Chapter 11: Sugars and Polysaccharides

Voet & Voet: Chapter 11
Carbohydrates (saccharides) are essential components of all living organisms

- carbohydrate means “carbon hydrate” and reflects the chemical composition of simple monosaccharides
- polyhydroxyl aldehyde or polyhydroxyl ketose are particularly important in biological systems

Structural and functional studies of carbohydrates are less advanced than for nucleic acids and proteins as:

1) complex carbohydrates are heterogeneous in size and composition
2) saccharide sequences are not subject to standard genetic analysis
3) difficult to establish functional assays as typically have structural roles
Saccharide Classification

**Monosaccharides** are the basic unit of carbohydrates

- synthesized from simpler substances in gluconeogenesis or photosynthesis
- major energy source & components of nucleic acids and many lipids

**Oligosaccharides** consist of a few (up to 20) covalently linked monosaccharides

- associated with proteins (glycoproteins) and lipids (glycolipids)
- serve structural and regulatory roles

**Polysaccharides** consist of many covalently linked monosaccharides

- structural function in all organism (*ie* cellulose in plants)
- nutritional reserve (*ie* starch in plants, glycogen in animals)
Monosaccharide Classification

Classified according to chemical nature of carbonyl group and number of C atoms

- Aldose or Ketose
- Triose, tetrose, pentose, hexose

Figure: D-aldose family of monosaccharides
Saccharide Stereochemistry

Based upon configuration of chiral C in glyceraldehyde

- chiral C furthest from carbonyl for sugars with n > 3
- Number of stereoisomers is $2^n$ (n is number of chiral centers)

Stereochemical terminology (review)

- **Enantiomers**: differ at all chiral centers (mirror image molecules)
- **Diastereomers**: differ at one or more chiral centers
- **Epimers**: differ at one chiral center

Example of epimers

Circles: Epimeric Carbons

Squares: D-configuration
Reactivity (review)

- Alcohols react with aldehydes (1:1 ratio) to form hemiacetals and (2:1 ratio) acetals
- Alcohols react with ketones (1:1 ratio) to form hemiketals and (2:1 ratio) ketales
Saccharide Configurations

- Aldoses can react with self forming cyclic hemiacetals (left) and ketoses can react with self forming cyclic hemiketals (right)
  - Saccharides forming 5 and 6 member rings are referred to as a furanose and pyranose, respectively

\( \text{d-Glucose} \) (linear form) \( \xrightarrow{\text{Haworth projection}} \) \( \alpha-\text{d-Glucopyranose} \) (Haworth projection) \( \text{d-Fructose} \) (linear form) \( \xrightarrow{\text{Haworth projection}} \) \( \alpha-\text{d-Fructofuranose} \) (Haworth projection)

Pyranose

Furanose
Cyclization of saccharides can generate two diastereomers or anomers

- hemiacetal or hemiketal carbon is referred to as the anomeric carbon

\( \alpha \) anomer: anomeric carbon OH is on the opposite side of the ring from the \( \mathrm{CH}_2\mathrm{OH} \) of the chiral center defining D- or L-

\( \beta \) anomer: anomeric carbon OH is on the same side of the ring as the \( \mathrm{CH}_2\mathrm{OH} \) of the chiral center defining D- or L-

Need to learn the structures of glucose (an aldose) and fructose (a ketose) and their anomers
An equilibrium exists between the $\alpha$ and $\beta$ anomeric forms of saccharides.

- Interconversion between anomeric forms is referred to as mutarotation.

\[ \text{~33\%} \quad \text{~1\%} \quad \text{~66\%} \]
Conformational Variability

- Pyranose adopt “chair” or “boat” conformations due to the tetrahedral configuration of carbon atoms

![Diagram of chair and boat conformations of pyranose]

Boat form is only observed when bulky substituents are present (rare in biological saccharides).
Saccharide Derivatives

Sugar Alcohols – alcohol replaces aldehyde or ketone (suffix -itol)

Sugar Acids – C1 oxidized (suffix -onic); C6 oxidized (suffix -uronic)

Sugar Amines – amine or acetylated amine replaces a hydroxyl

You must be able to recognize the different saccharide derivatives and the appropriate suffix. You are not responsible for learning the exact names of the derivatives.
Important Hexose Derivatives

For information only
Glycosidic Bonds

Condensation reaction between anomeric carbon and any other hydroxyl containing compound produces a glycosidic bond

- In disaccharides, the glycosidic bond is typically between C1 and C4
- Glycosidic bonds between C1 & C6, C1 & C1 of aldoses are also common
Disaccharides

Examples of glycosidic bonds between sugars

- lactose – milk sugar (β1-4)
- trehalose – insect hemolymph (α1-α1)
- sucrose – common sugar (α1-β2)
Polysaccharides

Polysaccharides are variable in length, can be composed of one or more types of monosaccharide and can be linear or branched

- **Homopolysaccharides** are composed of one monosaccharide type
- **Heteropolysaccharides** are composed of two or more monosaccharide types
Homopolysaccharides

**Cellulose:** unbranched $\beta 1$-$4$ linked glucose; serves structural role in plants; indigestible by mammals

**Amylose:** unbranched $\alpha 1$-$4$ linked D-glucose

**Glycogen:** amylose with $\alpha 1$-$6$ branch every $8$-$12$ residues
**Heteropolysaccharides**

Glycosaminoglycans: family of linear polymers composed of repeating disaccharide units

- one saccharide is N-acetylglucosamine (or N-acetylgalactosamine) and the other is an acid sugar (D-glucuronic or L-iduronic)
- hydroxyl groups can be esterified with sulfate

- Covalently attach to proteins forming proteoglycans
Proteoglycans: macromolecules of cell surface or extracellular matrix

- composed of a membrane or secreted protein and one or more glycosaminoglycan chains covalently attached to Ser-Gly-X-Gly sequence

Proteoglycans are one type of glycoconjugate – an oligo- or polysaccharide attached to protein or lipid
**Glycoproteins**: glycoconjugates composed of a protein and one or more oligosaccharides

- oligosaccharides are smaller and structurally diverse
- covalently attached to Ser/Thr (O-linked) or Asn (N-linked)
**Glycolipids**: glycoconjugates composed of a membrane lipid and an oligosaccharides (eg. gangliosides)

- oligosaccharides are attached to polar head group
- specific recognition site for carbohydrate binding proteins