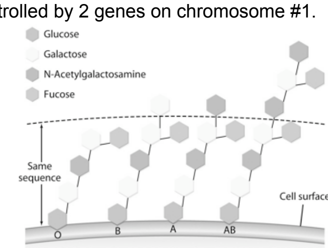
Polysaccharides

Blood Group Type

http://anthro.palomar.edu/blood/Rh_system.htm

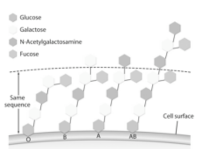
Involves a large number of different antigens on the surface of red cells whch are genetically controlled by 2 genes on chromosome #1.



Also, proteins on the cell surface: Rh factor, + or -

Blood Histocompatibility

http://anthro.palomar.edu/blood/Rh_system.htm

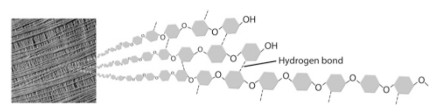


Red blood cell compatibility table[58][59]

Recipient[1]	Donor[1]									
	O−	O+	A−	A+	B−	B+	AB−	AB+	US	WORLD
O−	✓								6.6	4.5
O+	✓	✓							37	36
A−	✓		✓						6.4	3.5
A+	✓	✓	✓	✓					36	28
B−	✓				✓				1.5	1.5
B+	✓	✓			✓	✓			8.5	21
AB−	✓		✓		✓		✓		0.6	0.5
AB+	✓	✓	✓	✓	✓	✓	✓	✓	3.4	5

Cellulose: a glucose polymer

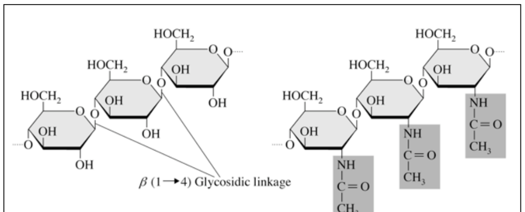
- *Can animals in the isoptera family feed on it?*
- *Can homo sapiens feed on it?*



(a) Cellulose fibrils in a plant cell wall

(b) Structure of cellulose in a fibril

The structures of cellulose (a) and chitin (b). In both substances, all glycosidic linkages are of the β-(1, 4) type.



(a)

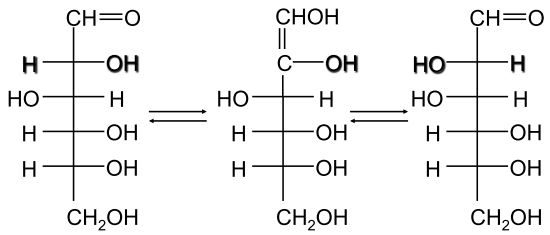
(b)

Epimerization, Isomerization, and Biological Aldol/Retro-Aldol Reactions of Carbohydrates

Enol Forms of Carbohydrates

- Enolization of an aldose scrambles the stereochemistry at C-2.
- This process is called *epimerization*. Diastereomers that differ in stereochemistry at only one of their stereogenic centers are called epimers.
- D-Glucose and D-mannose, for example, are epimers.

Epimerization



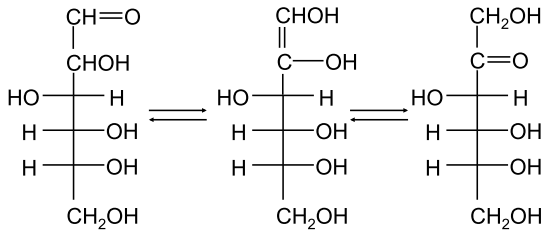
D-Glucose Enediol D-Mannose

This equilibration can be catalyzed by hydroxide ion.

Enol Forms of Carbohydrates

- The enediol intermediate on the preceding slide can undergo a second reaction. It can lead to the conversion of D-glucose or D-mannose (aldoses) to D-fructose (ketose).

Isomerization



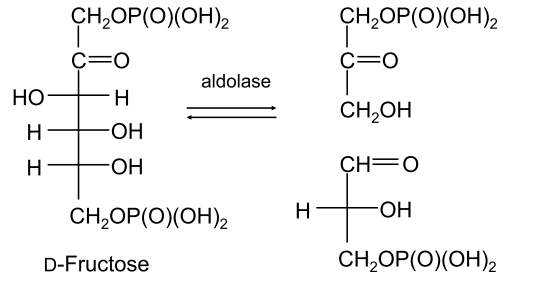
D-Glucose or D-Mannose Enediol D-Fructose

Glycolysis / Retro-Aldol reactions

- D-fructose 6-phosphate undergoes phosphorylation of its free CH_2OH group to give D-fructose 1,6-diphosphate.
- D-Fructose 1,6-diphosphate is cleaved into two 3-carbon products by a reverse aldol reaction.
- This *retro-aldol* reaction is catalyzed by the enzyme *aldolase*.

Glycolysis occurs metabolically in nearly every organism, both aerobically and anaerobically. The released energy is used to form the high energy compounds, ATP and NADH.

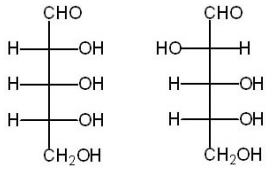
Isomerization



D-Fructose 1,6-phosphate

Question

- What is the relationship between the structures shown?

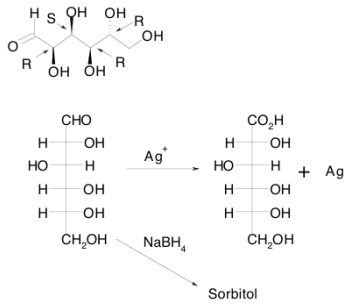


- A) constitutional isomers B) meso forms
- C) enantiomers D) epimers
- E) diastereomeric disaccharides

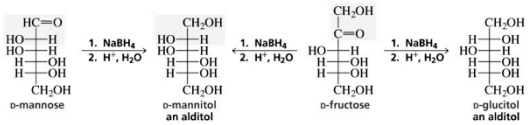
Reactions of Sugars

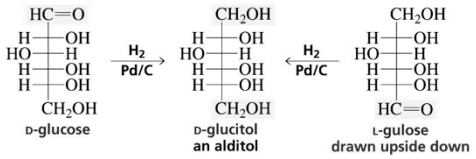
Monosaccharides

Oxidation-Reduction Products

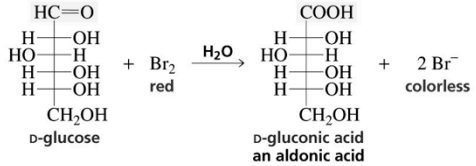


Redox Reactions of Monosaccharides





Oxidation

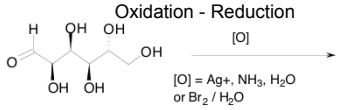


Ketones and alcohols cannot be oxidized by Br_2

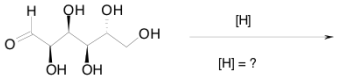
Questions to Consider:

Reactions of Monosaccharides

Oxidation - Reduction

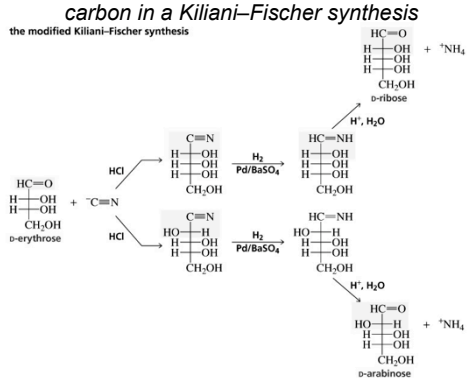


Aldoses are "reducing" sugars, that is, they are oxidized under very mild conditions. (Only the aldehyde is oxidized.)

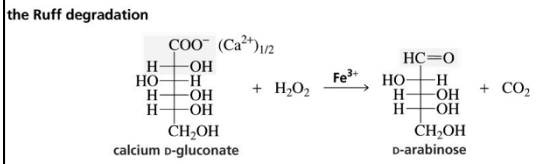


1) Identify the starting sugar as D- or L-.
2) Draw Fisher projections for the products.
3) Draw a Haworth projection of the beta pyrano anomer.

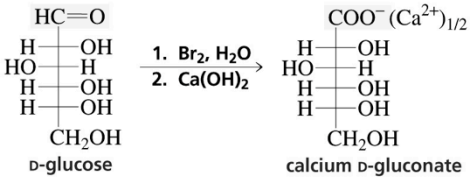
The carbon chain of an aldose can be increased by one carbon in a Kiliani–Fischer synthesis



The Ruff degradation shortens an aldose chain by one carbon

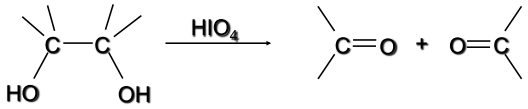


Preparation of the Calcium D-Gluconate for the Ruff Degradation



Periodic Acid Oxidation

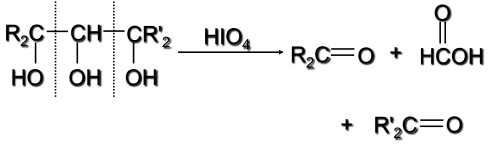
Vicinal diols are cleaved by HIO_4.



- Cleavage of a vicinal diol consumes 1 mol of HIO_4.

Also Cleaved by HIO_4

Compounds that contain three contiguous carbons bearing OH groups



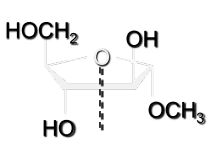
- 2 mol of HIO_4 are consumed. 1 mole of formic acid is produced.

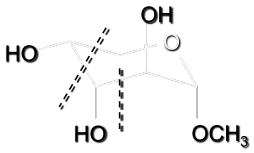
Question

- How many moles of formic acid and formaldehyde, respectively, would be produced when D-arabinitol is oxidized with periodic acid (HIO_4)? (*(2R,4R)-pentane-1,2,3,4,5-pentol)*
- A) 0 moles of formic acid: 5 moles of formaldehyde
- B) 1 moles of formic acid: 4 moles of formaldehyde
- C) 2 moles of formic acid: 3 moles of formaldehyde
- D) 3 moles of formic acid: 2 moles of formaldehyde

Structure Determination Using HIO_4

Distinguish between furanose and pyranose forms of methyl arabinoside

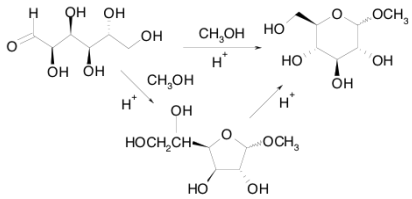




2 vicinal OH groups; consumes 1 mol of HIO_4

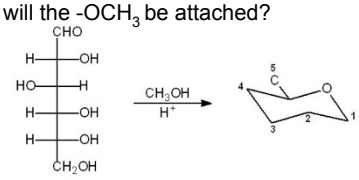
3 vicinal OH groups; consumes 2 mol of HIO_4

Reactions of Monosaccharides
Glycoside (acetal) formation



Question

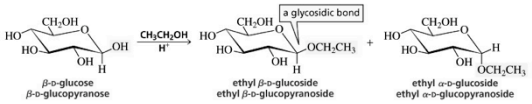
- When glucose is allowed to react with methanol in the presence of a catalytic amount of acid, to which carbon of the ring will the -OCH_3 be attached?
-



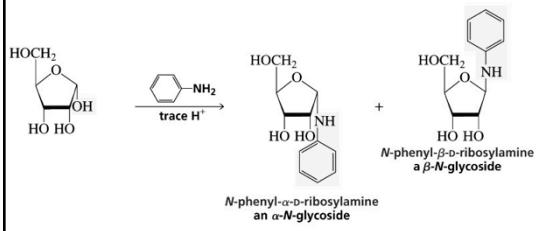
- A) 1 only B) 1 and 5
- C) 1, 2, 3, and 4 D) 2, 3, 4 and 5

Formation of Glycosides

The acetal (or ketal) of a sugar is called a glycoside



Formation of an N-Glycoside

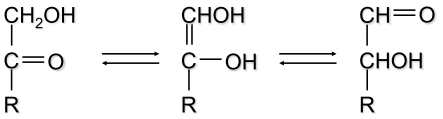


Reducing Sugars

A sugar with an aldehyde, a ketone, a hemiacetal, or a hemiacetal group is a reducing sugar

Examples of Reducing Sugars

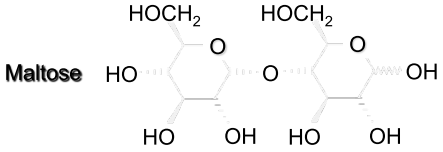
- Aldoses: because they have an aldehyde function in their open-chain form.
- Ketoses: because enolization establishes an equilibrium with an aldose.



oxidized by Cu^{2+}

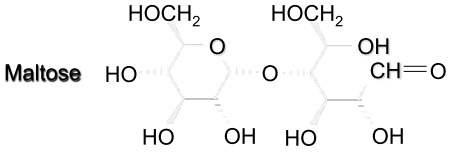
Examples of Reducing Sugars

- Disaccharides that have a free hemiacetal function.



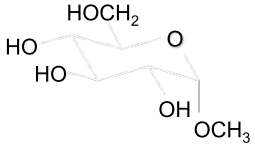
Examples of Reducing Sugars

- Disaccharides that have a free hemiacetal function.



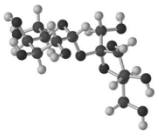
oxidized by **Cu^{2+}**

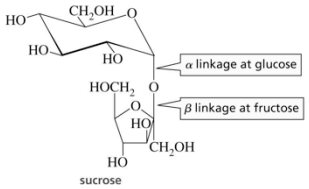
Glycosides are not reducing sugars



Methyl α-D-glucopyranoside lacks a free hemiacetal function; cannot be in equilibrium with a species having an aldehyde function

The most common disaccharide sucrose:

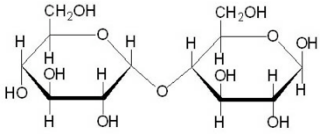




Sucrose is not a reducing sugar

Question

- The disaccharide below is maltose. Maltose is a reducing sugar.



A) True B) False