

Carbohydrate Structure

FDSC400

Carbohydrates

- $C_x(H_2O)_y$
- 70-80% human energy needs (US~50%)
- >90% dry matter of plants
- Monomers and polymers
- Functional properties
 - Sweetness
 - Chemical reactivity
 - Polymer functionality

Simple Sugars

- Cannot be broken down by mild acid hydrolysis
- C3-9 (esp. 5 and 6)
- Polyalcohols with aldehyde or ketone functional group
- Many chiral compounds
- C has tetrahedral bond angles

Nomenclature

Functional group

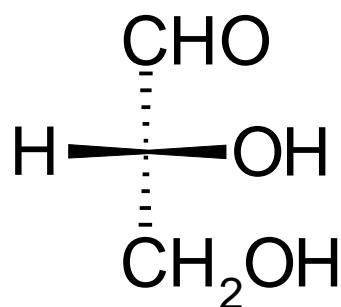
Number of carbons

	Ketone	Aldehyde
4	Tetrose	Tetrulose
5	Pentose	Pentulose
6	Hexose	Hexulose
7	Heptose	Heptulose
8	Octose	Octulose

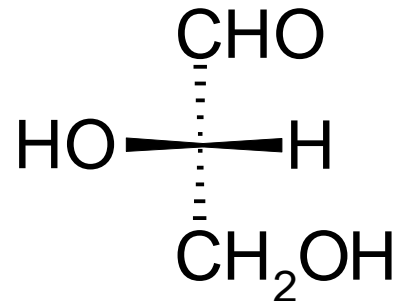
Table 1

Chiral Carbons

- A carbon is chiral if it has four different groups
- Chiral compounds have the same composition but are not superimposable
- Display in Fisher projection



D-glyceraldehyde

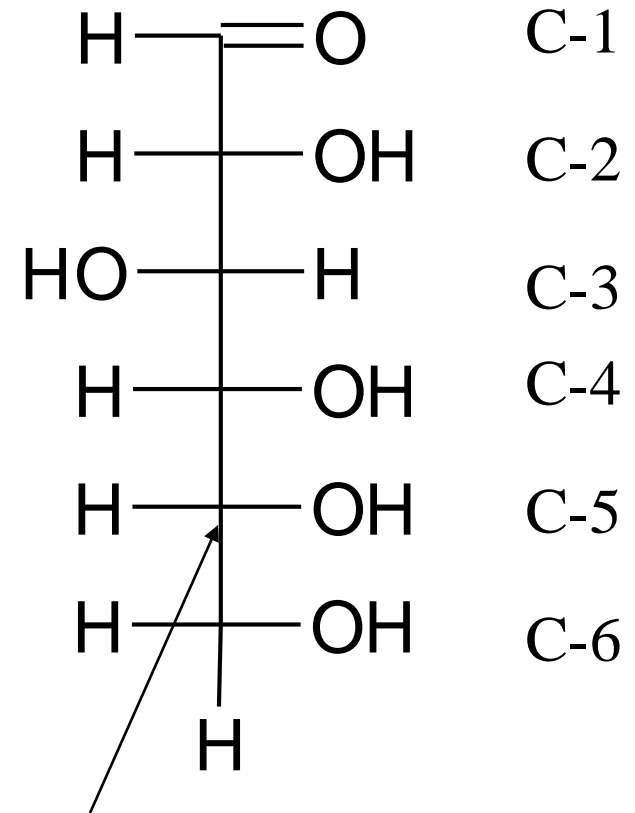


L-glyceraldehyde

ENANTIOMERS

Glucose

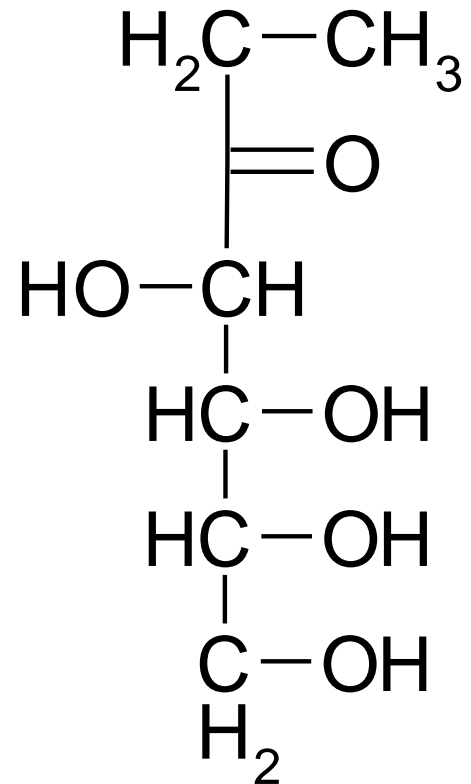
- Fisher projection
- D-series sugars are built on D-glyceraldehyde
- 3 additional chiral carbons
- 2^3 D-series hexosulose sugars (and 2^3 L-series based on L-glyceraldehyde)



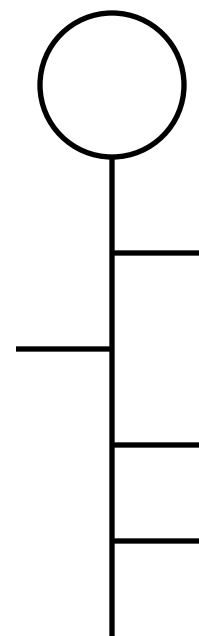
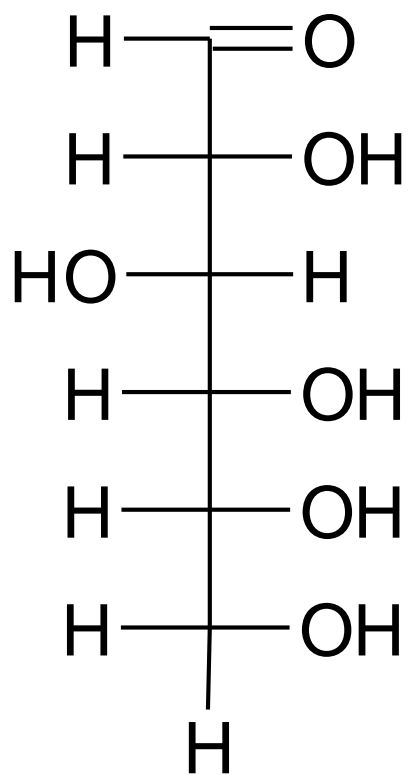
Original D-glyceraldehyde carbon

D-Fructose

- A ketose sugar
- One less chiral carbon than the corresponding aldose
- Sweetest known sugar



The Rosanoff Projection



D-Hexosulose Isomers

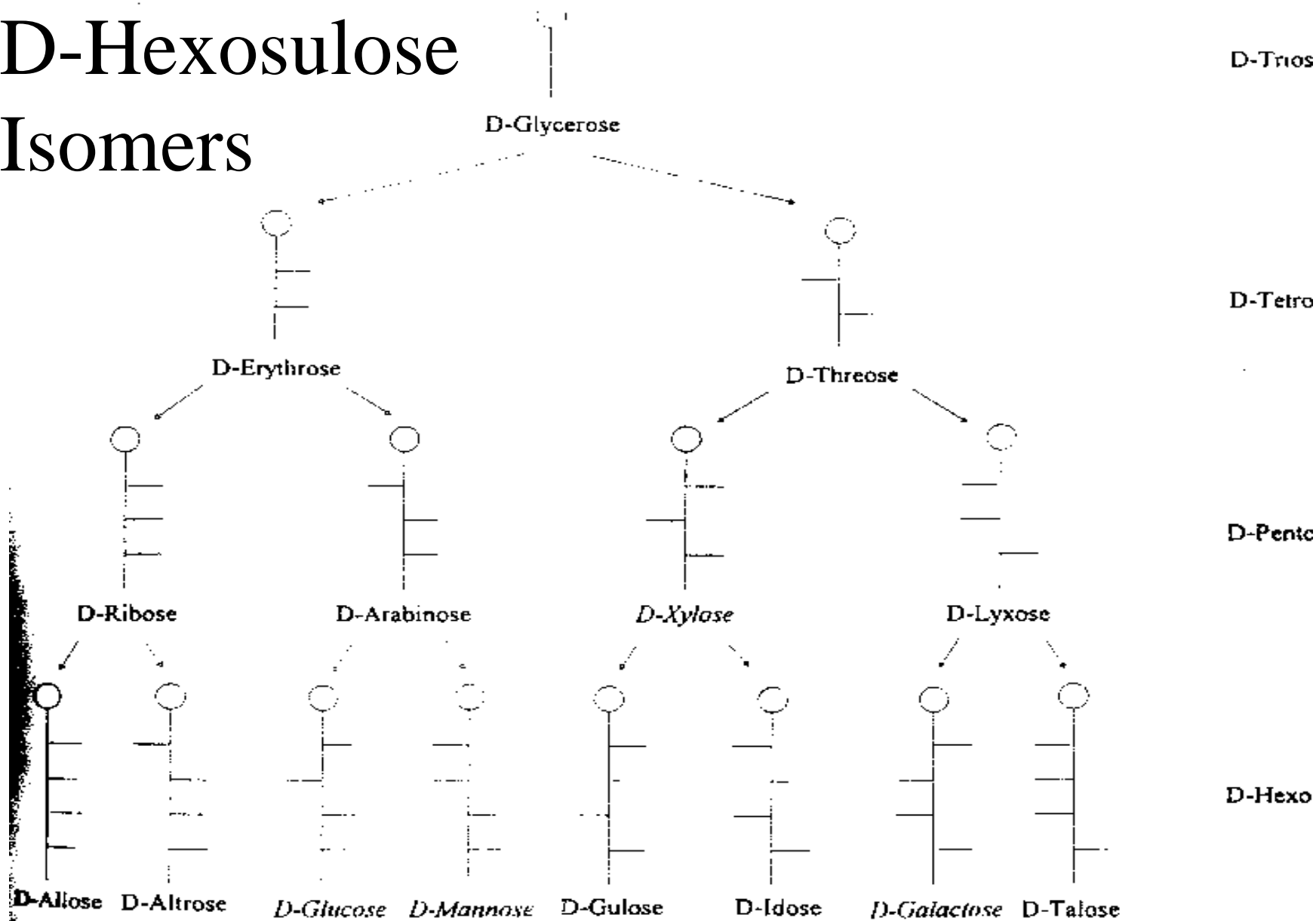


FIGURE 3 Rosanoff structure of the D-aldoses containing from three to six carbon atoms

D-Hexosulose Isomerization

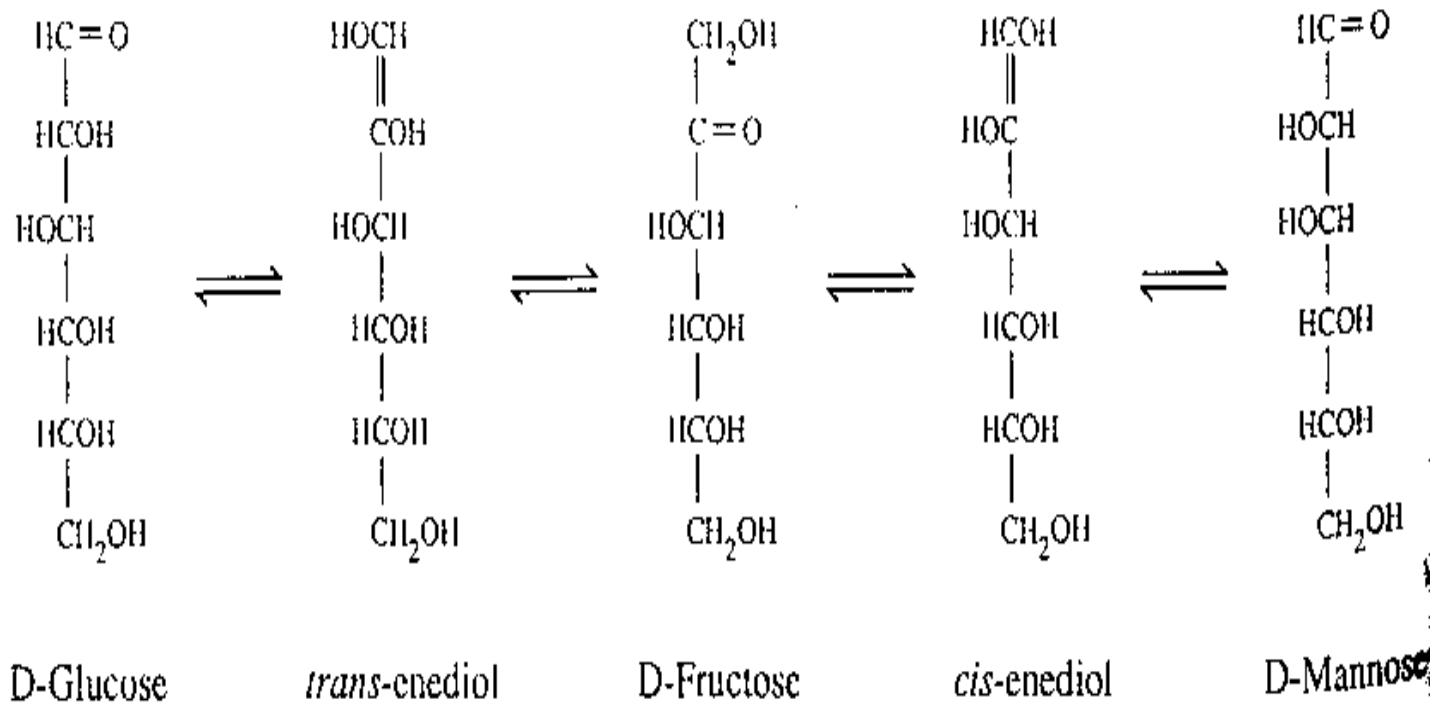


FIGURE 5 Interrelationship of D-glucose, D-mannose, and D-fructose via isomerization.

Ring Formation

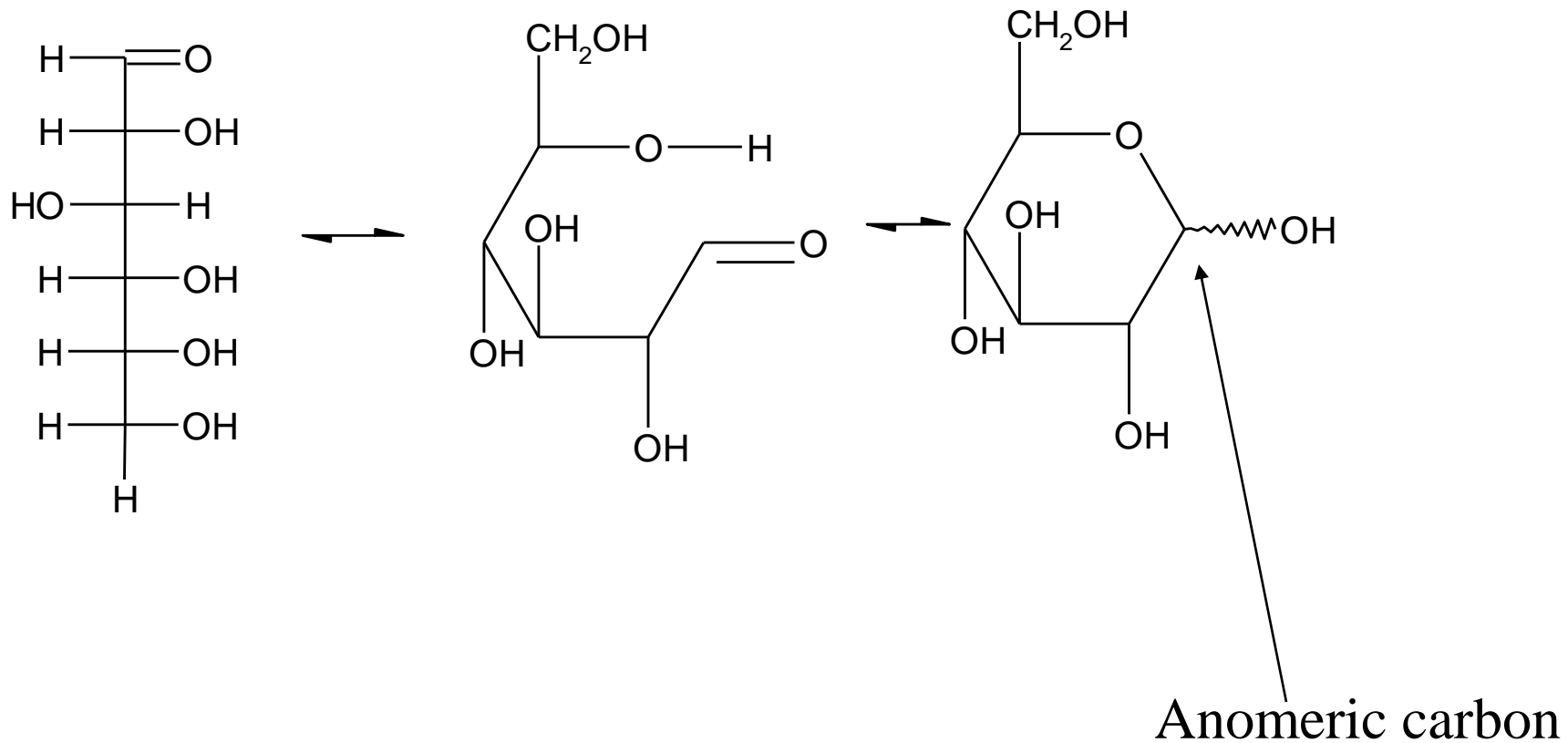
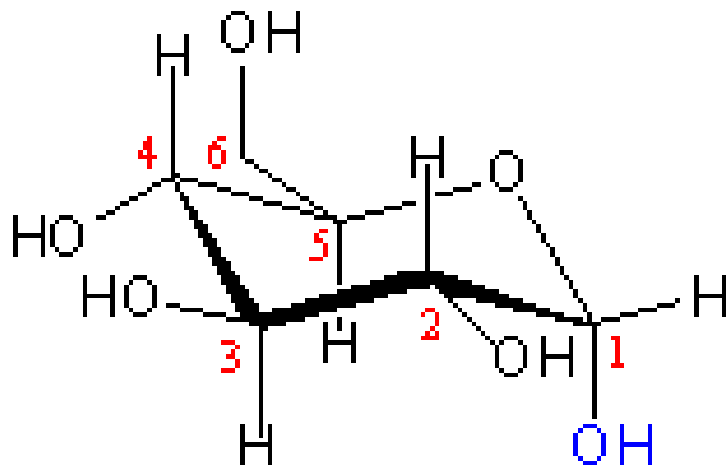
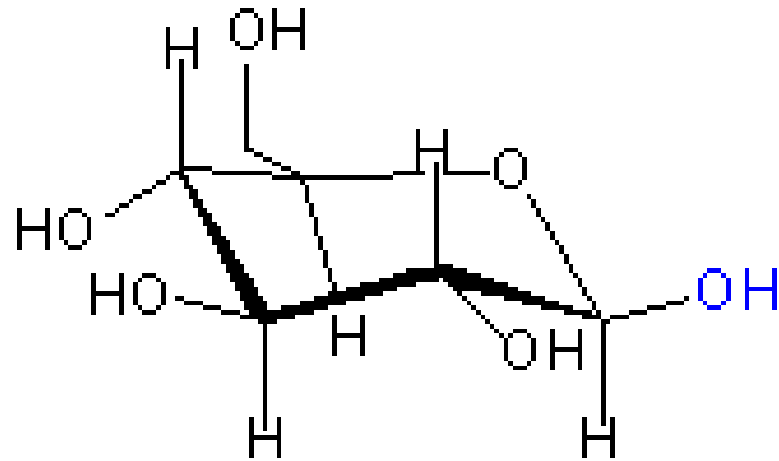


Figure 7

Anomeric Structures



α -D-glucopyranose



β -D-glucopyranose

Acyclic and Cyclic Glucose

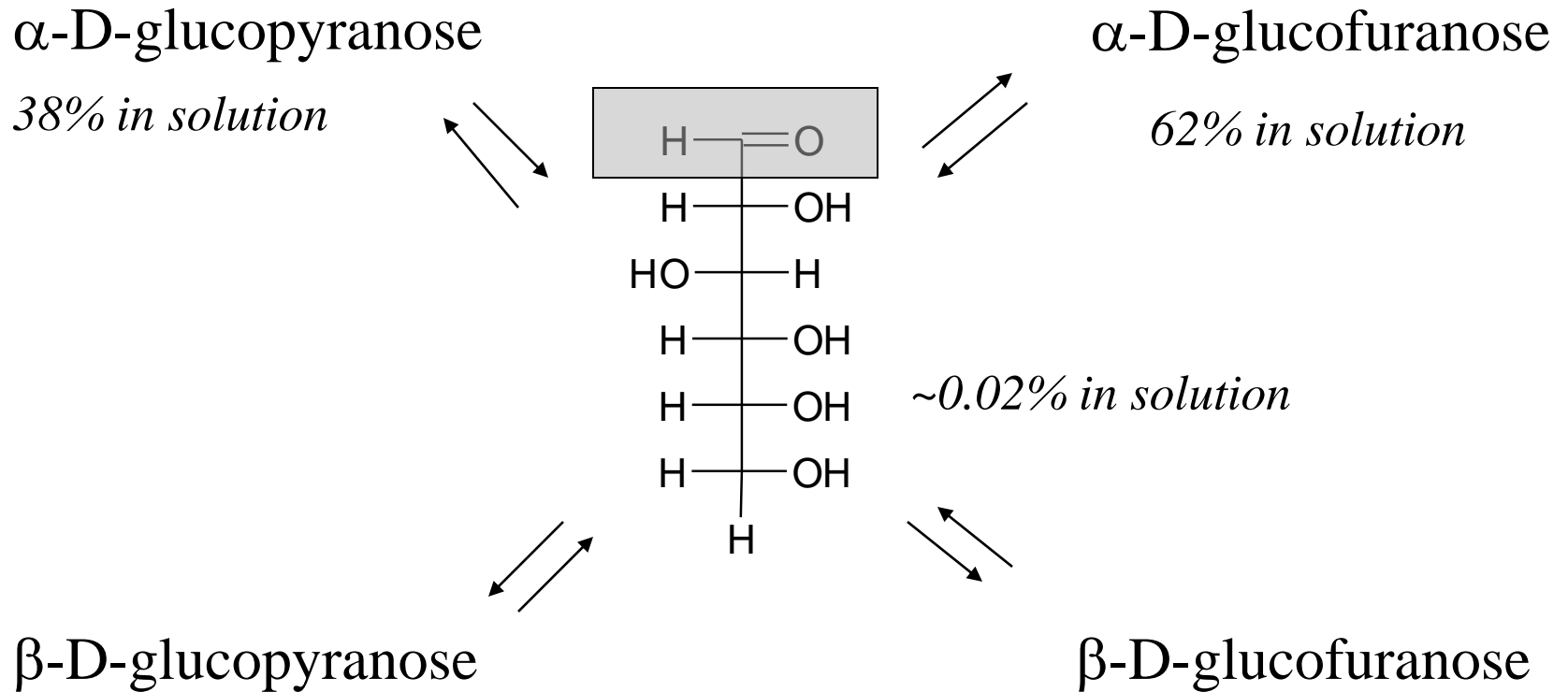


Figure 12

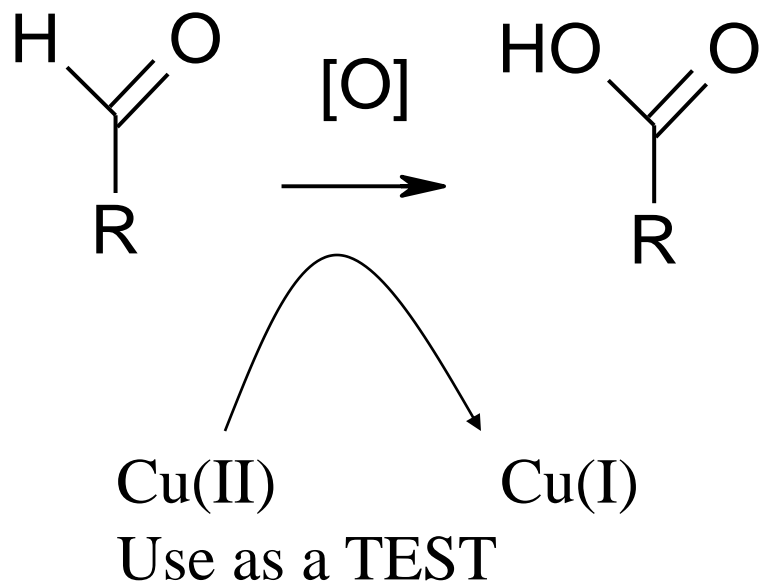
Ring Formation

- Intramolecular reaction between alcohol and carbonyl to form a ring
 - 6-membered rings are **pyranose**
 - 5-membered are **furanose**
- Generates a new α -carbon and two additional anomers (α - and β -)

Oxidation

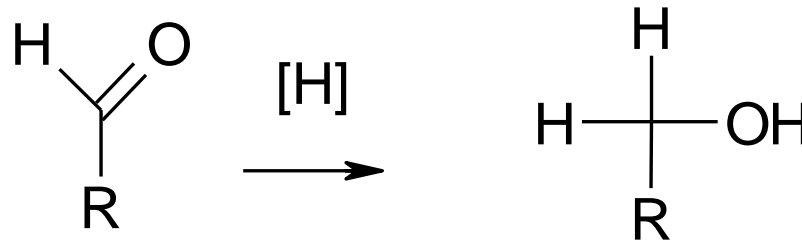
(or “*What does it mean to be a reducing sugar*”)

- Aldehydes can be oxidized to corresponding carboxylic acids



Reduction

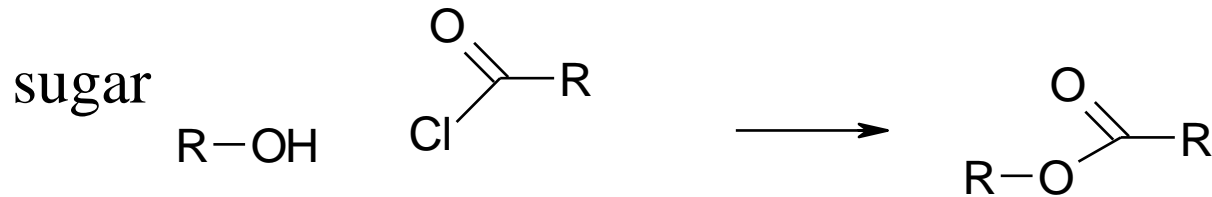
- Carbonyl groups can be reduced to alcohols (catalytic hydrogenation)



- Sweet but slowly absorbed
- Glucose is reduced to sorbitol (glucitol)
- Xylose can be reduced to xylitol
- Once reduced – less reactive; not absorbed

Esterification

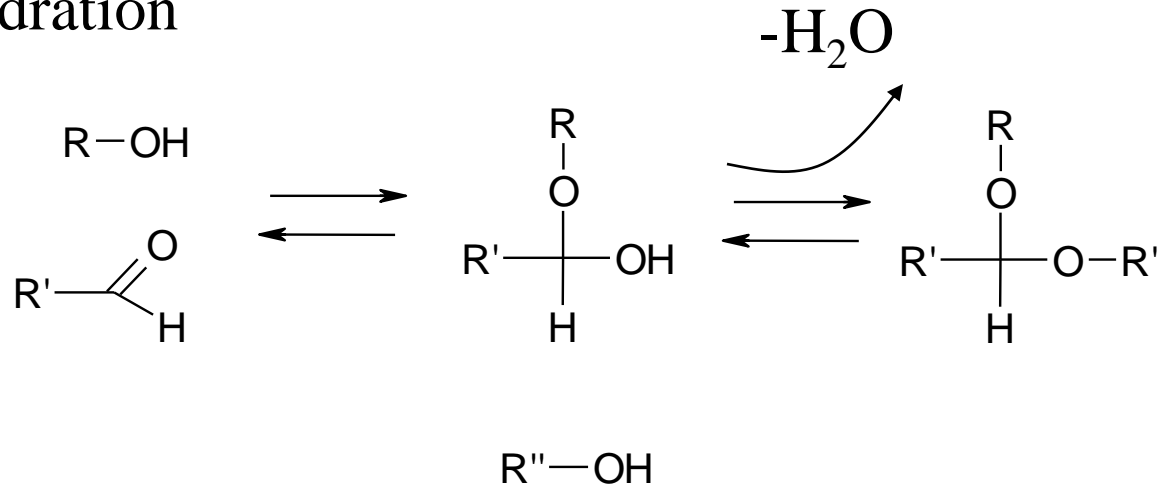
- An acid chloride or acid anhydride can add to an alcohol to form an ester



- Frequent way to react with a fatty acids
 - A few substituents to form a surfactants
 - 6-8 to form OLESTRA

Dimerization

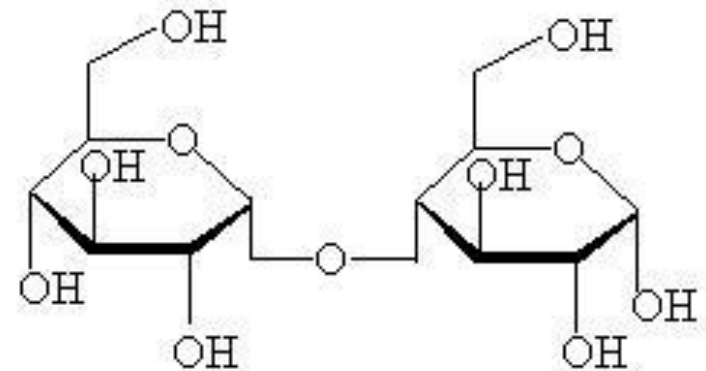
- An alcohol can add to the alcohol of a hemiacetal (formed after ring formation) to form an acetal
- Dehydration



- Depending which conformation the hemiacetal is, the link can either be α - or β -, once link is formed it is **fixed**

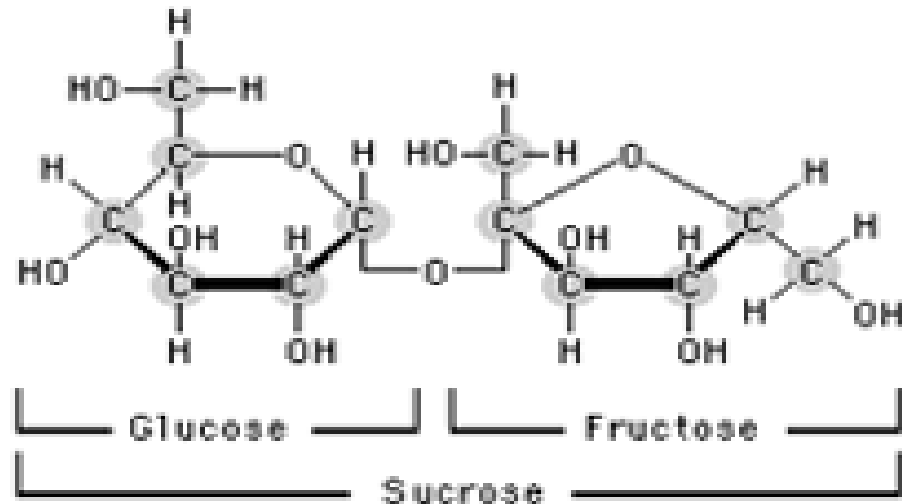
Example Simple Sugars

- **Maltose**
- Malt sugar, enzymatic degradation product from starch
- Mild sweetness characteristic flavor
- Two glucose pyranose rings linked by an α -1-4 bond
- Ring can open and close so a **REDUCING SUGAR**



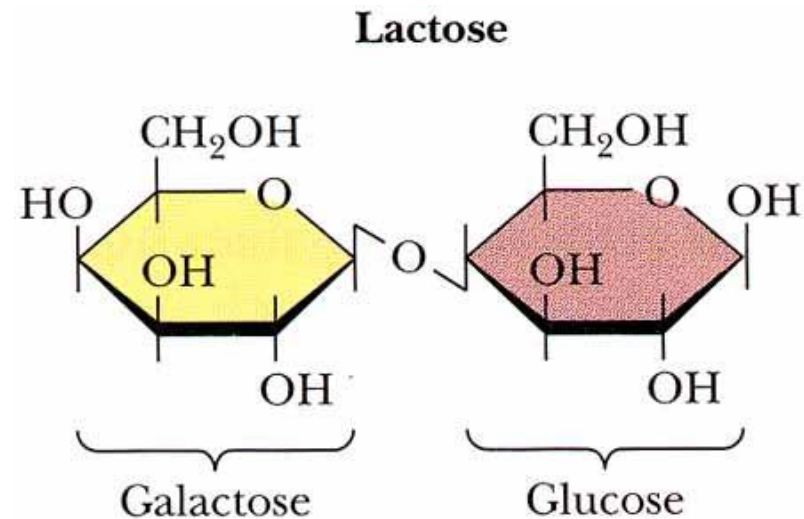
Example Simple Sugars

- **Sucrose**
- Table sugar
- α -glucopyranose and β -fructofuranose in an α , 1-1 link
- The rings cannot open so NOT a reducing sugar
- Easily hydrolyzed
- Used to make caramels



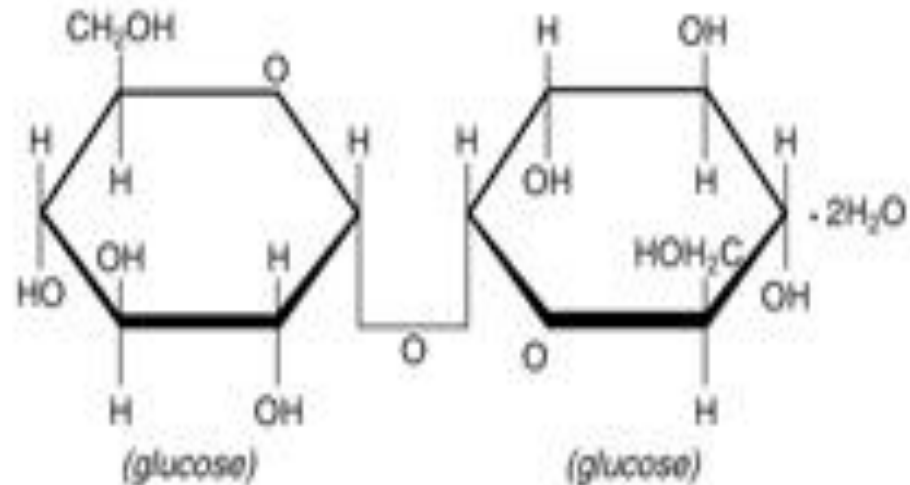
Example Simple Sugars

- **Lactose**
- ~5% milk (~50% milk solids). Does not occur elsewhere
- Glucose-galactose linked by 1-4 β glycosidic bond.
- Galactose opens and closes so REDUCING sugar
- Lactase deficiency leads to lactose intolerance. (More resistant than sucrose to acid hydrolysis).



Example Simple Sugars

- **Trehalose**
- Two glucose molecules with an a 1,1 linkage
- Non reducing, mild sweetness, non-hygroscopic
- Protection against dehydration



Browning Chemistry

- What components are involved? What is the chemistry?
- Are there any nutritional/safety concerns?
- Are there any positive or negative quality concerns?
- How can I use processing/ingredients to control it?

Types of Browning

- Enzymatic
- Caramelization
- Maillard
 - Ascorbic acid browning
- (Lipid)

Polymers lead to color – Small molecules to flavor

Caramelization

- Heat to 200°C
 - 35 min heating, 4% moisture loss
 - Sucrose dehydrated (*isosacchrosan*)
 - 55 min heating, total 9% moisture loss
 - Sucrose dimerization and dehydration → *caramelan*
 - 55 min heating. Total 14% moisture loss
 - Sucrose trimerization and dehydration → *caramelen*
- More heating → darker, larger polymers
→ insolubilization
- Flavor

Maillard Browning

- “the sequence of events that begins with reaction of the amino group of amino acids with a glycosidic hydroxyl group of sugars; the sequence terminates with the formation of brown nitrogenous polymers or melanoidins”
 - John deMan

Maillard Browning

1. Formation of an N-glucosamine

Esp LYSINE

2. Amadori Rearrangement

3. (*Formation of diketosamine*)

4. Degradation of Amadori Product

Mild sweet flavor

5. Condensation and polymerization

color

Involvement of Protein -Strecker Degradation-

- Amine can add to dicarbonyl
 - Lysine particularly aggressive
- Adduct breaks down to aldehyde
 - Nutty/meaty flavors
 - Nutritional loss

Nutritional Consequences

- Lysine loss
- Mutagenic/carcinogenic heterocyclics
- Antioxidants

Control Steps

- Rapidly accelerated by temperature
- Significant acceleration at intermediate water activities
- Sugar type
 - Pentose>hexose>disaccharide>>polysaccharide
- protein concentration (free amines)
- Inhibited by acid
 - amines are protonated
 - and used up, pH drops
- Sulfur dioxide