

Carbohydrates

Oligosaccharides and Polysaccharides

I. Oligosaccharides – Definitions

- A. Def. - From 2-10 monosaccharides connected together**
- B. Disaccharides - Two monosaccharides connected together**
- C. Trisaccharides - Three monosaccharides connected together**
- D. Tetrasaccharides - Four monosaccharides connected together**
- E. Pentasaccharides - Five monosaccharides connected together**
- F. Hexasaccharides - Six monosaccharides connected together**

II. Oligosaccharides- How To Connect Rings & Types of Glycosidic Linkages

A. Beta (1 ---> 4)

1. Note that glycosidic linkage is beta type
2. Anomeric carbon is on right side
3. - OH at anomeric carbon can be up (β) or down (α)
 - a. So can have α - D – Sugar
or β - D –Sugar
4. Hemiacetal end is free to open or close
5. Acetal end is not free to open or close

B. Alpha (1 ---->4)

C. Alpha (1 -----> 6)

III. Oligosaccharides – Examples

A. D-Cellobiose - from partial hydrolysis of cellulose

1. Cellobiose + HCl -----> 2 Glucoses
2. Type of linkage β (1 \rightarrow 4)
3. Note α -D-cellobiose and β -D-cellobiose
4. Enzyme *cellulase* in microbes that reside in termites or in the rumen of the cow's stomach

B. D- Maltose - from partial digestion of starch

1. Maltose + HCl -----> 2 Glucoses
2. Type of linkage α (1 \rightarrow 4)
3. Note α -D-maltose and β -D-maltose
4. Compare maltose to cellulose
5. Used in baby foods and in malted milk
6. In body there is an enzyme ***mal-tase*** that converts maltose to 2 glucoses

C. D-Isomaltose

1. Isomaltose + HCl -----> 2 Glucoses
2. Type of linkage $\alpha(1 \text{ ---->}6)$
3. Note α -D-isomaltose and β -D-isomaltose
4. Enzyme ***maltase*** will not break the $\alpha(1 \text{ --->}6)$ link

D. D- Gentiobiose

1. Gentiobiose + HCl -----> 2 Glucoses
2. Type of linkage is $\beta(1 \text{ -----} > 6)$
3. Note α -D-gentiobiose and β -D-gentiobiose

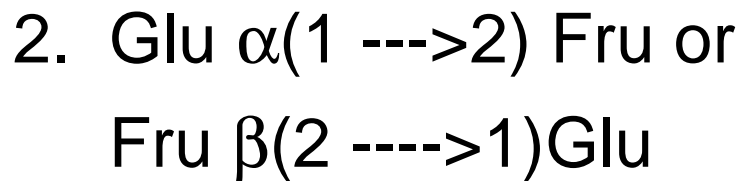
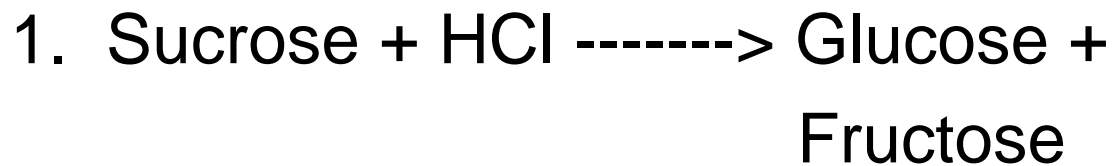
E. D-Trehalose

1. Trehalose + HCl -----> 2 Glucoses
2. Type of linkage (α 1 -----> α 1)
3. Note that there is no α or β -D-trehalose; only D-trehalose
 - a. Both rings are locked shut
4. Function - It is a major constituent of the circulating fluid (hemolymph) of insects. As such it serves as an energy storage compound

F. D- Lactose (Milk Sugar)

1. Lactose + HCl -----> Galactose +
Glucose
2. Connected by $\beta(1 \text{ ----} \rightarrow 4)$ link
3. Order of sugars is important
 - a. Gal $\beta(1 \text{ ----} \rightarrow 4)$ Glu is not same as Glu $\beta(1 \text{ ----} \rightarrow 4)$ Gal
4. Note there is α -D-Lactose and β -D-Lactose
5. Lactose may be hydrolyzed by an enzyme called ***lactase*** .
 - a. Enzyme can recognize the difference between
Gal $\beta(1 \text{ ----} \rightarrow 4)$ Glu and
Glu $\beta(1 \text{ ----} \rightarrow 4)$ Glu

G. D-Sucrose



3. Note that both anomeric carbons
are locked shut

4. No α or β anomers possible

IV. Oligosaccharides- Reactions

A. Benedict's reaction and Reducing Sugars

1. Aldehyde + Benedict's agent ---->
Salt of carboxylic acid + Cu_2O
(brick red)
2. Observe conversion of clear blue solution to cloudy, red (yellow, green)
3. All aldoses have the -CHO group on carbon #1 - known as reducing sugars

4. Formation of ring ties up the -CHO group, but the opening and closing of the ring and the equilibrium that exists keeps some straight chained sugars around.
 - a. True for tetrose, pentose, hexose, heptose, etc. aldoses

5. Ketoses are reducing sugars too
 - a. In basic solution (NaOH) there is an enediol equilibrium that creates -CHO on carbon # 1

 - b. The -CHO formed is what reacts

6. Many disaccharides are reducing sugars
 - a. While one of the rings is locked shut, the other is free to open and close

B. Benedict's Reaction and Nonreducing sugars

1. Monosaccharides that are locked shut ie methyl glycoside
2. Disaccharides that have their anomeric -OH tied up –
 - a. Glycosides of disaccharides
 - b. Also Trehalose and Sucrose

V. Polysaccharides - Definitions and Types

A. Definition - Polymers in which monosaccharides are joined together by glycosidic linkages to form chains of > 10 monosaccharides

B. Two Classification Systems

1. Classification by function

2. Classification by number of kinds of monosaccharides in the polysaccharide

C. Classification By Function

1. Structural - Involved as a part of an organism's structure
 - a. Examples: Cellulose and hemicellulose (wood fiber), peptidoglycan (cell walls of bacteria), chitin (exoskeleton of insects), hyaluronic acid (Holds cells together)

2. Storage - Polymers to store units of Glu, Fru, Man, Gal
 - a. Examples: Starch in plants, glycogen in animals, fructans (inulans), mannans, galactans

D. Classification by number of kinds of sugars in the polysaccharide

1. Homopolysaccharide - only one kind of monosaccharide unit in the chain - all the units linked together are identical.
 - a. Starch, glycogen, fructans, mannans, galactans, cellulose, chitin

2. Heteropolysaccharide - more than one kind of monosaccharide unit in the chain
 - a. Hemicellulose, pectin, hyaluronic acid, chondroitin sulfate, heparin

E. Characteristics of Polysaccharides

1. Heterogeneous group - The name of a polysaccharide takes in a wide number of compounds-

Not all celluloses have the same number of glucoses in them. The name cellulose denotes that the polysaccharide is made up of glucoses connected by $\beta(1 \rightarrow 4)$ glycosidic linkages, and that the number of glucoses are within certain limits. Not all cellulose molecules have the same number of glucoses.

2. Identified by types of sugars within and the linkages that hold them together and by size range

VI. Polysaccharides- Structural

A. Cellulose

1. Complete hydrolysis yields only glucose
2. -Glu β (1 \longrightarrow 4)Glu β (1 \longrightarrow 4)Glu-
3. See transparency for linear structure
4. Abbreviation
$$-(\text{Glu } \beta (1 \longrightarrow 4)\text{Glu})_n-$$
5. Molecular Weight between 50,000 and 500,000
 - a. Ave number of glucoses per molecule \sim 300-2500

6. Chemical Properties

a. Water Solubility

b. Reaction with Benedict's reagent

c. Reaction with Iodine

B. Chitin - Chief Component of Exoskeleton of Insects

1. Complete hydrolysis yields N-acetylglucosamine
2. Structures of N-acetylglucosamine
3. Linking of N-AcGlu together by β (1 \longrightarrow 4) linkages

4. Comparison to cellulose

5. Chemical Properties

a. Water Solubility

b. Reaction with Benedict's Reagent

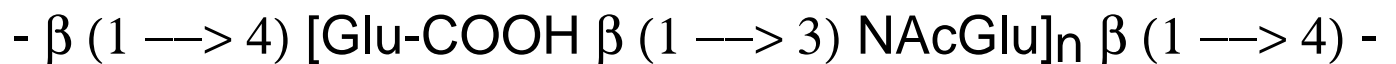
C. Hyaluronic Acid

1. Components

a. D-glucuronic acid

b. N-acetylglucosamine

2. Structure showing linkages



3. Function

- a. Serves as lubricant in synovial fluid of the joints
- b. Part of extracellular matrix

D. Chondroitin Sulfate

VII. Polysaccharides – Storage

A. "Starch" – Facts

1. Plants - Amylose and Amylopectin
2. Animals – Glycogen
3. Serves as nutritional reserve

B. Amylose

1. Known as linear starch
2. alpha (1--->4) linkage
3. Helical Structure
4. Size
 - a. Ave MW 10,000 - 50,000
 - b. Range 2,000 - 500,000
 - c. Ave 60 - 300 Glu / molecule

5. Compare To Structure of Cellulose

- a. Has 300 - 2500 Glu per molecule or MW of 50,000 - 500,000

6. Reactions

- a. Water Solubility
- b. Benedict's Reagent
- c. Iodine

7. Alpha and beta amylases

- a. Alpha amylase attacks at random ----> mixture of Glu and maltose

- b. Beta amylase attacks in organized fashion ----> maltose

- c. Can alpha or beta amylase attack beta (1--->4) or alpha (1 ---> 6) linkages? **NO**

C. Amylopectin

1. Structure

a. Glu connected by alpha (1--->4) and alpha (1--->6)

b. Frequency of branches

1. 1 terminal Glu per 24 - 30 Glu units

c. Size of polysaccharide

1. MW = 300,000 or ~ 1800 Glu's

2. ~ 60 branching points

d. Comparing Size of Amylopectin to other polysaccharides

1. Amylose Ave MW 10,000 - 50,000

2. Amylopectin MW 50,000 - 500,000

2. Reactions of Amylopectin

a. With Benedict's reagent

b. With Iodine - no helix possible

c. Digestibility

1. Dextrin - Partially digested starch
2. Limit Dextrin - Digested to alpha (1--->6) linkages
3. Debranching enzyme

D. Glycogen

1. Animal Starch

2. Structure

a. Glu connected by alpha
(1--->4) and alpha (1--->6)

b. Frequency of branches

1. 1 branch per 12- 20 glu

2. Amylopectin - 1 branch per
24 - 30 glu

c. Size of polysaccharide

1. Range 250,000 - several million
2. 1500 - 20,000 Glu / molecule
3. Compare to Amylopectin
MW = 300,000
4. Amylose MW = 10,000 - 50,000 but varies from 2000-500,000
5. Cellulose = 50,000 - 500,000

3. Reactions of Glycogen
 - a. With Benedict's reagent
 - b. With Iodine
 - c. Digestibility
 1. Dextrin - Partially digested starch
 2. Limit Dextrin - Digested to alpha (1--->6) linkages
 3. Debranching enzyme

E. Galactans, Mannans, & Fructans (Inulin)

1. Galactans (Galactogen) made up of galactose residues
 - a. Similar to glycogen except all residues are made up of galactose rather than glucose
 - b. β (1 \longrightarrow 4) or α (1 \longrightarrow 4) linking galactoses together in straight chain part and α (1 \longrightarrow 6) at the branches
 - c. Found in slug eggs - presumably a nutritional reserve for developing slugs

2. Mannans made up of mannose residues
 - a. Mannans may be found in some berries, vegetable ivory, endosperm of palm nuts

3. Fructans (Inulin)

- a. Fru held together by β (1 \rightarrow 2) linkages