Carbohydrates

Learning Objectives

As we study this chapter, you should...

1) Know how to draw and interpret Fisher projections. Straight-chain (acyclic) carbohydrates are usually drawn using Fisher Projections. In a Fisher projection, the horizontal lines come out of the page and the vertical lines go behind the page.

the most oxidized carbon is drawn at the top
* each intersection is a stereocenter
the lowest stereocenter is called the penultimate carbon

the numbering system starts at the topmost carbon

2) Know the rules for manipulating Fisher projections. The fact that horizontal lines in a Fisher projection come out of the page and vertical lines go behind the page limits what you can do with the drawing. Essentially, Fisher projections may only be rotated 180° on the plane of the paper. Any other rotation that lifts the molecule off the paper yields a different molecule.

3) Know the “Nomenclature” and classifications of acyclic carbohydrates. Nearly all carbohydrates have common names. For example, the carbohydrate used in the item #1 (above) is known as "glucose" and is rarely called "(2R,3S,4R,5R)-2,3,4,5,6-pentahydroxyhexanal." Straight chain carbohydrates are given the prefix “aldo” (for aldehydes) or “keto” (for ketones). They are then classified according to their number of carbon atoms (see table). So glucose (shown above in #1) is an aldohexose. Other examples are shown below:

<table>
<thead>
<tr>
<th>No. of carbons</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>triose</td>
</tr>
<tr>
<td>4</td>
<td>tetrose</td>
</tr>
<tr>
<td>5</td>
<td>pentose</td>
</tr>
<tr>
<td>6</td>
<td>hexose</td>
</tr>
</tbody>
</table>

4) Understand the definition of D and L carbohydrates. Capital “D” and “L” are another classification of carbohydrates. In straight chain carbohydrates, a compound is classified as a D-sugar if the OH at the penultimate carbon is on the right side, and a compound is classified as an L-sugar if the OH at the penultimate carbon is on the left side. These are not to be confused with lower case “d” and “l,” which are used to indicate the rotation of plane polarized light. One thing the D/L classification has in common with the d/l classification is that they both can be used to describe pairs of enantiomers.
5) **Understand how carbohydrates come to be cyclic carbohydrates.** Although we initially study the straight-chain form of carbohydrates, most carbohydrates are in equilibrium with two possible cyclic forms which arise from an intramolecular hemiacetal-forming reaction between one of the alcohols and the carbonyl carbon. The two possible forms are called “alpha” and “beta” depending on the relative relationship (anti and syn, respectively) between the former carbonyl oxygen and the CH$_2$OH group. The former carbonyl carbon (C-1) is called the anomeric carbon. The $\alpha$ and $\beta$ isomeric forms of the cyclic carbohydrates are called anomers. Because hemiacetal formation is reversible, all three forms of glucose are in equilibrium with each other.

To convert an acyclic $D$-carbohydrate into a cyclic $D$-carbohydrate:

- a) decide which hydroxyl group will be attacking the carbonyl
- b) rotate the carbohydrate 90° clockwise
- c) transpose the hydroxyl groups to the cyclohexyl ring as shown below (Any OH group that is “up” in the rotated Fisher projection, will be “up” in the ring. Any OH group that is “down” in the rotated Fisher projection, will be “down” in the ring).

6) **Know the classifications of cyclic carbohydrates and be able to draw and interpret Haworth projections.** Aside from the $\alpha$ and $\beta$ designations, a cyclic carbohydrate is also named according to ring size. The two most common ring sizes are 5 and 6, furanoses and pyranoses, respectively. The drawings shown below are called Haworth projections. They are used to give a 3-D perspective of the carbohydrate, while also being quick to draw. Note that the pyranose rings don’t provide information regarding the axial or equatorial orientation of the bonds.
7) **Understand the formation of glycosides.** Carbohydrates can also cyclize in the presence of an alcohol or amine to form acetals known as glycosides (glycoside: any O- or N-acetal of a carbohydrate). As we know from our studies on ketones & aldehydes, acetals are more stable than hemiacetals, so glycosides are not generally in equilibrium with their open chain forms (unless under acidic conditions).

Examples of glycosides

- Lactose
- Cytosine (from RNA)

8) **Be familiar with the concept of complex carbohydrates.** Sugars can exist as dimers (a molecule made up of 2 sugars covalently bonded), oligomers (a molecule made up of 3-10 sugars covalently bonded), or polymers (a molecule made up of more than 10 sugars covalently bonded). These are known as disaccharides, oligosaccharides, and polysaccharides, respectively. The individual sugar units can be connected at various locations, but are usually connected via a glycosidic bond.

Examples of complex sugars

- Sucrose
- Maltose
- Cellulose

9) **Be familiar with these definitions.**

   **Epimers:** Sugars that differ only in the configuration of one stereocenter. Epimers are also diastereomers.

   **Anomeric Carbon:** In cyclic sugars, this is the carbon that used to be the ketone or aldehyde.

   **Anomers:** Cyclic sugars that differ only in the configuration at the anomeric carbon. Each anomer is referred to as either α or β. α and β are relative designations and refer to the relationship between the anomeric OH and the stereochemistry at the penultimate carbon.

   **Mutarotation:** Conversion of one anomer to another and establishment of an equilibrium between the two such that a constant optical rotation is obtained.

   **Pyranoside:** A 6-membered ring glycoside.

   **Furanoside:** A 5-membered ring glycoside.

   **N-Glycoside:** A glycoside in which the anomeric OR group has been replaced by a bond to an amine.