

Chem 191: Biochemistry

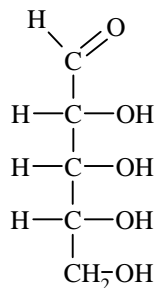
Lecture 7 – Carbohydrates

I. Introduction

- A. Carbohydrates are one of the four major classes of biological molecules, which include:
1. Carbohydrates
 2. Proteins
 3. Lipids
 4. Nucleic Acids
- B. Carbohydrates play many important roles.
1. For biological organisms:
 - a. They are a source of chemical energy
 - b. They are a source of carbon for the biosynthesis of new molecules.
 - c. They provide a way of storing energy as glycogen and starch.
 - d. They are used for structural purposes, such as the *chitin* shells of crustaceans and the *cellulose* cell walls of plants.
 2. Commercially
 - a. They are used to make paper and cotton fabrics.

II. Classes of Carbohydrates

- A. Carbohydrates
1. Heating produces carbon (carbo-) and water (-hydrate).
 2. They have a large number of functional groups.
 - a. Each carbon is involved in a functional group.
 - b. Every carbohydrate molecule is either an aldehyde or a ketone
 - c. All the carbons which are not involved in the aldehyde or ketone group have hydroxyl groups attached to them
 - i. A carbohydrate is either a *polyhydroxylated aldehyde* or a *polyhydroxylated ketone*.
 - d. Aldehydes
 - e. Ketones
 - f. Alcohols
 3. The example shown on page 502 in your text is the carbohydrate *ribose*.



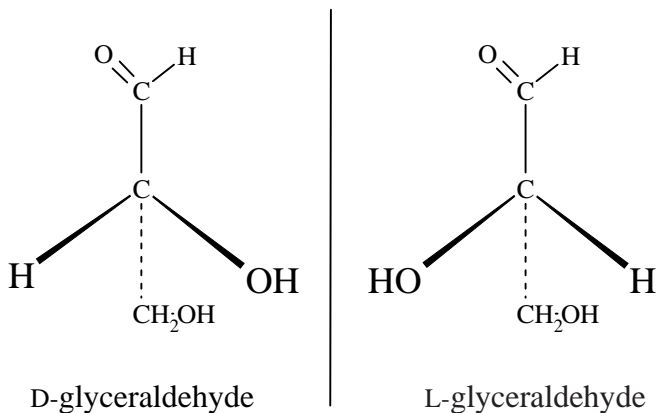
ribose

- a. It contains 5 carbons

- i. The one terminal carbon is part of an aldehyde group.
 - ii. The remaining 4 carbons each have a hydroxyl group.
- B. Classification according to sized.
 - 1. A single carbohydrate molecule is called a **monosaccharide**.
 - 2. Monosaccharides can join together to form *polymers*.
 - a. **Disaccharides** contain 2 monosaccharide units.
 - b. **Trisaccharides** contain 3 monosaccharide units.
 - c. ...
 - d. **Oligosaccharide** contain 3-10 monosaccharide units.
 - e. **Polysaccharides** contain 10's to 100's of monosaccharide units.

III. Stereochemistry of Carbohydrate.

- A. Carbohydrates present us with a new kind of isomer, the **optical isomer**.
 - 1. Optical isomers are a type of stereoisomer
 - a. Stereoisomers have the same chemical *and* structural formulas, but a different spatial arrangement of their atoms.
 - i. This means that they contain the same elements, and that these elements have the same types bonds connecting them
 - ii. The *cis/trans* isomers is another example of a stereoisomer,
 - 1) Because there is no rotation about a double bond, there are two possible spatial arrangements of groups attached to the carbon atoms that participate in the double bond.
 - b. A molecule has an optical isomer when its mirror image is non-superimposable on itself.
 - i. The non-superimposable mirror images are called **enantiomers** of one another.
 - c. A non-molecular example of a pair of objects that are not superimposable on one another, and which are mirror images of one another, are your left and right hands.
 - 2. An object that can not be superimposed on its mirror image is said to be **chiral**.
 - a. Glyceraldehyde is an example of a molecule that is chiral.



- i. D and L glyceraldehyde are non-superimposable on each other.
 - 1) They are *enantiomers* of one another.
 - 2) Both D and L glyceraldehyde are *chiral* molecules.
3. Chiral organic molecules can be identified by examining the carbon atoms.
 - a. Tetrahedral carbon atoms that have 4 *different* groups attached to it are chiral.
 - b. The central carbon of glyceraldehyde has four different groups attached to it:
 - i. -CHO
 - ii. -OH
 - iii. -CH₂OH
 - iv. -H
 - c. If a molecule contains a carbon that has 4 different groups attached to it, it is a *chiral* molecule.
 - i. The carbon that makes it a chiral molecule is called a *chiral carbon*.
 - 1) It is also called an *asymmetric carbon*.

Work some examples from the Exce

- B. Calculating the number of stereoisomers that glucose and fructose have.
 1. Each chiral carbon has two possible configurations.
 - a. If a molecule has two chiral carbons then there are 4 possible optical isomers.
 - i. There will be two pairs of enantiomers.
 - 1) Enantiomers share the same name
 - b. The number of possible optical isomers a molecule has is equal to 2^n , where n is the number of chiral carbons it contains.

IV. Fisher projections

- A. Provides a way of representing 3-dimensional information in 2-dimensions.
 1. The aldehyde or ketone group is placed at the top with the carbon chain extending downward.
 - a. The hydrogen and hydroxyl groups attached to the left and right of each of the other carbons, are assumed to project outward from the plane of the paper (board).
 - i. If the OH is on the *left*, a chiral carbon is in the L configuration.
 - ii. If the OH is on the *right*, a chiral carbon is in the D configuration.
 - iii. The chiral carbon furthest from the aldehyde or ketone group is used to designate a member of a pair of enantiomers as D or L.
- B. **Optical activity**
 1. Chiral molecules can be detected experimentally by using polarized light.
 - a. Dextrorotatory

- i. Bends the plane of polarization for plane polarized light to the right (clockwise)
- ii. A lowercase *d* is used in naming a chiral molecule that bends plane polarized light to the right.
- b. Levorotatory
 - i. Bends plane of polarization for plane polarized light to the left (counterclockwise).
 - ii. A lowercase *l* is used in naming a chiral molecule that bends plane polarized light to the left.
- c. The *l* and *d* designations do not imply whether a molecule is L or D.

V. Classifications Monosaccharides

- A. Aldoses
- B. Ketoses
- C. Hexoses
- D. Pentoses
- E. Tetroses

Fig 17.8

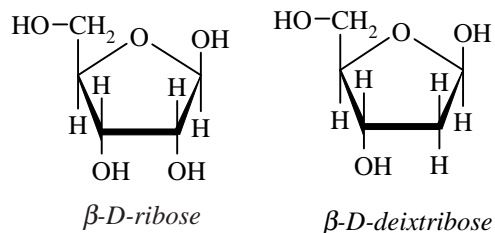
VI. Properties of Monosaccharides

- A. Physical properties
 - 1. Monosaccharides and disaccharides are called sugars because they taste sweet.
 - a. Fructose, which is found in honey and corn syrup, is the sweetest tasting sugar.
 - 2. Solids at room temperature
- B. Chemical properties
 - 1. Cyclization
 - a. Puranose and furanose rings
 - i. Formation of hemiacetals and hemiketals.
 - b. Anomeric carbon is the one that was formerly the aldehyde or ketone.
 - i. It now becomes a chiral carbon
 - 0) The Greek letters α and β to designate the two new isomers
 - c. The different forms of D-glucose: the open chain, the α -D-glucose ring and the β -D-glucose ring are in rapid equilibrium with each other.
 - i. In a solution of D-glucose the percentage of each form present is 0.02%, 36% and 64%, respectively.
 - d. The ring-like structures are

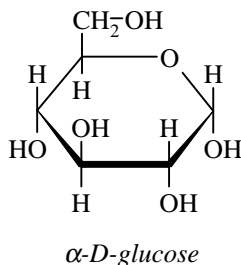
VII. Important monosaccharides

- A. Ribose and deoxyribose

- Are used to make ribonucleic acids (RNA) and deoxyribonucleic acids (DNA), respectively.



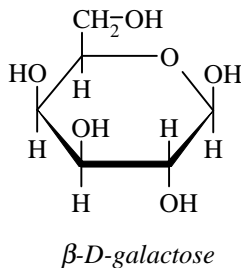
B. Glucose



- Is nutritionally one of the most important sugars
- Is found in fruits
- Is sometimes called dextrose, because the D isomer bends plane polarized light to the right (dextrorotatory)

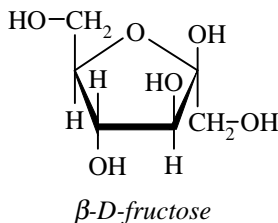
C. Galactose

- It is synthesized in the mammary glands and combined with glucose to form the disaccharide *lactose*.



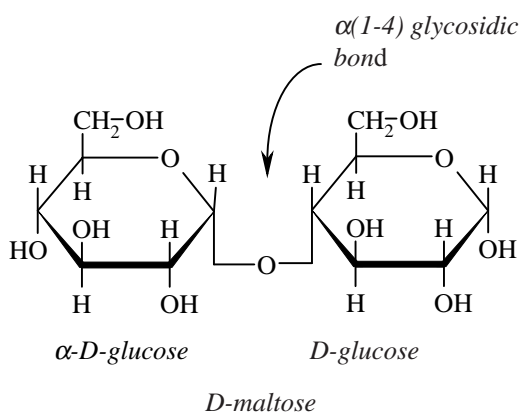
D. Fructose

- It is the sweetest of the common sugars
- It is found in honey
- It is combined with glucose to form the disaccharide *sucrose*.



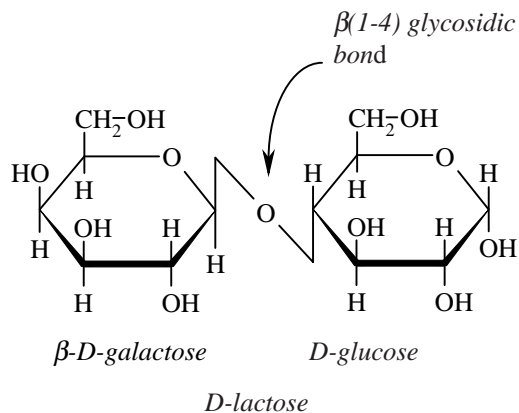
VIII. Disaccharides

- A. Disaccharides are sugars composed of two monosaccharides joined by a glycosidic bond.
 1. The -OH of the hemiacetal or hemiketal on the one monosaccharide reacts with an -OH from another monosaccharide.
 - a. The -OH can be either a hydroxyl group or the -OH from the hemiacetal or hemiketal on the other monosaccharide.
 - b. The reaction leads to the release of a water molecule
- B. The glycosidic bond connecting the monosaccharides can be easily hydrolyzed (broken) with mild acid and heat or using enzymes (biological catalysts).
- C. The most important nutritional disaccharides are *maltose*, *lactose* and *sucrose*.
- D. Maltose
 1. Glucose α (1-4) Glucose



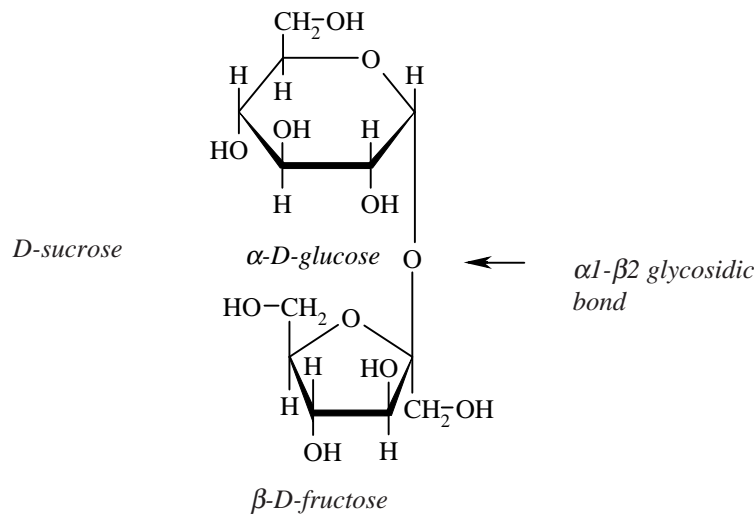
2. The -OH from the hemiacetal of D-glucose in its α configuration combines with the -OH from the hydroxyl group on the fourth carbon of a second D-glucose to form the glycosidic bond.
 - a. This is called a α (1-4) glycosidic bond.
3. Maltose is produced from the break down of starch when seeds germinate.
 - a. If the seeds are roasted soon after they germinate the process is called malting and the resulting product will have high concentrations of maltose.
 - b. This process is used in the production of beers, ales, and malt liquors. Yeast are used to convert the maltose to ethanol and carbon dioxide.
2. Lactose is still considered a reducing sugar
 - a. Even though the D-glucose on the left is no longer capable of reducing Cu^{2+} , the D-glucose on the right, which still contains a hemiacetal group, can open up to expose an aldehyde group.

B. Lactose

1. Galactose β (1-4) Glucose

2. The -OH from the hemiacetal of D-galactose in its β configuration combines with the -OH from the hydroxyl group on the fourth carbon of D-glucose to form the glycosidic bond.
 - a. This is called a β (1-4) glycosidic bond.
3. Lactose is called “milk sugar” because it is found in milk.
4. Individuals who have the condition called *lactose intolerance* lack the ability to break the glycosidic bond connecting the galactose to the glucose monosaccharides.
5. Lactose is still considered a reducing sugar
 - a. Even though the D-galactose is no longer capable of reducing Cu^{2+} , the D-glucose on the right, which still contains a hemiacetal group, can open up to expose an aldehyde.

C. Sucrose

1. Glucose α 1- β 1 Fructose

2. The -OH from the hemiacetal of D-glucose in its α configuration combines with the -OH from the hemiketal of D-fructose in its β configuration to form the glycosidic bond.

- a. This is called a $\alpha 1\text{-}\beta 2$ glycosidic bond.
2. Sucrose is also called table sugar.
3. Sucrose is not a reducing sugar
 - a. This is because both the hemiacetal of the D-glucose and the hemiketal of the D-fructose are involved in the formation of the glycosidic bond.
 - i. Both monosaccharides are locked in their closed ring form.

II. Polysaccharides

A. Starch

1. Is a polymer that contains hundreds to thousands of glucose monosaccharide connected together
 - a. The amylose form is unbranched and the glucose monosaccharides are connected by $\alpha(1\text{-}4)$ glycosidic bonds.
 - b. The amylopectin form is branched; in addition to long chains of glucose monosaccharides connected by $\alpha(1\text{-}4)$ glycosidic bonds, every 24-30 monosaccharide units along the chain there is an additional $\alpha(1\text{-}6)$ glycosidic bond.
 - i. Amylopectin is therefore a branched polymer.
 - c. Glucose $\alpha(1\text{-}4)$ glucose (amylose unbranched)
2. Starch is found in plants and is a storage form of glucose.

B. Glycogen

1. Glycogen is similar to amylopectin but more highly branched (every 8 - 12 units).
2. It is found in animals, primarily in the muscles and liver, and is also a storage form of glucose to be used for energy purposes

C. Cellulose

1. Cellulose is also a polymer of glucose
 - a. Like amylose it is unbranched, but the glucose monosaccharides are connected instead by $\beta(1\text{-}4)$ glycosidic bonds.
2. This gives cellulose markedly different physical and chemical properties than starch or glycogen.
 - a. It is a very linear polymer and is quite insoluble, unlike starch or glycogen.
3. Can only be digested by a few microorganisms, making it quite resistant to biological degradation.
4. Cellulose is used primarily by plants for structural purposes.