

## BCH 4053 Summer 2001 Chapter 7 Lecture Notes

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# Chapter 7

## Carbohydrates

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### Carbohydrates: Nomenclature

- Hydrates of carbon
  - General formula  $(\text{CH}_2\text{O})_n$  (simple sugars) or  $\text{C}_x(\text{H}_2\text{O})_y$
- Monosaccharides (simple sugars)
  - Aldoses and ketoses
  - Sugar derivatives
    - Sugar acids, sugar alcohols, deoxy sugars, sugar esters, amino sugars, glycosides
- Oligosaccharides
- Polysaccharides

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### Monosaccharides

- Carbon chain, 1 oxygen for each carbon
- One oxygen is carbonyl, rest are alcohols
  - Aldose—carbonyl on carbon-1 (aldehyde)
  - Ketose—carbonyl on carbon-2 (ketone)
- Number of carbon atoms can vary
  - Triose, tetrose, pentose, hexose, heptose

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## Monosaccharides, stereochemistry

- Chiral carbons
  - n-2 for aldoses (trioses have one, tetroses two, etc)
  - n-3 for ketoses (tetroses have one, pentoses two, etc)
  - Fischer projection
    - D correlates with d-glyceraldehyde
    - L correlates with l-glyceraldehyde
      - See Figure 7.1

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## Stereochemistry, con't.

- Number of isomers =  $2^n$ 
  - where n = number of chiral centers

	Aldoses		Ketoses	
	n	isomers	n	isomers
Trioses	1	2	0	1
Tetroses	2	4	1	2
Pentoses	3	8	2	4
Hexoses	4	16	3	8

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## Monosaccharide, nomenclature

- Sugar class refers to the **penultimate** (n-1) carbon configuration
  - D sugar if n-1 position has D configuration
  - L sugar if n-1 position has L configuration
- Isomers at other positions distinguished by different names
  - See Figure 7.2 for aldoses, 7.3 for ketoses

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## Monosaccharide, nomenclature, con't.

- Learn the following structures:
  - Trioses: all
  - Tetroses: all
  - Pentoses: ribose, ribulose, xylulose
  - Hexoses: glucose, mannose, galactose, fructose

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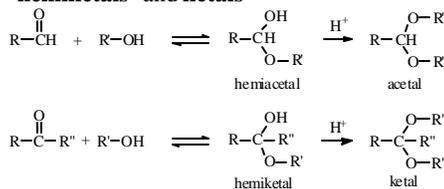
## Some stereochemical terms

- Enantiomers, mirror image isomers
  - Configuration at **every** chiral carbon is different
    - See Figure 7.4
- Diastereomers, isomers with one or more configuration differences that are **not** enantiomers
  - Epimers, isomers that differ only at **one** chiral center

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## Acetals and Ketals

- Aldehydes can react with alcohols to form **hemiacetals** and **acetals**
- Ketones can react with alcohols to form **hemiketals** and **ketals**



The aldehyde and hemiacetal are in equilibrium, and depend on the concentration of the alcohol. Heating with acid and excess alcohol can cause dehydration between the alcohol and the hemiacetal to occur to form an acetal, which is stable at room temperature under neutral conditions. Breaking the acetal linkage requires heating with acid and water. The same conditions apply to the formation of hemiketals and ketals.

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## Cyclic structures and anomeric forms

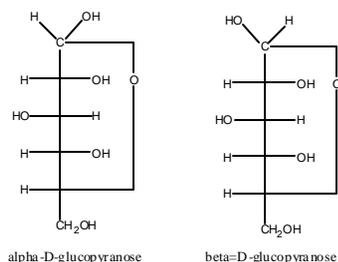
- Cyclization to form hemiacetal or hemiketal introduces an additional chiral carbon, called the **anomeric** carbon
  - Equilibrium favors the cyclic form
  - Isomers distinguished by prefix *alpha* or *beta*
- Isomers at the anomeric carbon are called **anomers**
  - (They are also **epimers** and **diastereomers**)
- Common ring structures contain five or six atoms
  - Five atoms = **furanose** ring (from furan)
  - Six atoms = **pyranose** ring (from pyran)
    - See Figure 7.5 for glucose

Sugars can form **cyclic** hemiacetals and hemiketals. Because the alcohol group involved is in the same molecule, the equilibrium mixture lies toward the cyclic structure.

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## Fischer Projection of ring structure

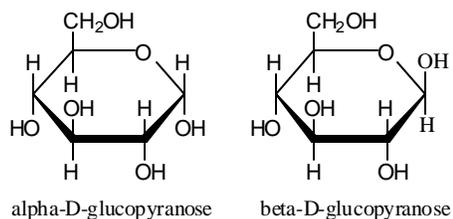
- Fischer projections of glucose anomers



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## Haworth Projection of ring structure

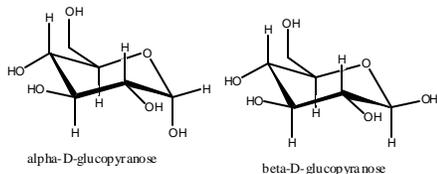
- Haworth projections of glucose anomers



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## Chair conformation of pyranose rings

- Chair conformation of glucose anomers



Note that for beta- D- glucose. All non-hydrogen atoms on the ring are in the **equatorial** position. That makes beta glucose more stable than alpha glucose, and the equilibrium mixture of the two contains more beta than alpha.

Note we most commonly find glucose and other aldohexoses in the pyranose ring form, while fructose, a keto hexose, is found in the furanose ring form, and ribose, an aldopentose, is found in the furanose ring form.

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## 3-D Structures of some Monosaccharides

- Alpha-D-glucopyranose
- Beta-D-glucopyranose
- Beta-D-fructofuranose
- Beta-D-ribofuranose
- (See “Course Related Web Sites” under “Resources” on the class web page for links to these structures).

The free sugars can exist as a mixture of ring forms, but the structures we encounter as metabolic intermediates are usually bound to phosphate and thus are locked into these ring forms. However, note in “A Deeper Look” on page 224 that honey contains a mixture of fructose ring forms in addition to some glucose, both produced by the hydrolysis of sucrose.

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## Mutarotation

- Hemiacetals are in equilibrium with the open chain form.
  - See Figure 7.5
- One anomer dissolved in water will equilibrate to a mixture of the two anomers
- Because the optical rotation of the solution changes as the anomers equilibrate, the phenomenon is called **mutarotation**.

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## Monosaccharide Derivatives

- Sugar acids from glucose (See Figure 7.10)
  - gluconic acid (C-1), glucuronic acid (C-6), glucaric acid (C-1 and C-6)
- Sugar alcohols (See Figure 7.11)
  - glucitol (sorbitol), mannitol, ribitol, xylitol, glycerol
  - *Myo*-inositol with closed carbon ring
- Deoxy sugars (See Figure 7.12)
  - 2-deoxyribose (DNA constituent)
  - rhamnose, fucose

Oxidation at C-1 is relatively easy for sugars with a free anomeric carbon (I.e. a hemiacetal or hemiketal) with oxidizing agents such as  $\text{Cu}^{+2}$  and  $\text{Ag}^+$ . Such sugars are referred to as **reducing sugars**.

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## Monosaccharide Derivatives, con't.

- Sugar esters (See Figure 7.13)
  - Glucose-1-phosphate, ATP
- Amino sugars
  - Hexosamines (See Figure 7.14)
  - Muramic acid and sialic acid
    - (See Figure 7.15)
- Glycosides—full acetals or ketals
  - (See Figures 7.16 and 7.17)
  - Alcohols attached to the **anomeric** carbon
  - Attached alcohol called the **aglycone**

For most sugar intermediates in metabolism the sugar residue is attached to phosphate in an ester linkage, or some derivative of phosphate.

Free amino sugars are very toxic, and so the amine group is usually **acetylated** with an acetyl ( $\text{CH}_3\text{CO}-$ ) group, though sometimes one finds a **glycolyl** ( $\text{HOCH}_2\text{CO}-$ ) group instead for sialic acid.

A sugar glycoside is no longer in equilibrium with the open chain aldehyde or ketone form of the sugar, and is therefore no longer as easily oxidized as the free sugar. Such sugars are therefore referred to as **non-reducing** sugars.

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## Disaccharides

- Glycosides in which the aglycone alcohol is an OH group from another monosaccharide.
- If only one anomeric carbon involved, we have a **reducing end** (the sugar with the free anomeric carbon) and a **non-reducing end** (the end with the full acetal or ketal at the anomeric carbon).
- Common examples (See Figure 7.18)
  - Maltose, isomaltose, cellobiose (glucose-glucose)
  - Lactose (galactose-beta-1,4-glucose)
  - Sucrose (glucose-alpha-1,2-fructose) **NON REDUCING!**

**Maltose** is the repeating unit of starch and glycogen by the action of the enzyme amylase.

**Cellobiose** is the repeating unit of cellulose, and can be obtained from acid hydrolysis of cellulose.

**Lactose** is milk sugar, formed by the interaction of a galactosyltransferase and lactalbumin in milk. To be digested, it must be broken down by an enzyme called **lactase**, and individuals lacking this enzyme have **lactose intolerance**.

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## Oligosaccharides

- A variety found free in nature (See Figure 7.19 for a few examples)
- Components of antibiotics where there is more complex organic aglycone (See Figure 7.20)
- Component residues of glycoproteins and glycolipids (we will discuss later).

Presumably this problem led to the development of fermentation processes to produce **yogurt** in which the lactose is hydrolyzed by microbial action. **Sucrose** is a major sugar produced by plants during photosynthesis. It is both an **alpha-glucoside** and a **beta-fructoside**, and since both anomeric carbons are involved in the linkage, it is a **non-reducing sugar**.

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## Polysaccharides

- Also known as **glycans**.
- Homopolysaccharides—polymer of one sugar
  - glucans—polymers of glucose
  - mannans—polymers of mannose
  - Others
- Heteropolysaccharides—more than one sugar in polymer chain

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## Homopolysaccharides

- Storage polysaccharides
  - Starch (Plants) (See Figure 7.21)
    - Amylose (*alpha* 1,4 glucose links)
    - Amylopectin (*alpha* 1,4 glucose links with *alpha* 1,6 branches every 12-30 residues)
  - Glycogen (Animals)
    - Similar to amylopectin, but *alpha* 1,6 branches every 8-12 residues
  - Dextrans (Yeast and Bacteria)
    - *Alpha* 1,6 glucose polymer, with branches at 2, 3, or 4 depending on species

Amylose forms a blue complex with iodine. The iodine fits into the hydrophobic center of the amylose helix. See Figure 7.22.

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## Homopolysaccharides, con't.

- Structural polysaccharides
  - Cellulose (*beta* 1,4 glucose polymer) the most abundant natural polymer in the world
    - Compare stereochemistry of *alpha* and *beta* linkage (Figure 7.26)
    - Sheet structure of cellulose (Figure 7.27)
    - Animals cannot digest cellulose
  - Chitin (*beta* 1,4 N-acetyl glucosamine polymer)
    - Structurally analogous to cellulose
    - Structural polymer for insects
- Alginates
  - *Beta* 1,4 mannuronate and *alpha* 1,4 poly glucuronate (See Figure 7.29)

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## Heteropolysaccharides

- Agarose from marine and red algae mixture called **agar**. Alternating D-galactose and 3,6 anhydro-L-galactose (See Figure 7.31)
- Glycosaminoglycans
  - Repeating disaccharides in which one unit is an amino sugar, and one or both contain either a carboxyl or a sulfonate group. (See Figure 7.33)
    - Heparin, Hyaluronate, chondroitin-4-sulfate, Chondroitin-6-sulfate, Dermatan sulfate, Keratan sulfate