Lecture 22 (11/7/25)

TODAY

•Reading: Ch7; 236-241

NEXT

•Reading: Ch7; 251-254, 258-

260, 241-250

•Homework: #21, #22

Carbohydrates

- A. Definition
- R Roles
- C. Monosaccharides-Chemistry
 - 1. Chirality
 - a. One or more asymmetric carbons
 - 2. Derivatives: the chemistry of carbohydrates
 - a. Oxidation
 - ii. C6
 - . Reduction
 - C1/C2 Other carbons
 - c. Ester formation
 - d. Amino sugars
 - 3. Polymerization
 - a. The Glycosidic Bond
 - b. Non-covalent bonds in macro-molecular structure
- D. Oligosaccharides
 - 1. Glycoproteins & glycolipids
 - 2. O-linked
 - 3. N-linked
 - 4. Sequence determination-ABO
- E. Polysaccharides
 - 1. Polymers of glucose
 - 2. Polymers of disaccharides

Carbohydrates

Relative amounts of tautomeric forms for some monosaccharide sugars at equilibrium in water at 40°Ca

Mono- saccharide		Relative Amount (%)				
	С	α-Pyranose	β -Pyranose	α-Furanose	β-Furanose	Total Furanose
Ribose	5	20	56	6	18	24
Lyxose -	5	71	29	Ь	Ь	<1
Altrose	6	27	40	20	13	33
→ Glucose	6	36	64	ь	b	<1
→ Mannose	6	67	33	Ь	Ь	<1
Fructose	6	3	57	9	31	40

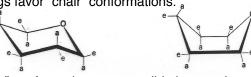
^aIn all cases, the open-chain form is much less than 1%. For data on other sugars, see S. J. Angyal, The composition and conformation of sugars in solution, *Angew. Chem.* 8:157–226(1969).

Why is the β -Glc more stable than α -Glc, and *visa versa* for Man? to answer this, we need to look at **ACTUAL** structures. These Haworth Projections are not the actual conformation.... What is?

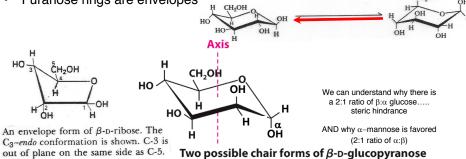
^bMuch less than 1%.

Actual Conformations of Cyclized Monosaccharides

- Cyclohexane rings have "chair" or "boat" conformations.
- Pyranose rings favor "chair" conformations.



- Multiple "chair" conformations are possible but require energy for interconversion (~46 kJ/mole).
- Furanose rings are envelopes



Carbohydrates

Monosaccharides: Chemistry

- Chemical Features:
 - Chirality
 - · One or more asymmetric carbons
 - · Linear and ring forms

- Derivatives: the chemistry of carbohydrates

- $\widehat{1}$ Oxidation
 - C1 C6
- (2) · Reduction
 - C1/C2
 - Other carbons
- 3 · Ester formation
- 4 · Amino sugars
- Polymerization
 - · The Glycosidic Bond
 - · Non-covalent bonds in macro-molecular structure

1

Monosaccharides: Derivatives

Oxidation: These make "sugar acids" or "acid sugars"

- Oxidation of aldehyde/ketone to acid (2e⁻ loss); reaction from the C1 of aldoses
 - named with "onic" suffix for acids ("onate" for conjugate base)
 - these sugars can reduce Cu²⁺ to Cu⁺ (Fehling's/Benedict's test) or Ag⁺ to Ag⁰ (Tollens' test)

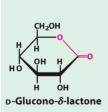
- Example: gluconic acid $^{HO}_{HO}$ $^{HO}_{OH}$ $^{HO}_{OH}$ $^{HO}_{OH}$ $^{+}$ $^{+}$ 2 Cu 99 $^{+}$ 5 OH $^{OH}_{HO}$ $^{OH}_{OH}$ $^{-}$ 2

Cu²⁺ + Reducing sugar → Cu⁺

This reaction is called Benedict's test

Cu⁺ → Cu₂O Red (ppt)

The copper is reduced and the sugar is oxidized. So, the sugar is called a **Reducing Sugar**. Reducing sugars have a free anomeric carbon.





Carbohydrates



Monosaccharides: Derivatives

Oxidation: These make "sugar acids" or "acid sugars"

Colorimetric Glucose Analysis

o-dianisidine (faint orange)

o-dianisidine (bright orange)

- Enzymatic methods are used to quantify reducing sugars such as glucose.
 - The enzyme glucose oxidase catalyzes the conversion of glucose to glucono-δ-lactone and hydrogen peroxide.
 - Hydrogen peroxide oxidizes organic molecules into highly colored compounds.
 - Concentrations of such compounds is measured colorimetricly.
- Electrochemical detection is used in portable glucose sensors.

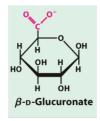


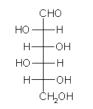
Monosaccharides: Derivatives

Oxidation: These make "sugar acids" or "acid sugars"

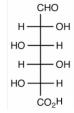
Oxidation of alcohol to acid (4e-loss)

- Reaction for C6 groups; like C1 oxidation, normally on aldoses
- Named as uronic acids ("uronate" for conjugate base)
- Many L-sugars are Uronic acids
- Examples: D-glucuronic acid, L-iduronic acid are among the most common acid sugars









OH OH

D-Idose

L-Idose

L-Iduronic acid

Carbohydrates



Monosaccharides: Derivatives

Reduction: These make "sugar alcohols" or "deoxysugars"

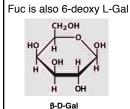
Reduction of aldehyde/ketone to alcohol (2e-gain)

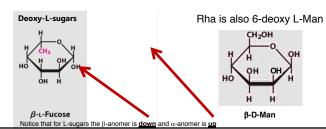
- Only carbon not already an alcohol is the anomeric carbon (C1/C2)
- Named as sugar "ol" or "itol"
- Examples: glycerol, mannitol, glucitol (sorbitol)



Reduction of alcohol carbon to methyl/methylene (2e-gain)

- Can react at any except the anomeric carbon
- Named as "x-deoxy" sugar with x being the reduced carbon
- Many are L-sugars are deoxy and have specific trivial names
- Examples: 2-deoxyribose, L-Fucose (Fuc) and L-Rhamnose (Rha)





Carbohydrates 3 Monosaccharides: Derivatives Esters: condensation of alcohol (sugar) and an acid Most important sugar esters use a phosphoric acid These are called phospho-sugars or sugar phosphates Examples: nucleotides, Glc 6-P, Fru 1,6-P₂, glycerol 3-phosphate ÇH₂OH HO HÓ HO ÓН **D-Glycerol 3-phosphate** α-D-Glucose 6phosphate **β-D-Fructose 1,6-bisphosphate**

Carbohydrates



Monosaccharides: Derivatives

Amines: condensation of alcohol (sugar) and ammonia

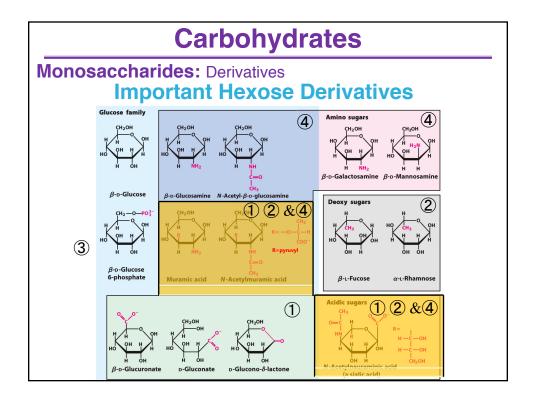
- · These are called amino-sugars
- · In biology, its ALWAYS at C2
- Often, the amino group will be further modified by an acetyl group (CH₃CO–) making an amide
- · Named as sugar"amine"

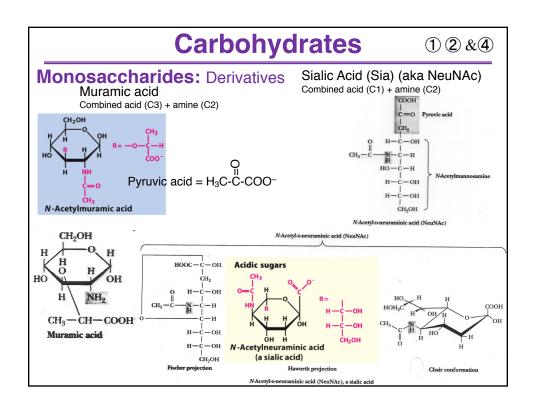
Example: glucosamine

when acetylated, the "N-acetyl" comes first Example: N-acetyl-glucosamine

when abbrev. is used, "NAc," it comes after Example: GlcNAc)

5





Monosaccharides: Chemistry

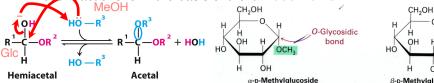
- Chemical Features:
 - Chirality
 - · One or more asymmetric carbons
 - · Linear and ring forms
 - Derivatives: the chemistry of carbohydrates
 - ① · Oxidation
 - C1
 - C6
- ② · Reduction
 - C1/C2
 - Other carbons deoxy-
- 3 · Ester formation
- 4 · Amino sugars
- Polymerization
 - · The Glycosidic Bond
 - · Non-covalent bonds in macro-molecular structure

Carbohydrates

Glycosidic Bond

Hemiacetals and Hemiketals are reactive to alcohols in condensation reactions

- Hemiacetals condense with alcohols to form Acetals.
- Hemiketals condense with alcohols to form Ketals.
- These reactions form the basis of the GLYCOSIDIC BOND.



- Two sugar molecules can be joined via a glycosidic bond between an anomeric carbon (the hemiacetal/nemiketal) and a hydroxyl carbon (the other sugar).
- The glycosidic bond between sugars is stable and does not readily hydrolyze.
- The anomeric carbon involved in the glycosidic linkage is fixed in its chirality and is non-reducing.
- The second monomer, with its unreacted hemiacetal, is still reducing.

HOOH
Adenosine
(B-D-adenine riboside)

HOHHOOH
Cellobiose
(Glucose- $\beta(1\rightarrow 4)$ -glucose)

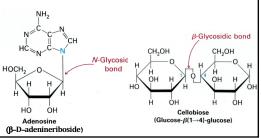
Carbohydrates

Hemiacetals and Hemiketals are reactive to alcohols in CONDENSATION reactions

- Hemiacetals condense with alcohols to form Acetals.
- · Hemiketals condense with alcohols to form Ketals.
- · These reactions form the basis of the GLYCOSIDIC BOND.

- Two sugar molecules can be joined via a glycosidic bond between an anomeric carbon (the hemiacetal/hemiketal) and a hydroxyl carbon (the other sugar).
- The glycosidic bond between sugars is stable and does not readily hydrolyze.
- The anomeric carbon involved in the glycosidic linkage is fixed in its chirality and is therefore nonreducing.
- The second monomer, with its unreacted hemiacetal, is still reducing.

The Glycosidic Bond

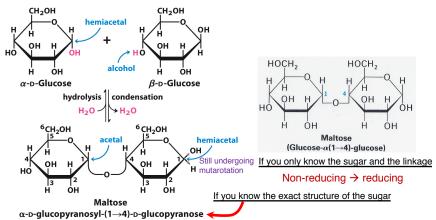


Disaccharides

Carbohydrates

Disaccharides:

- Disaccharides can be named by the organization and linkage or a common name.
 - The disaccharide formed upon condensation of two glucose molecules via a 1 → 4 bond is described as α-D-glucopyranosyl-(1→4)-D-glucopyranose.
 - The common name for this disaccharide is maltose.



As we make sugar-polymers, the convention is to have the non-reducing sugar to the LEFT and the reducing end at the RIGHT.

