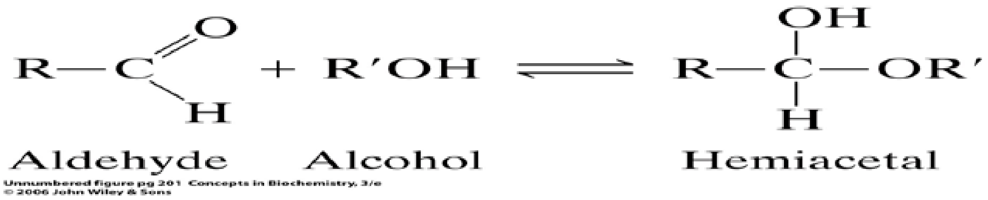
Ring structure of aldoses and ketoses (Cyclization)

- In solution, monosaccharides are cyclic – especially C_5 and C_6 sugars
- Less then 1% of carbonyl (C=O) exist in an open chain form.
- Predominantly found in **ring form**.
- involving reaction of C-5 OH group with the C-1 aldehyde group or C-2 of keto group.
- Drawn as **Haworth projections** - **Show all hydroxyls, oxygens, and hydrogens - no carbons**

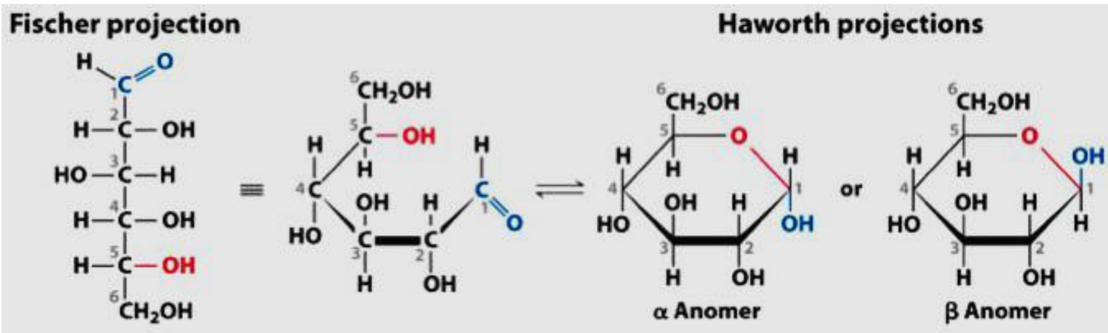
- **Two cases of cyclization**:

1- **Hemiacetals**:

Carbonyl reacting with hydroxyl group addition product called hemiacetal. Carbon center bonded to one R-group, a H atom, an -OH and an –OR



In D-Glucose C_1 carbonyl group (aldehyde) interacts with alcohol on C_5 to form a six-membered ring cyclic hemiacetal, with C_6 above the ring structure.



Reaction called an **aldol condensation**

o Form a 5 or 6 membered ring

o The C_1 carbonyl carbon becomes a new chiral center - a new C_1 hydroxyl

New C1 hydroxyl = anomeric carbon

• The carbonyl carbon in the straight chain form

• Carbon bonded to both the ring oxygen and a hydroxyl group in the cyclic form

o Hydroxyl group is either above or below the ring – **two forms (alpha) and (beta)**

for D-sugars:

• **α- anomer: hydroxyl group BELOW ring (down)**

• **β– anomer: hydroxyl group ABOVE ring (up)**

- Only anomeric carbon –OH is designated ***α*** or **β**

- **Going from Fischer projections to Haworth**

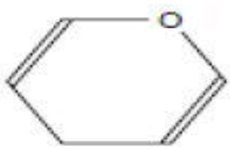
- **numbering** remains the same for the carbons .

- **If –OH is on the right, points DOWN in Haworth**

- **If –OH is on the left, points UP in Haworth**

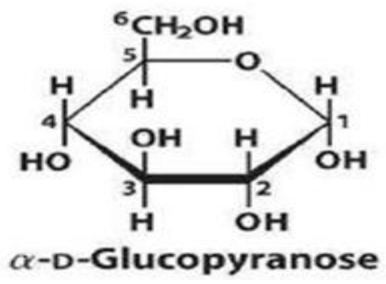
- Terminal CH_2OH **ALWAYS points UP relative to anomeric carbon in D sugars**

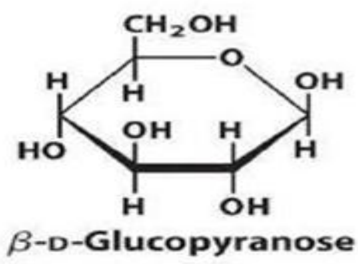
❖ Six membered rings are derived from cyclic compound pyran and **called pyranoses**



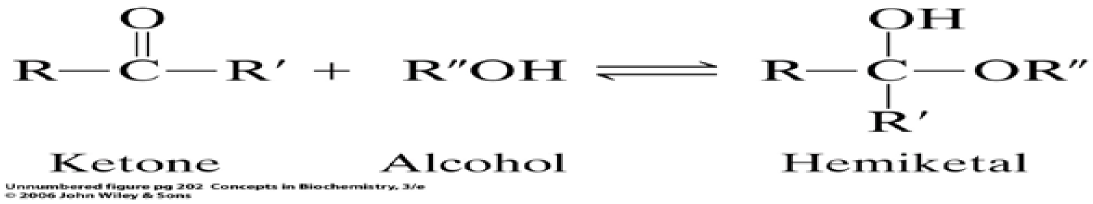
Pyran

IUPAC nomenclature of α-D-glucose is α-D-glucopyranose and β-D-glucose is β-D-glucopyranose



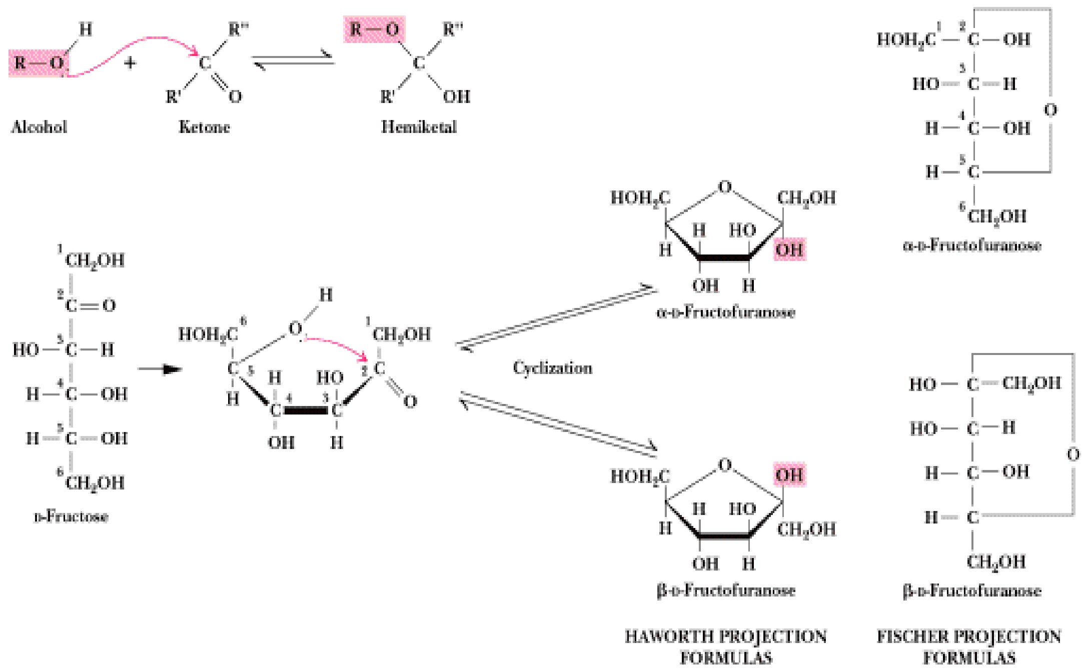


2- HEMIKETALS



Hemiketal functional group includes a carbon center with **2** R-groups, an –OH and an –OR'' group.

- Formed when C_5 hydroxyl interacts with C_2 carbonyl of a ketose
- Example: **D-fructose cyclization**



- Lone pair of electrons on –OH at position C_5 attacks carbonyl at C_2 forming the ring

- **Anomeric carbon is C_2**

- Hemiketals also have **α and β anomers**

- Depends on stereochemistry of –OH at **C_2**

o **Down = alpha**

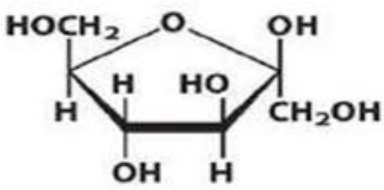
o **Up = beta**

- Note: Also have a CH_2OH at C_1 – becomes the other group off of the anomeric C_2 carbon

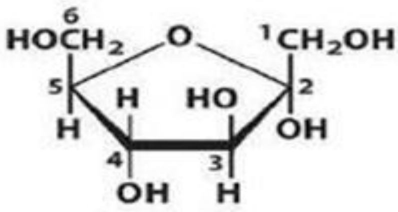
❖ five membered rings are derived from cyclic compound furan and **called furanoses**

Furan

IUPAC nomenclature of α-D-fructose is α-D-fructofuranose and β-D-fructose is β-D-fructofuranose



β-D-Fructofuranose

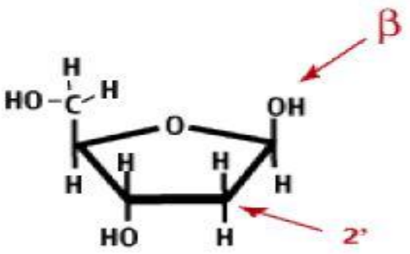


α-D-Fructofuranose

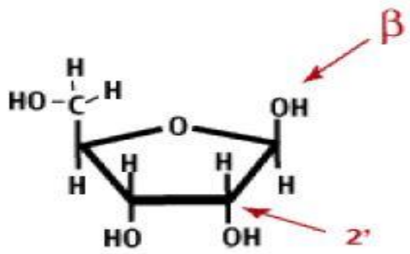
Deoxy sugars

- **Deoxy sugars** are carbohydrate derivatives that are lacking an -OH hydroxyl group at the 2'-Carbon of the sugar molecules.
- For example :

Deoxyribose is the most commonly known deoxy sugar because it is the exact sugar used in the backbone of our DNA double helices.



β -2-deoxyribofuranose



β - ribofuranose

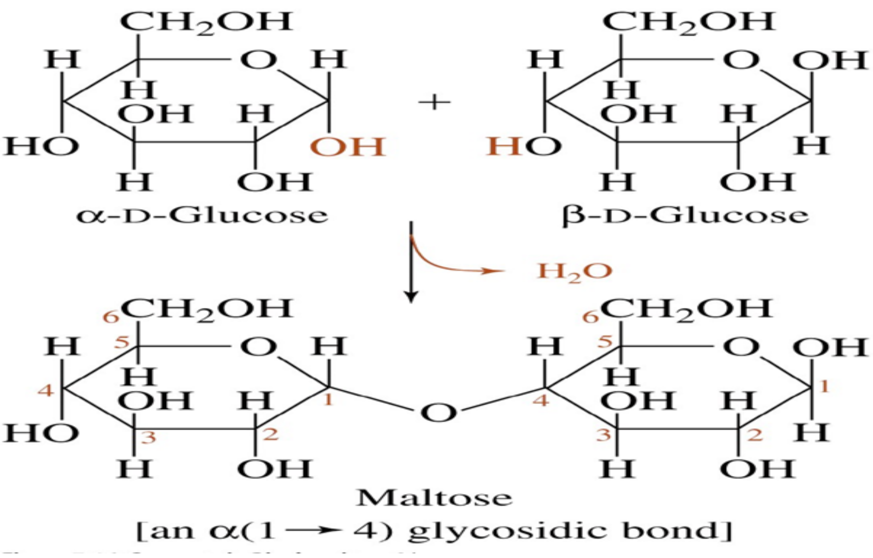
Disaccharides

- Formed between monosaccharides via a **glycosidic bond**
- involves OH of anomeric carbon and any other OH
- In the reaction, lose elements of H_2O
- **α (1−4)**
- **α** = alpha = configuration of anomeric carbon
- 1 = number of anomeric carbon
- 4 = denotes other carbon involved in glycosidic bond
- Anomeric carbon gets fixed/locked into either **α or β configuration** (**can't mutarotate**)
- Having lots of variation in monosaccharides and variation in how they are linked leads to many different disaccharides

For example :

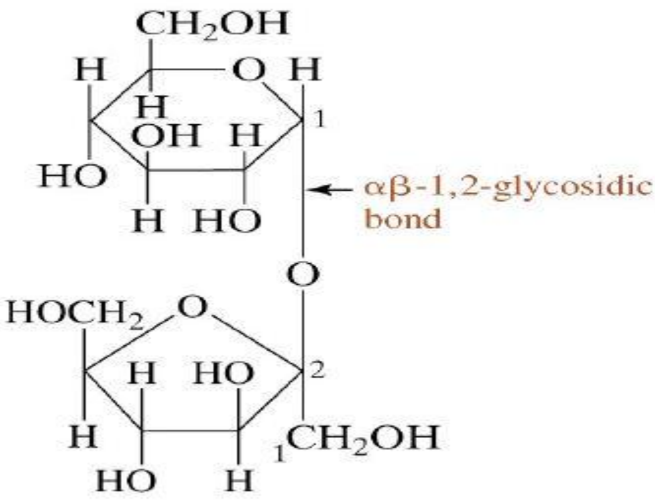
Maltose

- present in malt.
- maltose consists of two units of D-glucopyranose.
- α-1,4-glycosidic bond.
- maltose is a reducing sugar 2 glucose units.
- produced when starch breaks down.



Sucrose (table sugar or cane sugar)

- fructose and glucose
- sucrose is the most abundant disaccharide in the biological world; it is obtained principally from the juice of sugar cane and sugar beets
- Glucose in α,β (1-2) linkage with fructose
- sucrose is a non-reducing sugar.

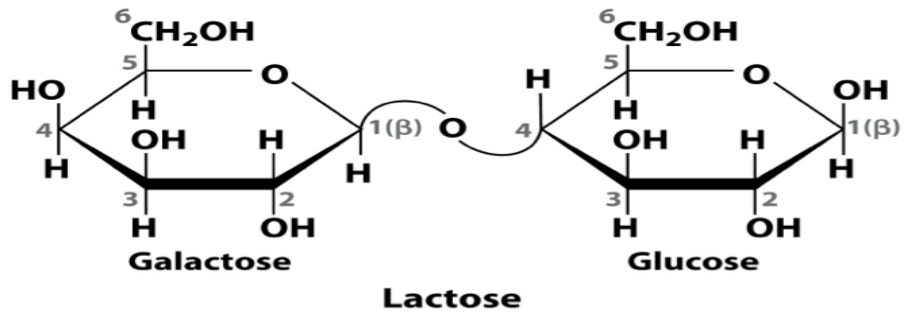


Sucrose [glucose-α, β (1→2)-fructose]

Lactose

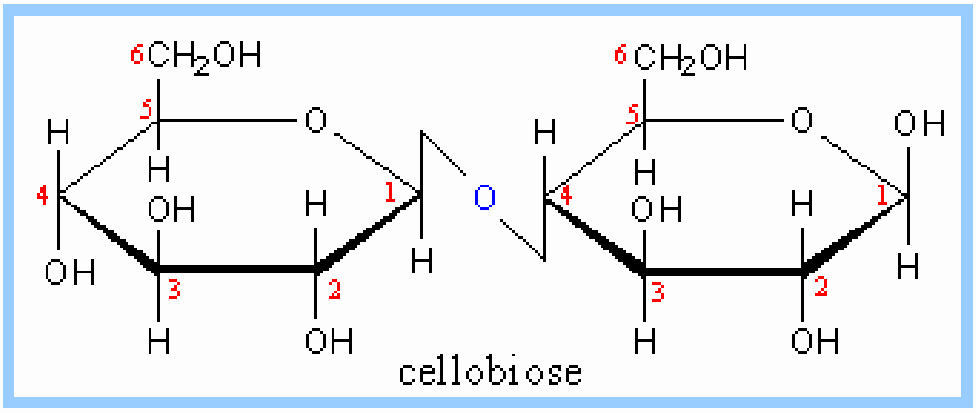
- Galactose in a **β(1-4)** linkage with glucose

- Galactose is converted by the body to glucose and glucose used for energy
- Found in dairy products
- Enzyme **Lactase** present in small intestine hydrolyzes lactose to galactose and glucose.



Cellobiose

- 1st glucose is β−linked to the 4th carbon of another glucose
- glucose β(1-4) glucose



POLYSACCHARIDES

A- Amylose

Linear, unbranched chain of **α(1-4) D-glucose molecules**

- Disaccharide repeating unit = **Maltose**
- Each amylose has 2 ends:
  - Non-reducing End (Glucose molecule with free –OH on C_4)
  - Reducing End (Glucose molecule with free –OH on C_1 – anomeric carbon

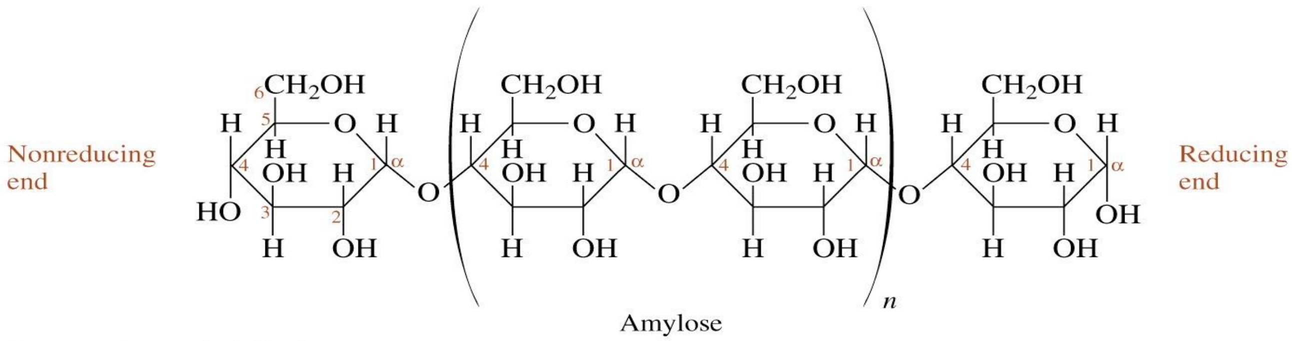
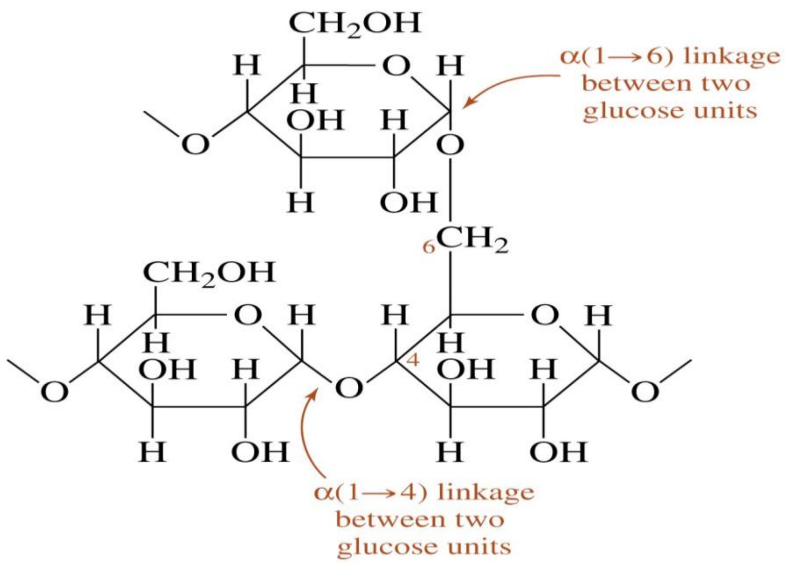


Figure 7-20a Concepts in Biochemistry, 3/e

B- Amylopectin

Main backbone is amylose (linear) with D-glucose molecules in α(1-4) linkage

- Also has **Branches: Connect to backbone and to each other by α(1-6) linkages**
- Branch points every 25-30 glucoses
- Has **one reducing end**
- Has many non-reducing ends



Cellulose

- Cellobiose is the repeating unit in long polymers of cellulose, the major structural component of plants especially wood and plant fibers
- Humans do NOT have the capacity to digest cellobiose or cellulose

- Can’t digest cellulose because we lack the enzyme
- **cellulase** that breaks β(1-4) linkages between glucose monomers .
- Ruminant animals (cattle, deer, giraffes, camels) CAN digest! Bacteria live in the rumen in GI tract and secrete **cellulase.**
- Termites also have bacteria in digestive tract that secrete **cellulase to digest wood** fibers.