Carbohydrates

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IMPORTANT FUNCTIONS OF CARBOHYDRATES

- To provide energy through their oxidation
- To supply carbon for the synthesis of cell components
- To serve as a stored form of chemical energy
- To form a part of the structural elements of some cells and tissues
- Biomolecule a general term referring to organic compounds essential to life
- Biochemistry a study of the compounds and processes associated with living organisms

CARBOHYDRATES

- **Carbohydrates** are polyhydroxy aldehydes or ketones, or substances that yield such compounds upon hydrolysis.
- Example:



CLASSIFICATION OF CARBOHYDRATES

- Carbohydrates are classified according to size:
- Monosaccharide a single polyhydroxy aldehyde or
 - ketone unit
 - Disaccharide composed of two monosaccharide units
 - Polysaccharide very long chains of linked monosaccharide units



STEREOCHEMISTRY

• Many carbohydrates exist as enantiomers (stereoisomers that are mirror images).



STEREOCHEMISTRY (continued)

- A chiral object cannot be superimposed on its mirror image.
- A chiral carbon is one that has four different groups attached to it.



STEREOCHEMISTRY (continued)

- The presence of a single **chiral carbon** gives rise to stereoisomerism.
- If a carbon atom is attached to four different groups, it is chiral.
- If any two groups are identical, it is not chiral.



STEREOCHEMISTRY (continued)

• Compounds can have more than one chiral carbon:



- The maximum number of stereoisomers is 2ⁿ where n= number of chiral carbon atoms.
- Therefore, this compound with two chiral carbon atoms has 2² or 4 stereoisomers.
- The compound on the previous slide with four chiral carbon atoms has 2⁴ or 16 stereoisomers.

FISCHER PROJECTIONS

 Fischer projections depict three-dimensional shapes for chiral molecules, with the chiral carbon represented by the intersection of two lines.



FISCHER PROJECTIONS (continued)

- Fischer projections of carbohydrates have the carbonyl (C=O) at the top. It is projecting away from the viewer behind the plane in which it is drawn as is the other vertical bond at the bottom of the image.
- The hydroxyl group on the chiral carbon farthest from the C=O group determines whether the carbohydrat is D (OH on right) or L (OH on left). The two horizontal bonds are coming toward the viewer out of the plane in which they are drawn.



ENANTIOMER PROPERTIES

- The physical properties of D and L enantiomers are generally the same.
- D and L enantiomers rotate polarized light in equal, but opposite directions.



ENANTIOMER PROPERTIES (continued)

- The enantiomer that rotates polarized light to the left is the levorotatory or (-) enantiomer.
- The enantiomer that rotates it to the right is the dextrorotatory or (+) enantiomer.
- The D and L designations do not represent **dextrorotatory** and **levorotatory**.
- The property of rotating the plane of polarized light is called optical activity, and the molecules with this property are said to be **optically active**.
- Measurements of optical activity are useful for differentiating between **enantiomers**.

ENANTIOMER PROPERTIES (continued)

- In some instances, only the D or L enantiomers are found in nature.
- If both D and L forms are found in nature, they are rarely found together in the same biological system.
- For example:
 - Carbohydrates and amino acids are chiral.
 - Humans can only metabolize the D-isomers of **monosaccharides**.
 - Most animals are only able to utilize the L-isomers of amino acids to synthesize proteins.

MONOSACCHARIDE CLASSIFICATION

- Questions to ask when classifying a **monosaccharide**:
 - Is the monosaccharide an aldehyde (aldose) or ketone (ketose)?
 - How many carbon atoms are in the **monosaccharide**?

Table 17.1MonosaccharideClassification Based on theNumber of Carbons in TheirChains

Number of Carbon Atoms	Sugar Class
3	Triose
4	Tetrose
5	Pentose
6	Hexose



- Most monosaccharides are aldoses.
- Almost all natural monosaccharides belong to the D series.
- The maximum number of possible stereoisomers is 2ⁿ, where n = number of chiral carbon atoms.
- Half of stereoisomers are D and the other other half are L.

# of Carbon	Name of	# of Chiral	# of Stereoisomers	# of D	# of L
Atoms	Sugar Class	Carbon Atoms (n)	(2^{n})	Stereoisomers	Stereoisomers
3	triose	1	2	1	1
4	tetrose	2	4	2	2
5	pentose	3	8	4	4
6	hexose	4	16	8	8







PHYSICAL PROPERTIES OF MONOSACCHARIDES

- Most are called sugars because they taste sweet.
- All carbohydrates are solids at room temperature.
- Because of the many –OH groups, they form hydrogen bonds with water molecules and are extremely water soluble.

Table 17.2 The Relative Sweetness of Sugars (Sucrose = 1.00)					
Sugar	Relative Sweetness	Туре			
Lactose	0.16	Disaccharide			
Galactose	0.22	Monosaccharide			
Maltose	0.32	Disaccharide			
Xylose	0.40	Monosaccharide			
Glucose	0.74	Monosaccharide			
Sucrose	1.00	Disaccharide			
Invert sugar	1.30	Mixture of glucose and fructose			
Fructose	1.73	Monosaccharide			

MONOSACCHARIDE REACTIONS

- All monosaccharides with at least five carbon atoms exist predominantly as cyclic hemiacetals and hemiketals.
- A Haworth structure can be used to depict the three-dimensional cyclic carbohydrate structures.



CYCLIZATION OF GLUCOSE



CYCLIZATION OF MONOSACCHARIDES

- The open-chain structure is numbered starting at the end closest to the carbonyl carbon atom.
- The alcohol group on the next to the last carbon atom adds to the carbonyl group.
- In the case of glucose, the alcohol group on carbon 5 adds to the aldehyde group on carbon 1 and a pyranose (six-membered ring containing an oxygen atom) forms.
- In the case of fructose, the alcohol group on carbon 5 adds to the ketone group on carbon 2 and a furanose (five-membered ring containing an oxygen atom) forms.
- The former carbonyl carbon atom is now **chiral** and called the **anomeric carbon** atom.



- Because the **anomeric carbon** atom is **chiral**, two possible stereoisomers can be formed during cyclization.
 - An α anomer (-OH on the anomeric carbon pointing down)
 - A β anomer (-OH on the anomeric carbon pointing up)
- Anomers are stereoisomers that differ in the 3-D arrangement of groups at the anomeric carbon of an acetal, ketal, hemiacetal, or hemiketal group.

CYCLIZATION OF FRUCTOSE



HAWORTH STRUCTURE RULES

- Draw the ring with its oxygen to the back.
- Put the anomeric carbon on the right side of the ring.
- Envision the ring as planar with groups pointing up or down.
- The terminal –CH₂OH group (position 6) is always shown above the ring for D-monosaccharides.



MONOSACCHARIDE REACTIONS (continued)

- A reducing sugar can be easily oxidized.
- All monosaccharides are reducing sugars.
- Benedict's reagent tests for reducing sugars: Reducing sugar + Cu²⁺ → oxidized compound + Cu₂O



blue

From left to right, three test tubes containing Benedict's reagent, 0.5% glucose solution, and 2.0% glucose solution

orange-red precipitate



The addition of Benedict's reagent produces colors (due to the red Cu₂O) that indicate the amount of glucose present.

MONOSACCHARIDE REACTIONS (continued)

 The –OH groups of monosaccharides can behave as alcohols and react with acids (especially phosphoric acid) to form esters.



MONOSACCHARIDE REACTIONS (continued)

 Cyclic monosaccharide hemiacetals and hemiketals react with alcohols to form acetals and ketals, referred to as glycosides.



- The new carbon-oxygen-carbon linkage that joins the components of the glycoside is called a glycosidic linkage.
- Glycosides do not exhibit open-chain forms.
- Glycosides are not reducing sugars.

IMPORTANT MONOSACCHARIDES

- Ribose and Deoxyribose
 - Pentoses
 - Used in the synthesis of DNA and RNA



IMPORTANT **MONOSACCHARIDES** (continued)

- Glucose is:
 - a hexose.
 - the most nutritionally important **monosaccharide**.
 - sometimes called dextrose or blood sugar.
 - the compound to which other sugars absorbed into the body must be converted in the liver.
 - used as a sweetener in confections and other foods.



IMPORTANT **MONOSACCHARIDES** (continued)

- Galactose is:
 - a hexose.
 - similar structure to glucose.
 - a component of lactose (milk sugar).
 - a component of substances present in nerve tissue.



IMPORTANT **MONOSACCHARIDES** (continued)

- Fructose is:
 - a ketohexose.
 - the sweetest monosaccharide.
 - sometimes called levulose or fruit sugar.
 - present in honey in a 1:1 ratio with glucose.
 - abundant in corn syrup.

