Lecture 25: Carbohydrates & Gibbs Free Energy

Assigned reading in Campbell: Chapter 16.3-16.5
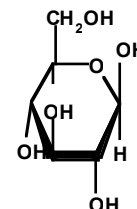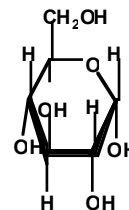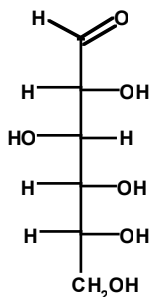
Key Terms:
- **Cellulose (β 1-4 glucose)**
- **Amylose (α 1-4 glucose)**
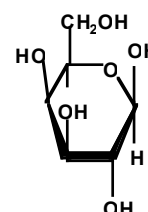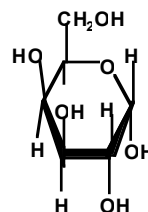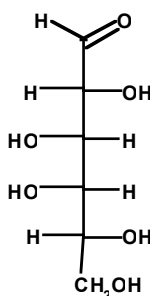- **Amylopectin & Glycogen (α1-4 and 1-6 glucose)**

A. Monosaccharides:

Presentation of structures

1. Fischer drawing - linear chain.
2. Haworth - Ring form, indicating chirality at each center.

Note: Glucose & Galactose are epimers because they differ in configuration about a single chiral center, C4.
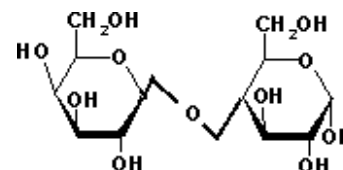
B. Disaccharides

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.***

Nomenclature: To describe dissacharides you need to specify the following:

1. The names of the two saccharides
2. Which OH group forms the link
3. The configuration of the anomeric carbons on both monosaccharides.

The Six Simple Rules for Naming Disaccharides are as follows:

1. Type of atom involved in linkage (Oxygen or nitrogen)
2. Configuration of the anomeric hydroxyl of the 1st sugar (α or β)
3. Name of 1st monosaccharide, root name followed by pyrano**syl** (6-ring) or furano**syl** (5-ring)
4. Atoms which are linked together, 1st sugar then 2nd sugar.
5. Configuration of the anomeric hydroxyl of the second sugar (α or β) (often omitted)
6. Name of 2nd monosaccharide, root name followed by pyran**ose** (6-ring) or furan**ose** (5-ring)

_____ ____ _____ _____ _____ _____
 1   2   3   4   5   6

O-β-galactopyranosyl-(1-4)-α-glucopyranose

**C. Polysaccharides:** Many monosaccharides linked by glycosidic bonds.

Most polysaccharides are polymers of either glucose, or modified glucose.

Shorthand notation. In the case of homo-polymers, the shorthand 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).
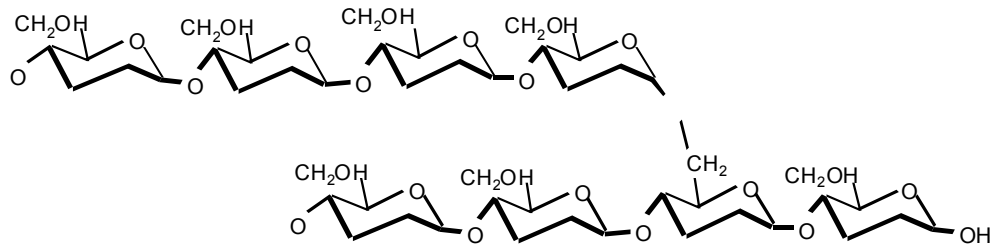
Energy Storage Polysaccharides

1. Starch [plants] (mixture of α amylose and amylopectin).
   - amylose = α(1-4) glucose.
   - Similar in structure to α-helix in proteins: forms a helix with extensive hydrogen bonding.
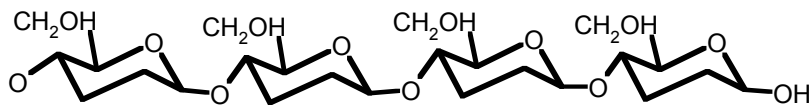

   - Amylopectin [plants] = branched polysaccharide consisting of linear amylose chains linked via α(1-6) linkages every 18-30 residues.

2. Glycogen [animals, mainly in the liver and skeletal muscle] =
   - Highly branched glucose chains linked by α(1-6) linkages every 8-10 glucose residues.
   - glucose units released by the enzyme glycogen phosphorylase, producing glucose-1-phosphate. Glucose-1-phosphate is used to generate energy.
   - more highly branched than amylopectin. What purpose might this serve?
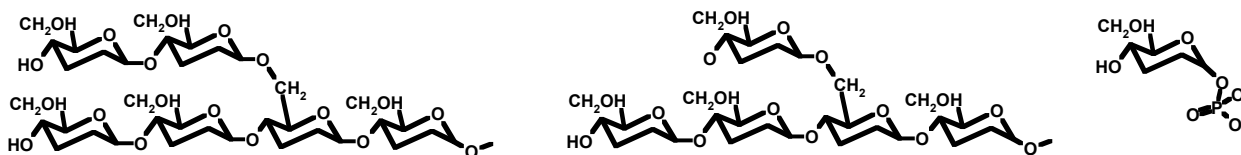
Structural Polysaccharides

Cellulose: Structural polysaccharide of plants.
- β(1-4) glucose, can't be digested by mammalian enzymes.
- Because the linkages are β(1-4) linkages, it forms flat sheets, similar in structure to β-sheets in proteins, with multiple hydrogen bonds between strands.
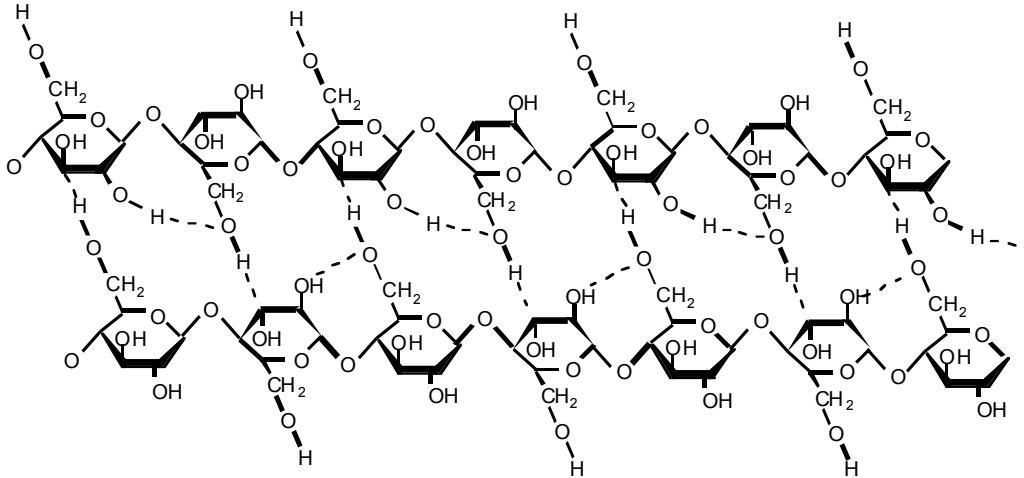

Bacterial Cell Walls:
- Polysaccharide chains of alternating N-acetylglucose amine (NAG) and N-acetylmuraminc acid (NAM)
- Muramic acid on NAM linked to a small peptide (Ala-Gln-Lys-Ala)
- NAM peptide chains are crosslinked with pentaglycine bridges that extend off of terminal Ala and join to Lys on adjacent chain, forming a tough crosslinked cell wall.
- Synthesis of bacterial cell walls is inhibited by penicillin.
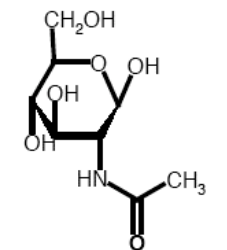
N-acetyl glucosamine (NAG)
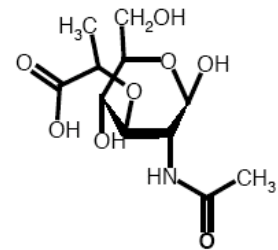
N-acetylmuramic acid (NAM)
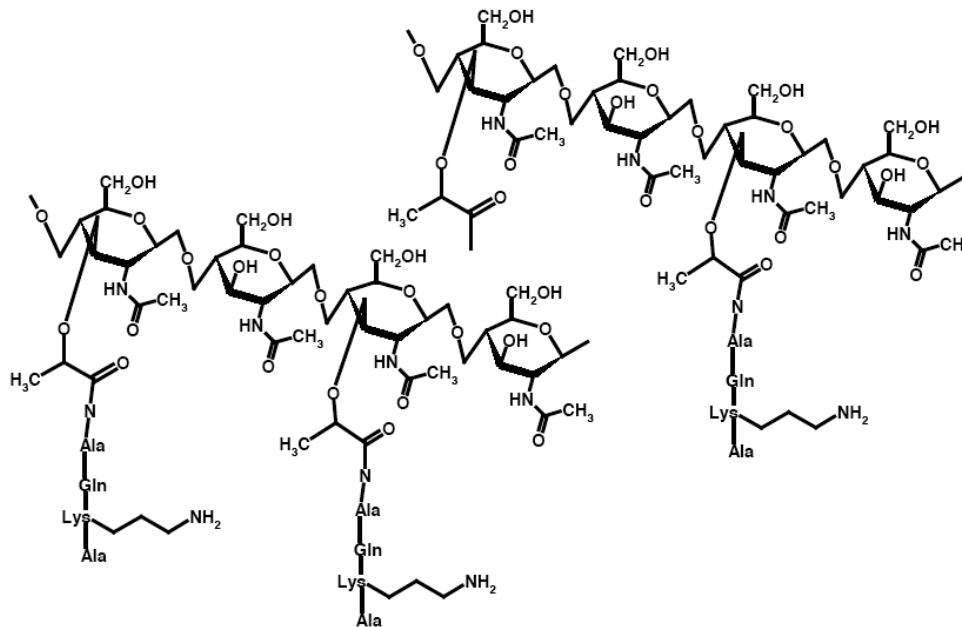
Cellular Biochemical Energetics:

Gibbs free energy (ΔG) versus standard free energy (ΔG°)

Whether a reaction is energetically favorable under cellular conditions depends, at least in part, on the relative concentrations of reactants and products.

Because cellular conditions can vary widely, a set of conditions called **standard state conditions**, have been agreed upon by biochemists to describe the extent to which conversion of a particular reactant to product is thermodynamically favored. This allows easy comparison of experimental results.
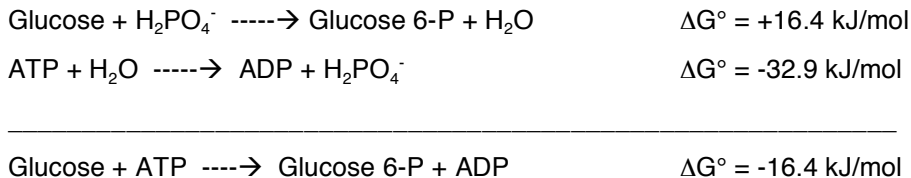

Concentration of each reactant: 1.0 M

pH: usually 7.0

Pressure: 1.0 atm

Temperature: usually 25°C or 298 K

For example, the first step of glycolysis involves the phosphorylation of glucose by hexokinase to form glucose 6-P. Formation of the high energy phosphoester is thermodynamically unfavorable and requires energy input. The energy comes from coupling the reaction to ATP hydrolysis.

Glucose + $H_2PO_4^-$ -----→ Glucose 6-P + H_2O ΔG° = +16.4 kJ/mol

ATP + H_2O -----→ ADP + $H_2PO_4^-$ ΔG° = -32.9 kJ/mol

_____

Glucose + ATP ----→ Glucose 6-P + ADP   ΔG° = -16.4 kJ/mol

The Gibbs Free Energy ΔG, an indication of spontaneity under *any given set of conditions*, is related to the standard free energy ΔG° by the following equation:

$$\Delta G = \Delta G^\circ + RT \ln \frac{[products]}{[reac\tan ts]}$$

$$\Delta G = \Delta G^\circ + RT \ln \frac{[G6P][[ADP]}{[Glu][ATP]}$$

$$\Delta G = -16.4 kJ/mol + (8.3 J/mol)(310K) \ln \frac{(8.3 \times 10^{-5} M)(1.4 \times 10^{-4} M)}{(5.0 \times 10^{-3} M)(1.85 \times 10^{-3} M)} = -33.9 kJ/mol$$

The reaction is significantly more favorable under cellular conditions than at standard state!