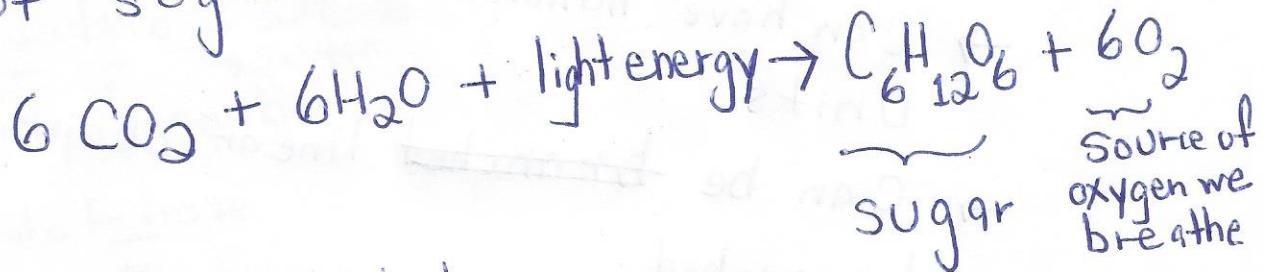


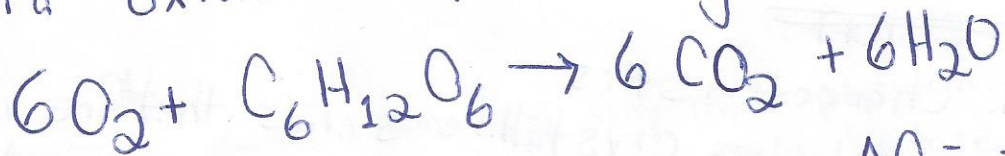
1. Carbohydrates

- Are the most abundant biomolecules on Earth
- Are a major dietary staple
- Provide an excellent source of energy
- ~~through oxidation of the carbohydrates in most photosynthetic cells~~

a. Photosynthetic organisms convert light energy to chemical energy and store it in the bonds of sugar.

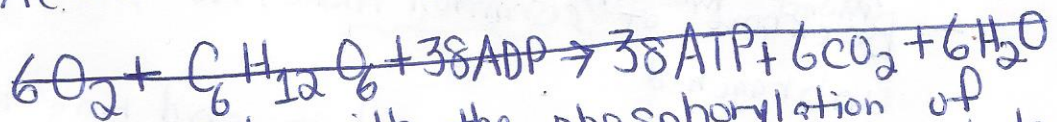


b. Non photosynthetic organisms utilize the energy stored in sugar via oxidation of the sugar.



$$\Delta G = -2870 \frac{\text{kJ}}{\text{mol}}$$

Actual reaction (Krebs cycle)



is coupled with the phosphorylation of adenosine diphosphate (ADP) to adenosine triphosphate

$$6\text{O}_2 + \text{C}_6\text{H}_{12}\text{O}_6 + X \text{ADP} \rightarrow 6\text{CO}_2 + 6\text{H}_2\text{O} + X\text{ATP}$$

Some energy loss in this process.

2. Types of carbohydrates

a. Monosaccharides - simple sugars

b. Oligosaccharides - Short chains of monosaccharide units linked by glycosidic bonds

↳ Disaccharides are the most abundant

c. Polysaccharides - Sugar polymers containing more than 20 or more monosaccharide units

↳ Can have hundreds or even thousands of units

↳ Can be ~~branched~~ linear chains or branched.

3) Monosaccharides

~~colorless~~

A. Characteristics

- colorless, crystalline solids that are very water soluble and insoluble in nonpolar solvents

- Are either aldehydes (aldoses) or ketones (ketoses) with two or more hydroxyl groups

- Backbone of common monosaccharides are unbranched

- Can exist in open-chain and ring forms

↳ In open-chain form, there is always a carbonyl group ($C=O$)

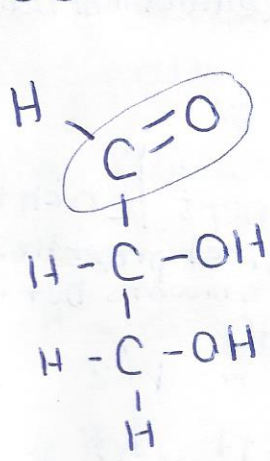
↳ other C are bound to hydroxyl groups

~~Divided into two classes~~

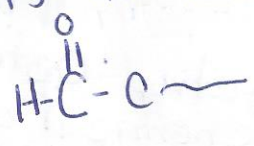
- a. Aldoses
- b. Ketoses

B. Aldose

General form



Carbonyl Aldehyde @ the end of the chain is an aldehyde

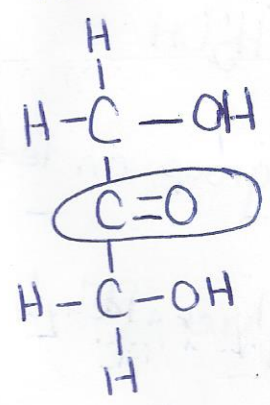


Glyceraldehyde

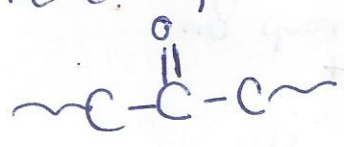
aldotriose suffix for sugar
 prefix 3-carbons

aldotetrose
 4-carbons

C. Ketose



Carbonyl @ any other position except the ends, it is a ketose

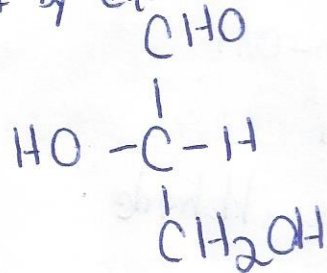
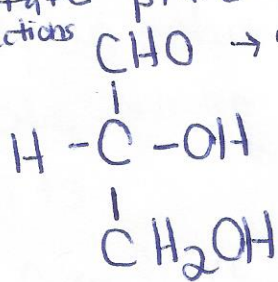


dihydroxyacetone
ketotriose
 prefix

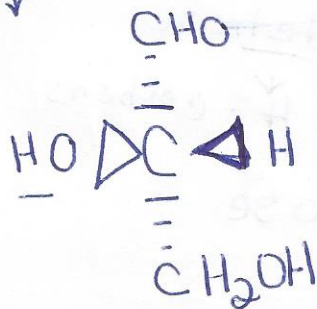
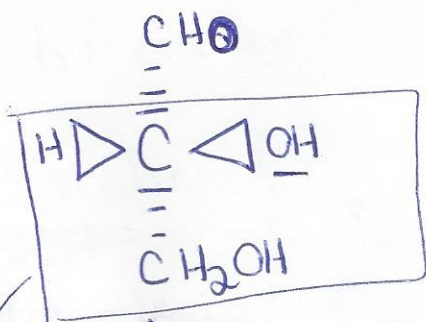
D. Chirality and nomenclature/numbering system

All monosaccharides except dihydroxyacetone contain one or more ~~asymmetric~~ (chiral carbons) → optically active.

- ~~Fisher projection~~ Optical isomers/enantiomers
 Have identical chemical and physical properties but rotate plane-polarized light by equal amounts but in opposite directions



Non-superimposable mirror images
 Fisher projection (perspective formulas)



Remains constant

All 3 Cs aligned; OH group on right

D-glyceraldehyde

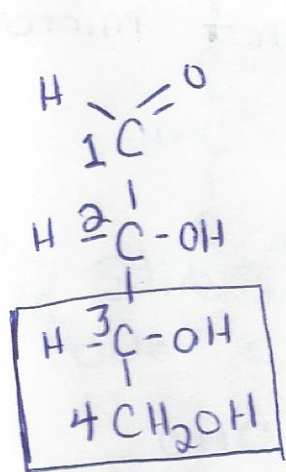
OH group on left

L-glyceraldehyde

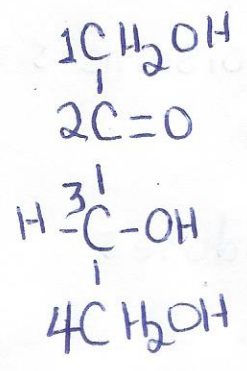
* → D-isomers tend to be more common especially for hexoses.
 6 C

b. Number system

The carbons of a sugar are numbered beginning at the end of the chain nearest the carbonyl group.



D-Erythrose



D-Erythrulose

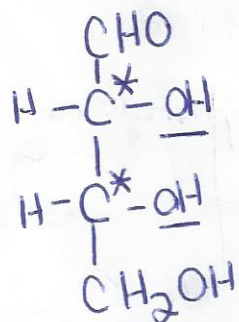
c. In general, a ^{sugar} molecule with n chiral centers can have 2^n stereoisomers.

a. Enantiomers

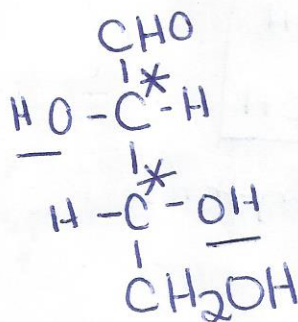
b. Diastereomers

→ Stereoisomers that are not mirror images

D- Aldoses



D-Erythrose



D-Threose

• Differ in the position of the hydroxyl groups

→ Have different physical properties + chemical reactivities.

D-Erythrose + D-Threose have different water solubilities

c. Epimers are two sugars that differ only in the configuration around one carbon atom.

⇒ Slide 2

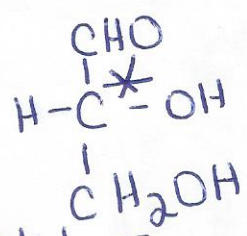
Identifying stereoisomers

In general, a molecule with n chiral centers can have 2^n stereoisomers.
Enantiomers
Diastereomers

→ Aldoses

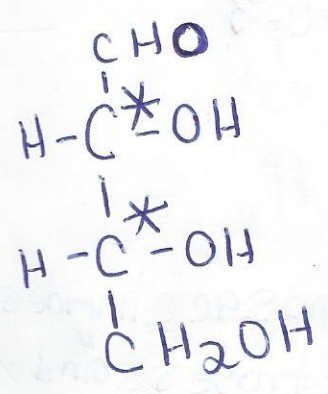
a. Three carbons have 1 chiral center

Glyceraldehyde ~~(only)~~ $2^1 \rightarrow 2^1 = 2$ isomers



⇒ Slide 3.

b. Four carbons have 2 chiral centers



$2^2 = 4$ isomers

D-Erythrose

General rule:

of chiral centers: $\# \text{C} - 2$

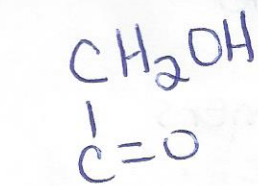
of stereoisomers: $\# \text{C} - 2$

⇒ Slide 4, 5 (5C+6C) 2
→ Ketoses

a. Three carbons have no chiral center
-Dihydroxyacetone

⇒ Slide 6

b. 4 C's have 1 chiral center



D-Erythrulose

General rule:

of chiral centers: #C - 3

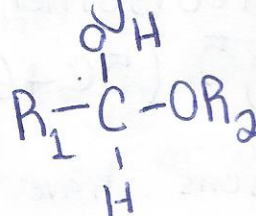
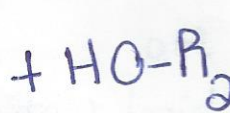
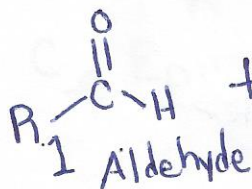
of stereoisomers: $2^{\text{\#C}-3}$

⇒ slide 7 + 8

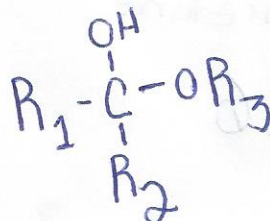
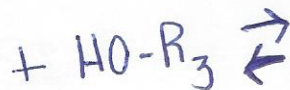
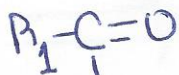
E. The Cyclic structure of monosaccharides

- In aqueous solution, aldotetroses and all monosaccharides with five or more carbon atoms in the backbone occur predominantly as cyclic (ring) structures

The result of the general reactions:



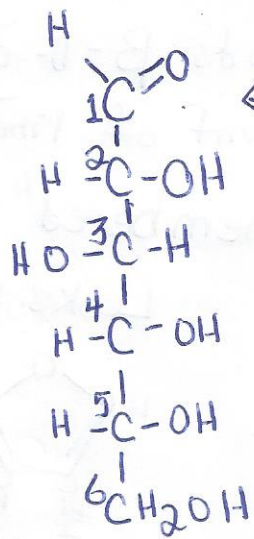
Hemiacetal



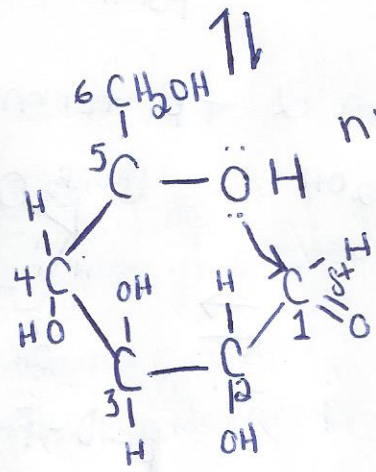
Hemiketal

- An additional asymmetric carbon atom forms that can exist in two stereoisomeric forms.

9. D-Glucose (~~Allose~~) (Aldohexose)

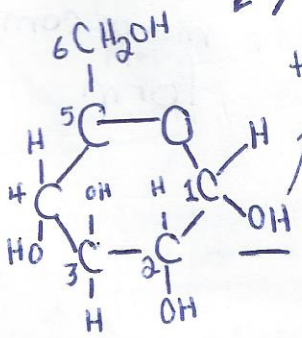
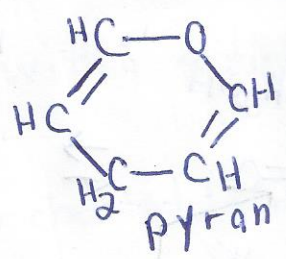


interact

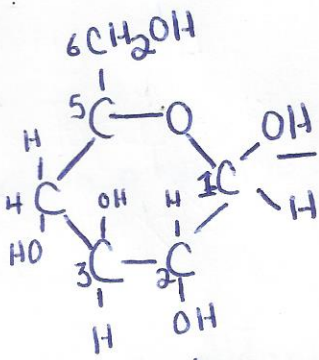


nucleophile

Looks like



trans to CH₂OH



cis to CH₂OH

Get inserted into the name.

α-D-glucopyranose

β-D-glucopyranose

anomer

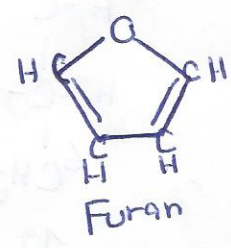
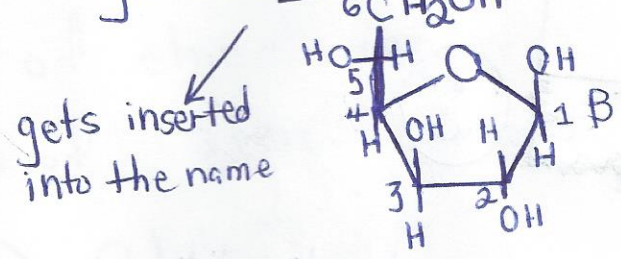
isomers of monosaccharides that differ only in their configuration about the hemiacetal/hemiketal C

C1 is the anomeric C

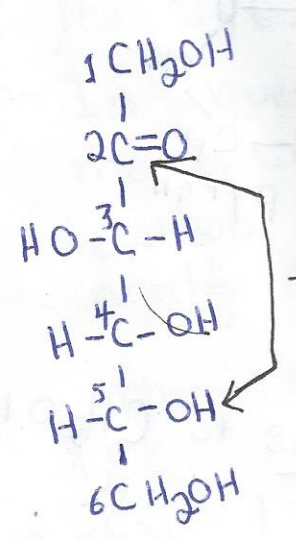
The α and β anomers of D-glucose interconvert in aqueous solution by a process called mutarotation, a C₁ bond breaking process.

@ equilibrium have one-third α -D-glucose
two-thirds β -D-glucose

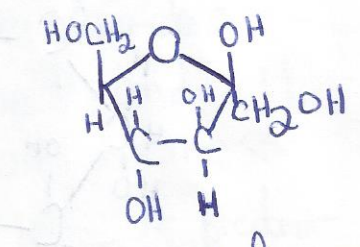
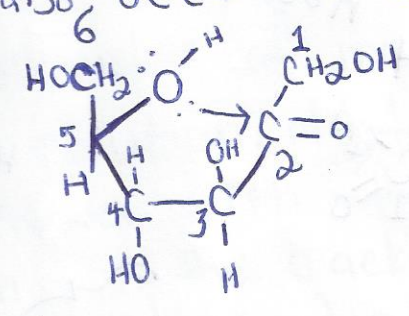
→ Also ^{have very little} not the five-membered ring
glucofuranose
Looks like:



b. Ketohexoses also occur in α + β forms

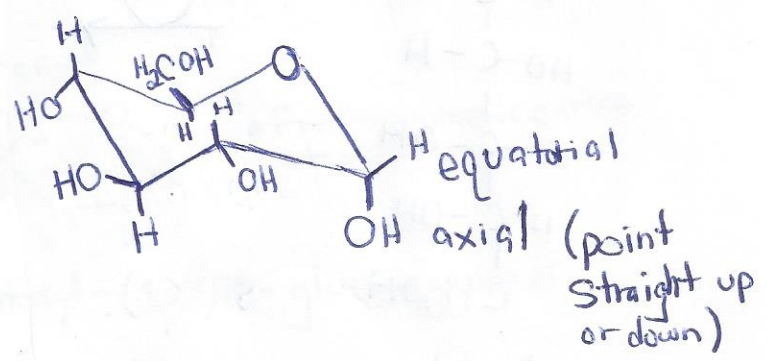
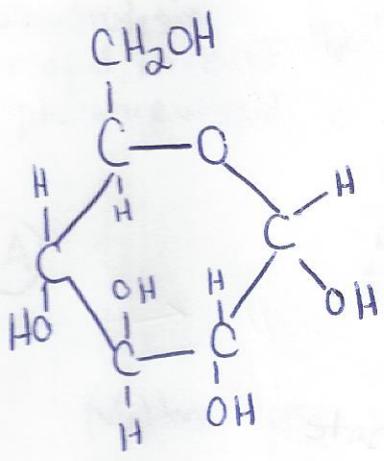


Interact



β -D-Fructofuranose
more common form

- The six-membered pyranose ring is not planar, exists in a "chair" conformation
Haworth perspective formula:



alpha-D-Glucopyranose

F. Organisms contain a variety of hexose derivatives

a. A hydroxyl group is replaced with a substituent

- Amino groups
- Phosphate groups → important for chemical transformation of sugars
- Acid groups (lactic acid)
- Alkyl groups

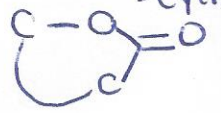
⇒ Slide 9

b. Oxidation of a carbon atom to a carboxyl group

⇒ Slide 10

- @ Carbonyl carbon → Aldonic acid
- @ C6 → Uronic acid

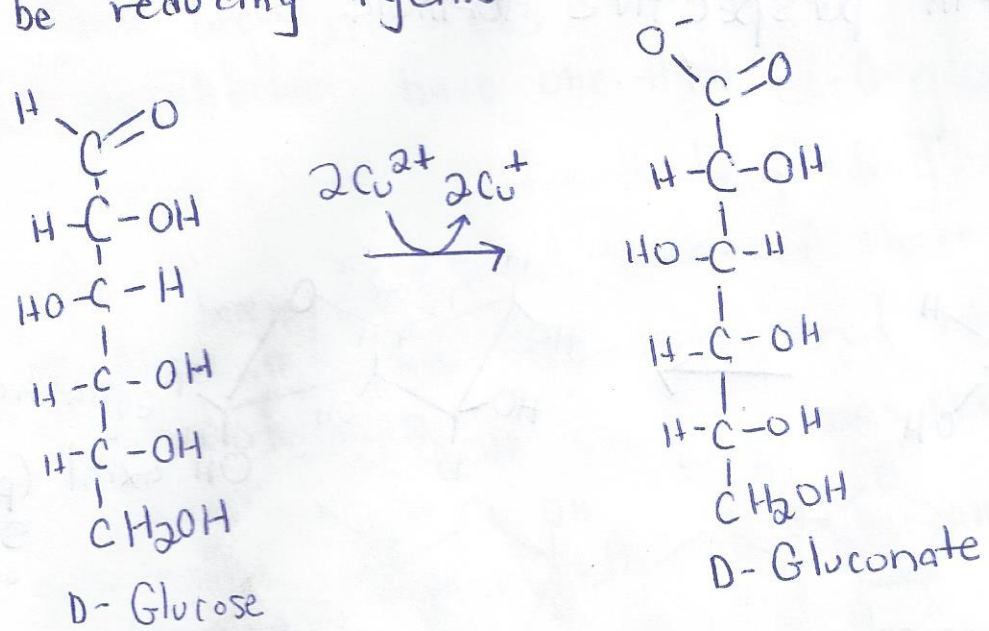
Can form stable intramolecular esters called lactones - cyclic ester



⇒ Slide 10

G. Monosaccharides are reducing agents

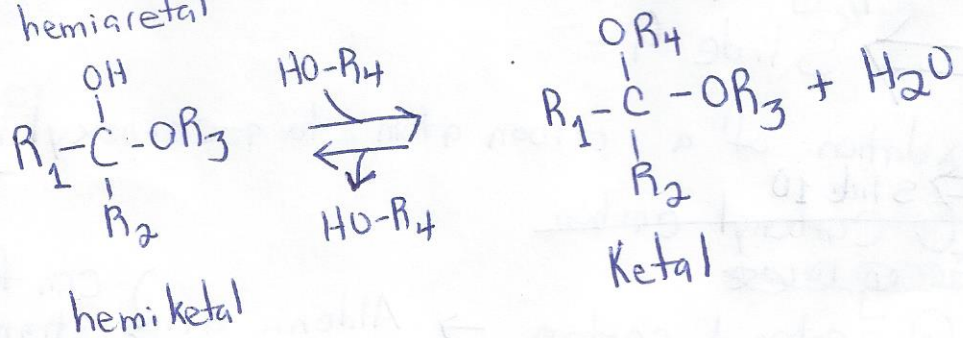
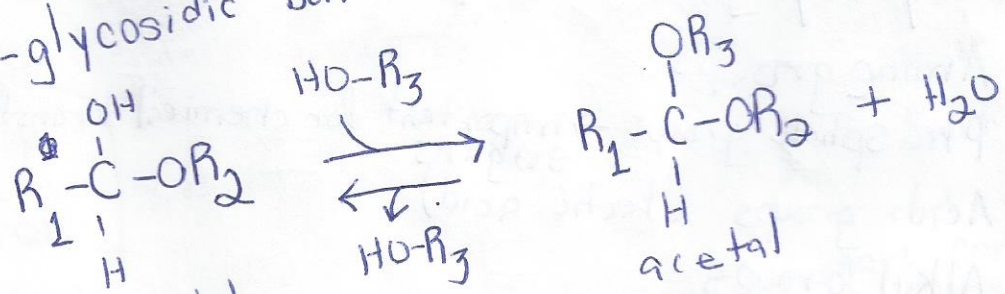
- Linear form is necessary for sugars to be reducing agents.

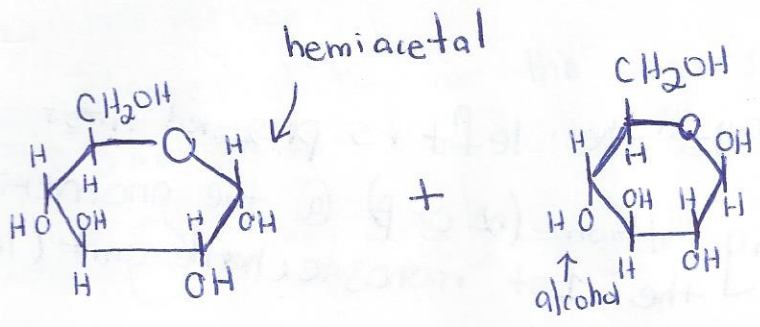


- This property can be used to quantify [sugar] by determining the amount of change of oxidizing agent. Fehling's test

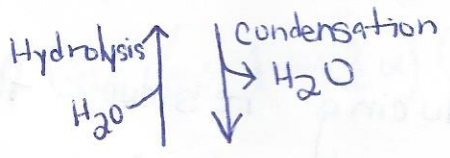
4. Disaccharides

- Consist of two monosaccharides joined by an O-glycosidic bond via the following reactions

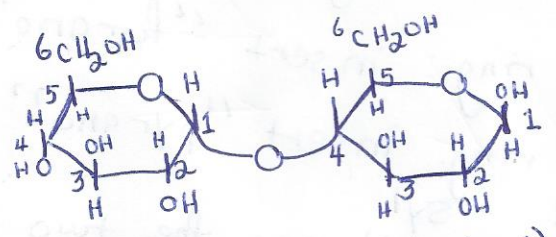




Hydrolysis is rapid in the presence of acid.



(A)



Free anomeric carbon atom

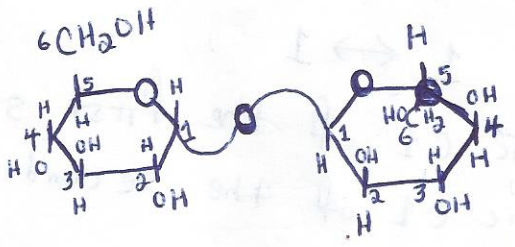
Maltose or α -D-glucopyranosyl-(1 \rightarrow 4)-glucopyranose

nonreducing end
 • Blocked anomeric carbon atom that can not be linearized

reducing end
 • can be α or β configuration

Another possibility:

(B)



Tetrahalose or α -D-glucopyranosyl-(1 \leftrightarrow 1)- α -D-glucopyranoside

nonreducing nonreducing
 • Both anomeric carbons are blocked

Nomenclature:

1) Nonreducing end to the left is presented first
• Give the configuration (α or β) @ the anomeric carbon joining the 1st monosaccharide unit (left) to the second.

2) Name the nonreducing residue then

• Five-membered ring: insert "furan"

• Six-membered ring: insert "pyrano"

3) Indicate in parentheses the two C atoms joined by the glycosidic bond and use arrow to indicate ~~reducing ability~~ anomeric C.

Example (A) $1 \rightarrow 4$

Anomeric C1 of the first sugar is joined to C-4 of the second sugar

Example (B) $1 \leftrightarrow 1$

Anomeric C1 of the first sugar is joined to anomeric C1 of the second sugar

4) Name the second residue.

~~5) If there is a that are subsequent~~

• Suffix -ose for reducing sugar

• Suffix -ide for nonreducing sugar

5) If there are additional residues then repeat the convention for subsequent residues ending with the suffix -syl unless it is the last residue.

Simplified version:

15

Use abbreviations for the sugars assuming all D isomers
→ Slide 11

