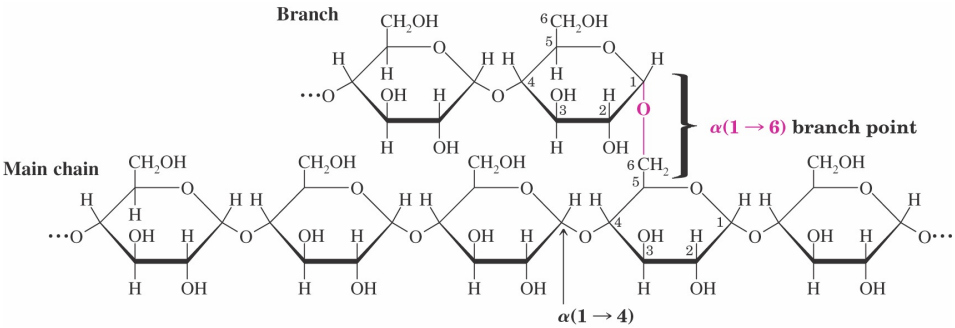
Starch (Amylose Form)

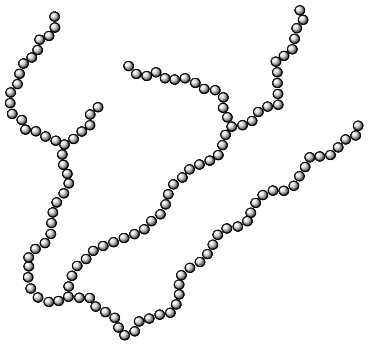
- **The storage form of glucose in plants is called starch. The two forms of starch are amylose (20%) and amylopectin (80%)**
- **Amylose consists typically >1000 D-glucopyranoside units connected by C1–C4 linkages**
- **Amylose adopts a very compact helical arrangement**

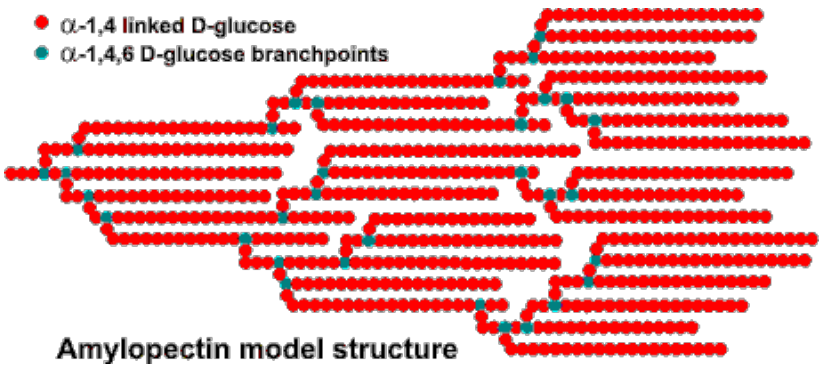




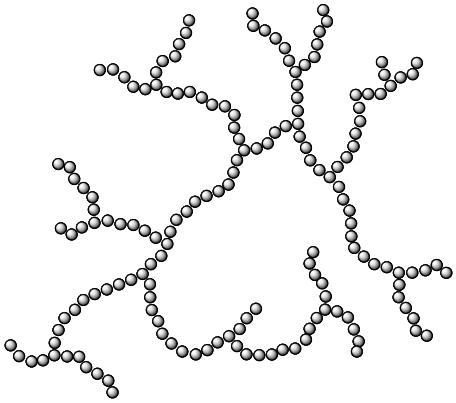
Amylopectin







Glycogen (animal starch)

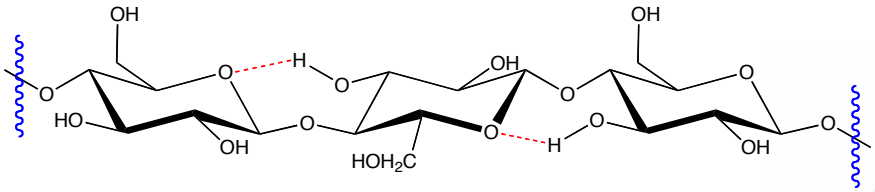


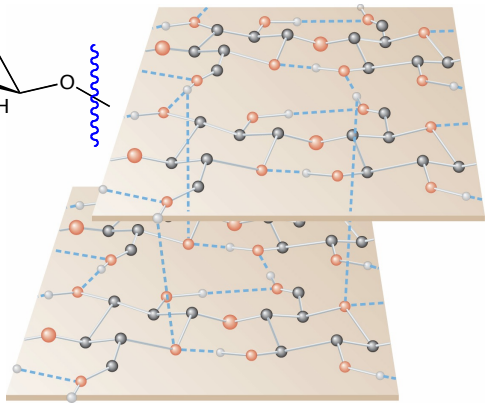
Branches ~10 units

- **Glycogen's large size prevents if from leaving the cell**
- **Linking tens of thousands of glucose molecules greatly relieves the osmotic problem for the storage**
- **The highly branched nature of glycogen allows hydrolytic enzymes to react at multiple sites. Thereby, releasing glucose quickly.**

Cellulose

- In cellulose, glucose units are joined by β-1,4'-glycosidic linkages
- Cellulose chains are relatively straight
- The linear chains of cellulose hydrogen bond with each other to give the rigid, insoluble fibers found in plant cell walls
  - ➢ The resulting sheets then stack on top of each other
- Humans lack enzymes to cleave the β linkages in cellulose and so cannot use cellulose as





Cellulose: makes up 90% of cotton and 50% of wood