Definition: Carbohydrates are polyhydroxyaldehydes or polyhydroxyketones and their derivatives.

Biologically important compounds include:
1. Monosaccharides: Simple sugars that are not broken down by mild hydrolysis. Monosaccharides have the general formula \( C_n(H_2O)_n \). (Fig 7-3, p. 93)
2. Oligosaccharides: Polymers of 2-10 monosaccharides (Fig 7-4, p. 94)
3. Polysaccharides: Polymers of >10 monosaccharides (Fig. 7-6, p. 95)
4. Important Macromolecules that incorporate carbohydrates: Glycoproteins, proteoglycans, nucleic acids, glycolipids, etc.

Nomenclature & Structure:
Monosaccharides have names that end in "ose". Most common monosaccharides contain 3-7 carbons and are named accordingly… triose, tetrose, pentose, hexose, heptose. (see "structure" handout). Aldehyde forms are aldoses. Ketone forms are ketoses. The simplest are glyceraldehyde and dihydroxyacetone.

By convention, in the Fischer projection, the carbonyl carbon is nearest the top of the structure as drawn and the top carbon is #1. Note that C2 of glyceraldehyde has 4 different substituents and is therefore "asymmetric" or "chiral", i.e., glyceraldehyde may exist in two stereoisomeric forms which are mirror images, i.e. enantiomers. Recall that in Fischer projection, substituents to the left and to the right of asymmetric carbons project out of the plane of the paper.

Again, by convention, if the penultimate (next to the last) carbon has its –OH projected to the left, it is in the L configuration; to the right, D configuration. Note that addition of carbons between the carbonyl carbon and the penultimate carbon introduces additional asymmetric carbons, each of which has two different configurations. Thus many different stereoisomers are possible (2n, where n is the number of asymmetric carbons), but only a few are important in biochemistry.

Isomers: same atomic composition, different structures
Enantiomers: Two chiral molecules that are mirror images of each other.
Epimers: Stereoisomers differing only in configuration around a single carbon atom are called epimers. Compare glucose and galactose. They differ only at C4 (the epimeric carbon); compare glucose and mannose, differing only at C2.

Ring formation: sugars containing 5 or more carbons tend to cyclize, forming internal hemiacetal or hemiketal linkages between the carbonyl group and one of the alcohols (hydroxyls). A new asymmetric carbon is thereby introduced, the anomeric carbon, whose configuration is defined as \( \alpha \) (hydroxyl projected to right [down]) or \( \beta \) (projected to left [up]). The carbonyl group, or potential carbonyl group, contains this anomeric carbon and the \( \alpha \) & \( \beta \) forms are called anomers. The \( \alpha \) & \( \beta \) forms are in equilibrium with the straight chain (carbonyl) configuration, and the process of interconversion is called mutarotation. 6-membered rings are related to pyran and are called pyranoses. 5-membered rings resemble furan and are called furanoses. Definition: Anomers are isomers that differ in configuration at the anomeric carbon of the hemiacetal or hemiketal linkage.

Definitions: Carbohydrates are polyhydroxyaldehydes or polyhydroxyketones and their derivatives.
Know aldoses, ketoses, isomers, stereoisomers, enantiomers, epimers, anomers, mutarotation, glycosidic linkages, & reducing sugars.

Haworth perspective: Pyranoses and furanoses are often shown in Haworth perspective, in which substituents shown to the right in Fischer projection are drawn below the plane of the ring; thus at the anomeric carbon, \( \alpha \) is down and \( \beta \) is up. For sugars in D configuration, the terminal-CH\(_2\)OH projects up in Haworth perspective.
Summary of Isomers:

**ISOMERS**: molecules made of the same atoms joined together into different structures

- **Stereoisomers**: Differ in configuration around one or more chiral carbons
- **Enantiomers**: mirror images
- **Anomers**: differ in configuration only at the anomeric carbon (α & β)…. In equilibrium with straight chain configuration.
- **Epimers**: differ in configuration at only one, non-anomeric, chiral carbons.

**Mutarotation**: interconversion of α & β anomers (α ↔ β)

**Glycosidic linkage**: an anomeric carbon covalently bonded to an alcohol, with elimination of water…no longer in equilibrium with carbonyl functional group.

**Reducing Sugar**: A sugar in equilibrium with "carbonyl" form. A reducing sugar reduces alkaline copper ions (Cu++ ⇌ Cu¹⁺)…. when the anomeric carbon becomes part of a glycosidic bond (linkage), it makes a sugar "non-reducing”

**Derivatives**:

1. Glycosides… reaction of a hemiacetal with an alcohol produces an acetal. The alcohol may be another sugar. With the glycosidic linkage, the cyclic form is no longer in equilibrium with the straight chain form, so mutarotation is blocked.
2. Acids… Oxidation at C6 produces uronic acid, e.g., glucuronic acid (see Fig 23-16, p. 480). Oxidation of glucose at C1 yields gluconic acid, which exists only in straight-chain configuration.
3. Phosphate ester e.g., glucose-6-phosphate, glucose-1-phosphate, fructose-6-phosphate
4. Amino sugars (see Fig. 23-16, p 480).
5. Disaccharides (Fig. 7-4, p. 94)
   a. Lactose (milk sugar)...galactosyl β-1,4 glucose
   b. Sucrose (table sugar)...glucosyl α-1,β-2 fructose
   c. Maltose (digestion product of starch)... glucosyl α-1,4 glucose.
6. Polysaccharides (Fig. 7-6, p. 95)
   a. Cellulose: glucose units in β-1,4 linkage. Plant structure.... "fiber" in human diet
   b. Starch: glucose units only ...20% amylase, straight, polymeric chains in α−1,4 linkage; 80% amylopectin, branched structures containing α−1,4 and α−1,6 linkages. Food source for animals, food storage in plants.
   c. Glycogen: glucose units in α−1,4 and α−1,6 linkage, similar to amylopectin, but more highly branched. Energy storage in animal tissues, especially liver and muscle.
   d. Dextrans: extracellular bacterial polysaccharides formed from sucrose, but containing only glucose units in a highly branched structure including many α−1,6, α−1,4, and α−1,3 linkages. An insoluble constituent of dental plaque.
   e. Glycosaminoglycans: heteropolysaccharides...repeating unit is uronic acid and an amino sugar, e.g., hyaluronic acid, ...D-glucuronic acid β−1,3 N-acetyl-D-glucosamine (β−1,4 ). And see Fig. 23-16, p. 480.