

Lecture 24: Carbohydrates 2

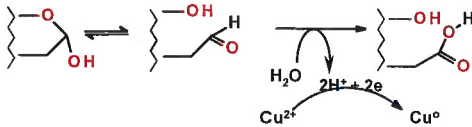
Goals:

- Glycosidic bond formation
- Disaccharide nomenclature
- Structure of lactose & fructose
- Energy storage polysaccharides
- Structural polysaccharides
- Modified glucose structure
- Bacterial cell walls

Disaccharides: Linkage of the anomeric carbon of one monosaccharide to the OH of another monosaccharide via a **condensation** reaction. The bond is termed a **glycosidic bond**.

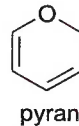
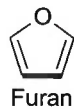
The anomeric carbon is the site of attack by another -OH group, why is this carbon the preferred site for nucleophilic attack?

Reducing End: The end of the disaccharide that contains the free anomeric carbon is referred to as the **reducing end** because it is capable of reducing various metal ions, such as Cu^{2+} .



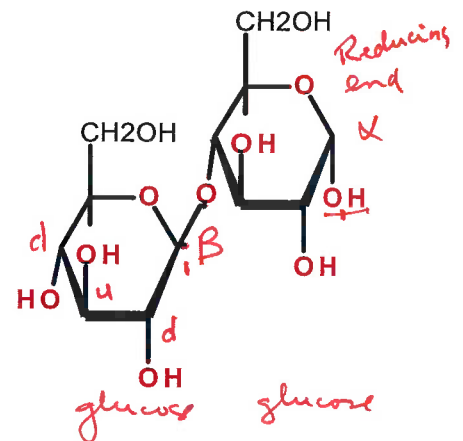
Nomenclature: To describe the chemical structure of disaccharides you need to specify the following:

1. The names of the two monosaccharides.
2. Their cyclic form:
 - a) furanose for 5 membered rings
 - b) pyranose for 6 membered rings
3. How they are linked together (one anomeric is *always* used)
4. The configuration of the anomeric carbon on *each* sugar.

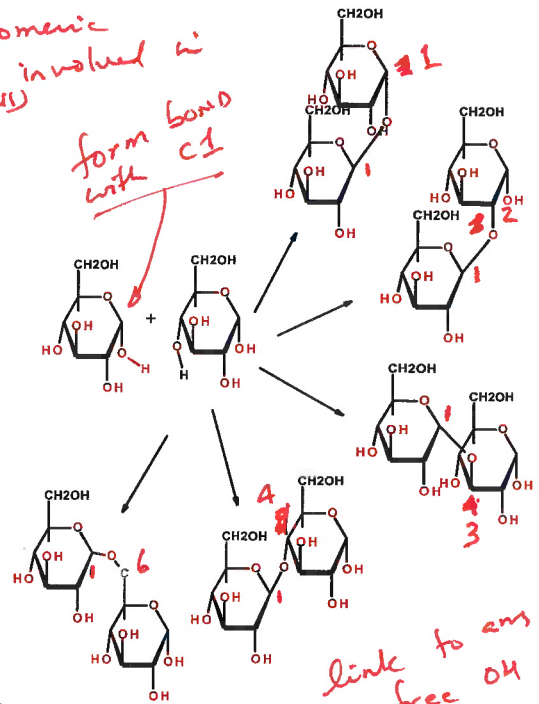
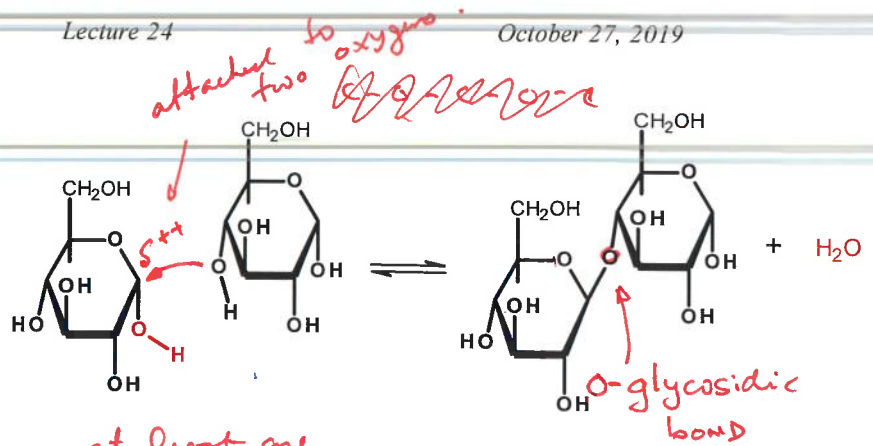


The six simple rules for naming disaccharides are as follows:

1. The **non-reducing** end defines the first sugar, if there is no reducing end, then either end can be used to begin naming.
2. Configuration of the anomeric carbon of the 1st sugar (α, β) ✓
3. Name of 1st saccharide, root name followed by pyranosyl (6-ring) or furanosyl (5-ring)
4. Atoms which are linked together, 1st sugar then 2nd sugar.
5. Configuration of the anomeric carbon of the second sugar (α, β) (Often omitted if the anomeric carbon is free since α & β forms are in equilibrium.)
6. Name of 2nd monosaccharide, root name followed by pyranose (6-ring) or furanose (5-ring). If both anomeric carbons are involved, then the name ends in 'oside', not 'ose')

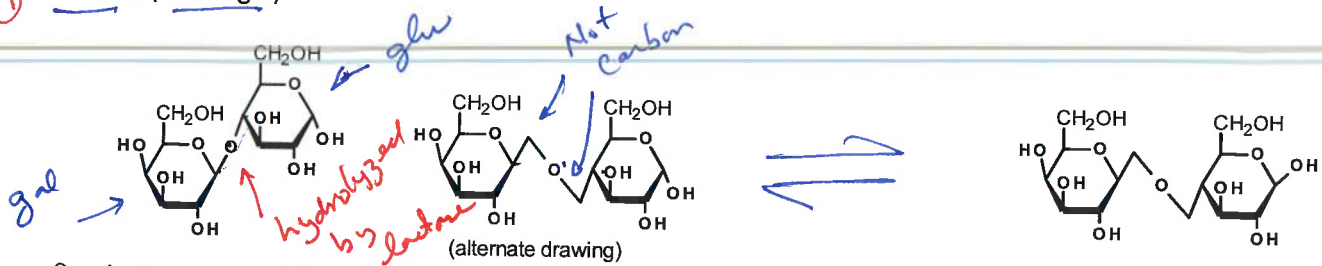


β -gluco pyranosyl (1-4) -
 α -gluco pyranose 1



link to any free OH 2nd sugar.

① Lactose (milk sugar):



β -galactopyranosyl-(1 \rightarrow 4)- α -glucopyranose

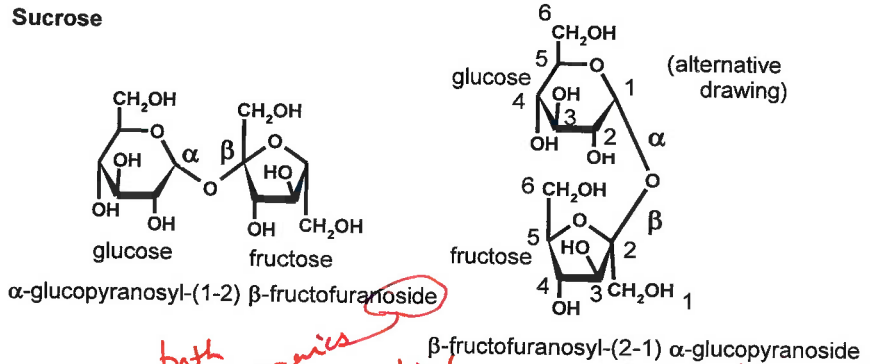
β -galactopyranosyl-(1 \rightarrow 4)- β -glucopyranose

Lactose is the major sugar in mammalian milk.

- Infants produce the enzyme lactase to hydrolyze the disaccharide to monosaccharides.
- Some adults have low levels of lactase. This leads to *lactose intolerance*. The ingested lactose is not absorbed in the small intestine, but instead is fermented by bacteria in the large intestine, producing uncomfortable volumes of CO₂. It is possible to purchase dairy products that have been treated with lactase.

② Sucrose (table sugar): The anomeric carbon of glucose forms a glycosidic bond to the anomeric carbon of fructose.

Sucrose



Polysaccharides: Many monosaccharides linked by glycosidic bonds. Most polysaccharides are polymers of either glucose, or modified glucose.

Short-hand nomenclature: In the case of homo-polymers, the short-hand notation is to simply describe the linkage between the glucose units: both the conformation of the anomeric carbon and the carbons participating in the glycosidic bond, i.e. β (1-4) instead of β -glucopyranosyl (1-4) β glucopyranose.

Energy Storage Polysaccharides

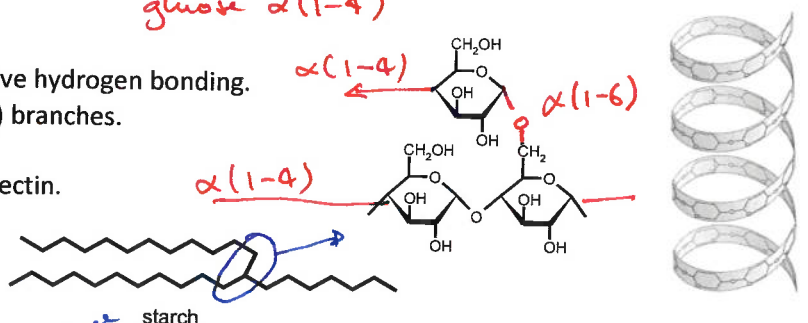
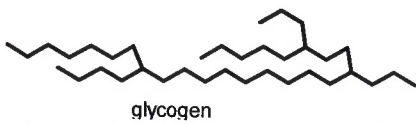
1. Starch [plants] (mixture of amylose and amylopectin).

- amylose = α (1-4) glucose.
- Similar in structure to α -helix in proteins: forms a helix with extensive hydrogen bonding.

2. Amylopectin [plants] = amylose plus α (1-6) branches.

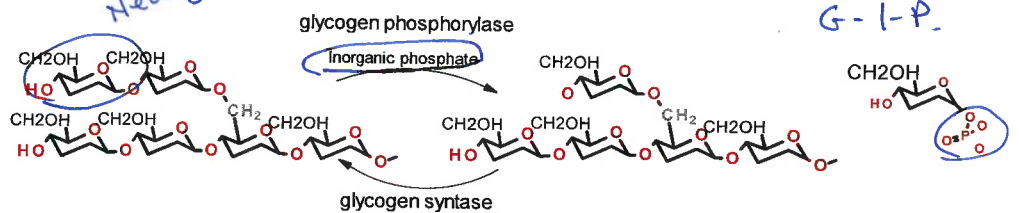
* 3. Glycogen [animals] =

- more highly branched than amylopectin.



Release of glucose from glycogen/Starch:

- glucose units released from **non-reducing end** by the enzyme **glycogen phosphorylase**, producing glucose-1-phosphate (G-1-P). G-1-P is used to generate energy in metabolism.

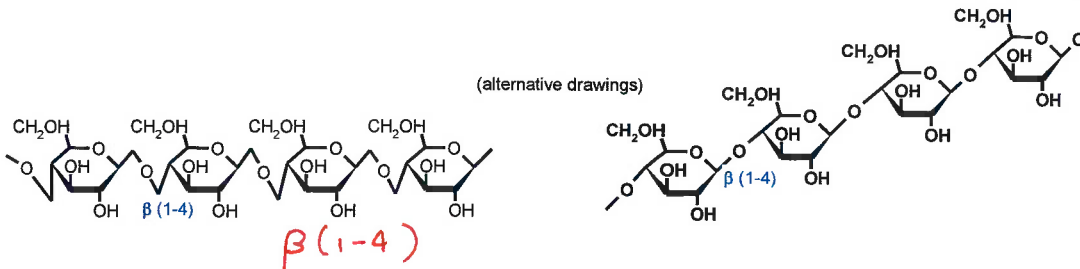
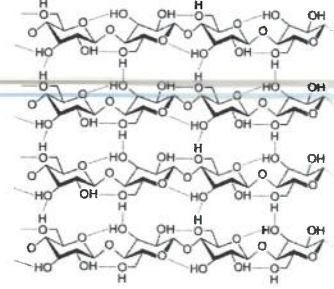


- The enzyme glycogen synthase adds the glucose to the non-reducing end.

Structural Polysaccharides

1. Cellulose: Structural polysaccharide of plants.

- β 1-4 glucose, can't be digested by mammalian enzymes.
- Similar in structure to β -sheets in proteins: forms flat sheets with multiple hydrogen bonds between strands.
- Digested by symbiotic microorganisms (such as those in termites)



2. Bacterial Cell Walls:

- Polysaccharide chains of alternating N-acetylglucosamine (NAG) and N-acetylmuramic acid (NAM)
- Muramic acid on NAM linked to a small peptide (L-Ala D-Gln L-Lys D-Ala)- note unusual D-amino acids.
- NAM peptide chains are crosslinked with pentaglycine bridges that extend off of terminal Ala and join to L-Lys sidechain on adjacent chain, forming a tough crosslinked cell wall.
- Synthesis of bacterial cell walls is inhibited by antibiotic penicillin.

