CHAPTER 23

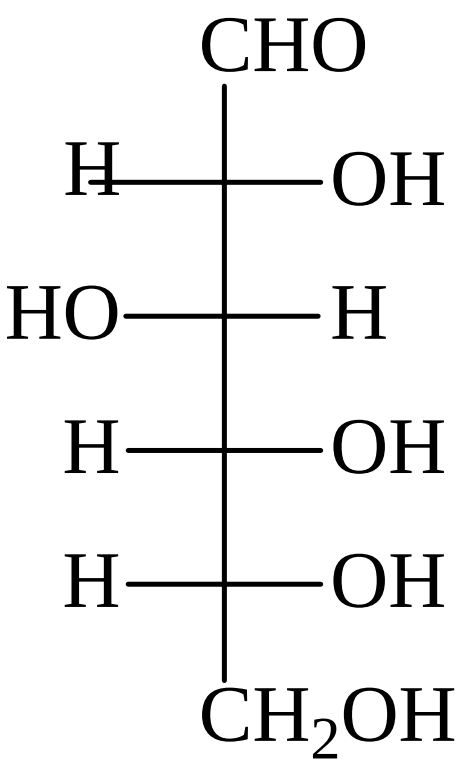
Carbohydrates

Introduction

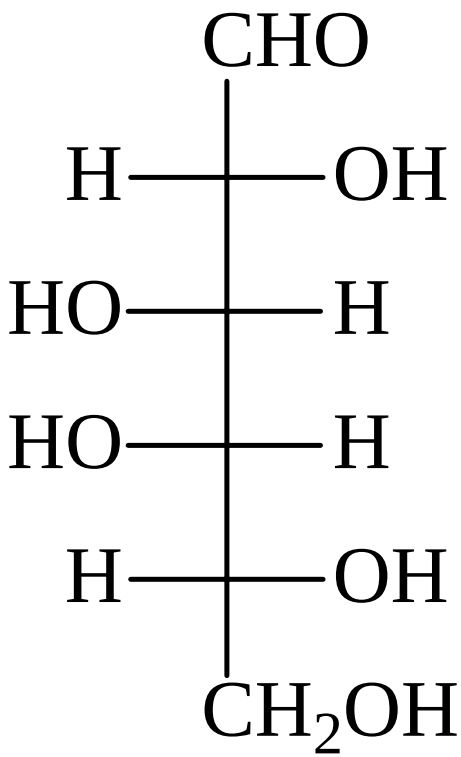
- Carbohydrates are naturally occurring compounds of carbon, hydrogen , and oxygen.
- Carbohydrates have the empirical formula CH_2O.
- Carbohydrates have the general formula $C_nH_{2n}O_{n.}$ eg. Glucose: $C_6H_{12}O_6$

- Carbohydrates are defined as polyhydroxy aldehydes or ketones or substances that hydrolyze to yield polyhydroxy aldehydes and ketones.
- Monosaccharides are carbohydrates that cannot be hydrolyzed to simpler carbohydrates = simple sugars.
- Disaccharides can be hydrolyzed to two monosaccharides.
- Oligosaccharides yield 2 to 8 monosaccharides.
- Polysacccharides yield >8 monosaccharides

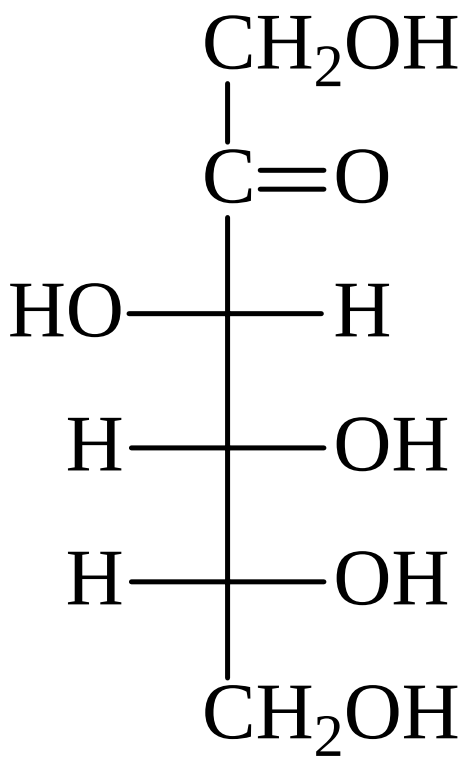
Some important monosacharides



D-glucose



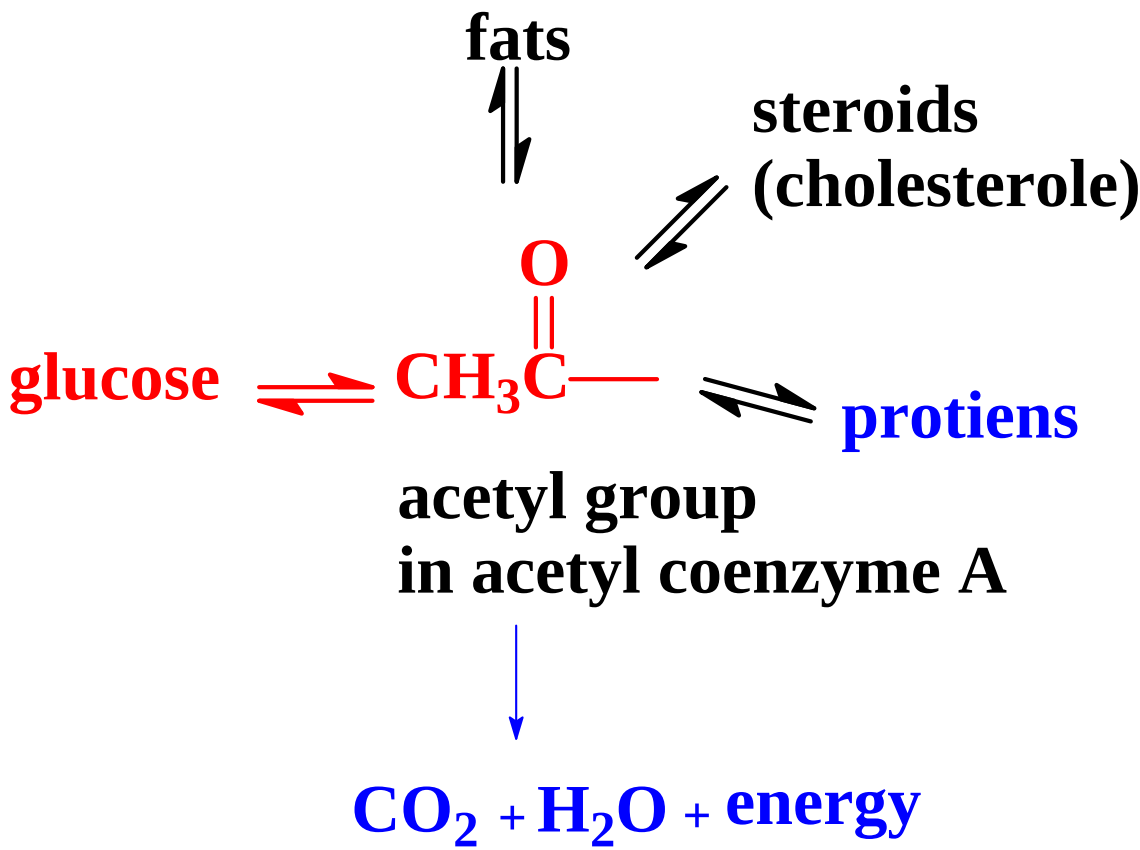
D- galactose



D-fructose

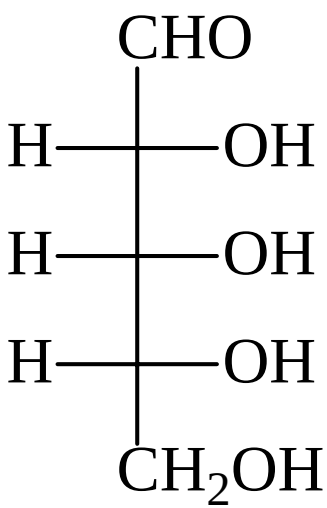
Glucose

- Blood sugar.
- Mammals convert sucrose, lactose, maltose, and starch to glucose which is then used for energy



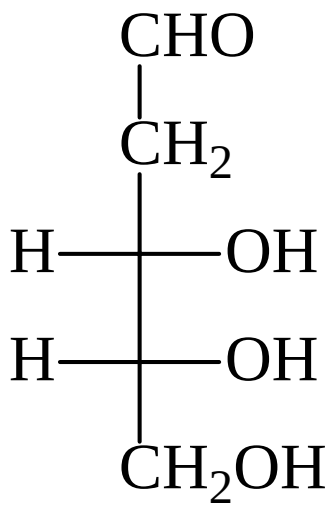
Other monosaccharides

- **Fructose** ➔ sweetest tasting sugar. It occurs in fruit and honey.
- **Galactose** ➔ found bonded to glucose in the disaccharide lactose.
- **Ribose and deoxyribose** ➔ form part of the polymeric backbone of nucleic acids.



D-ribose

$C_5H_{10}O_5$



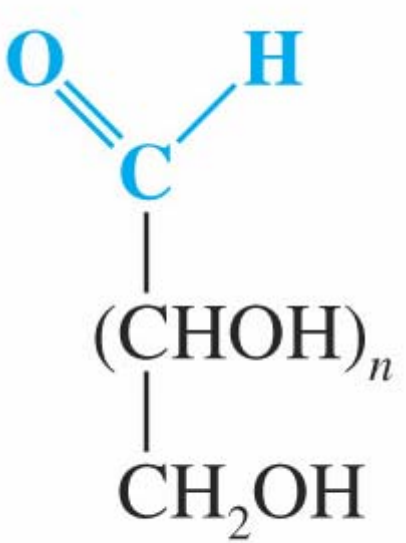
2-deoxy-D-ribose

deoxy = minus an oxygen

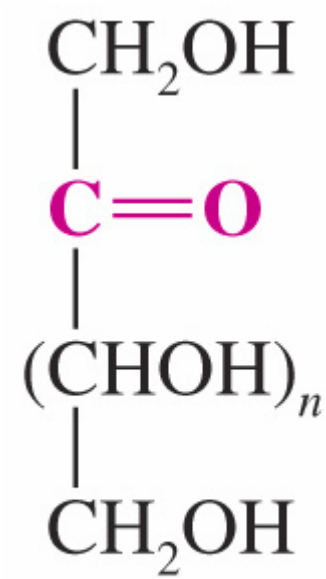
Classification of Monosaccharides

- The suffix **–ose** is used to designate a carbohydrate. Carbohydrate names ending in **–ose** (eg. Glucose, galactose).
- Mononsacchrides that contain aldehyde group ➔ **Aldoses** (aldehyde + ose) (glucose and ribose).
- Monosacchrides with ketone group ➔ **Ketoses** (ketone + ose) (frctose)

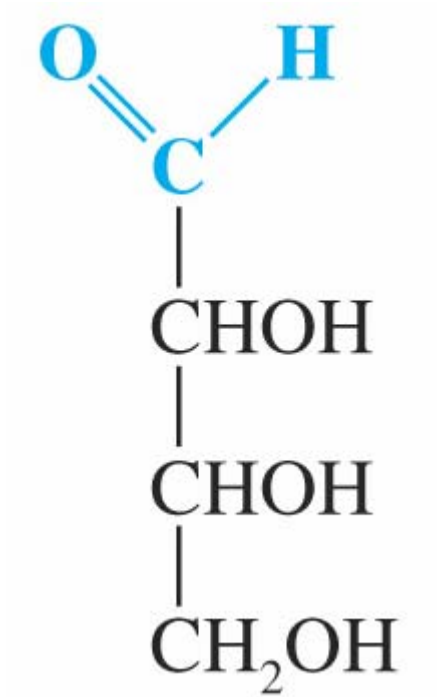
- The number of carbon atoms are designated by tri, tetr-, etc (for example a **triose** is three carbons)



An aldose

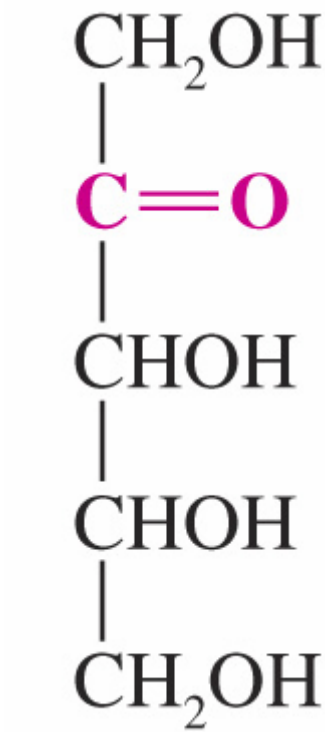


A ketose



An aldotetrose

C_4

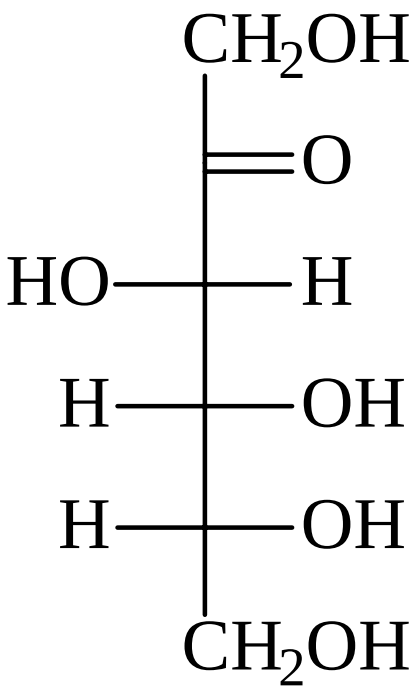


A ketopentose

C_5

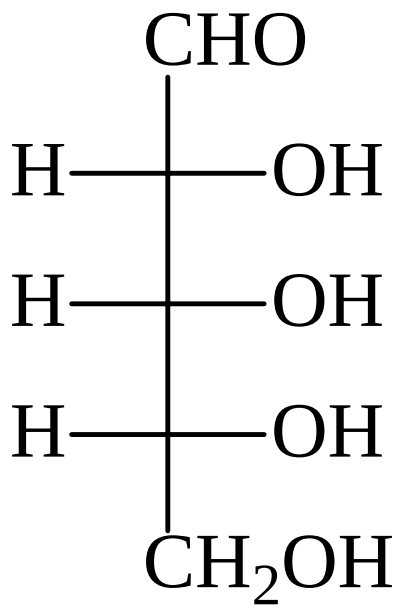
- Ketones are often given the ending –**ulose**.

example. Fructose,



Ketohexose or hexulose

Ketopentose or pentulose



D-ribose

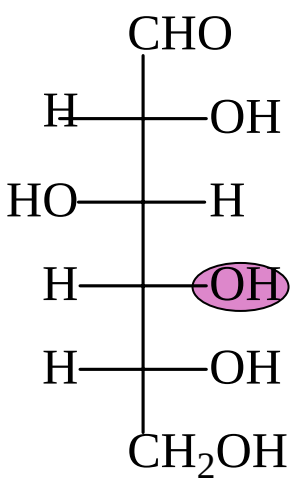
aldopentose

Configuration of monosaccharides

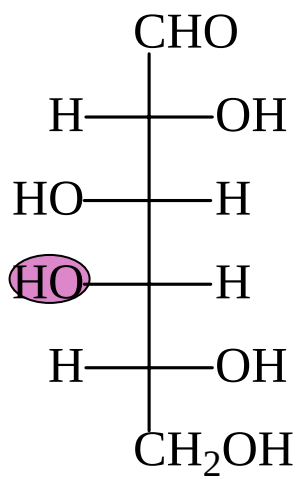
- Mpnpsaccharides with the same number of carbons are structural isomers or diastereomers.
- Diastereomers are nonenentiomeric stereoisomers with two or more chiral centers but differ in the projection of at least one of them.
- If two diastereomers differ in the projection of only one chiral center ➔ **epimers**

Examples

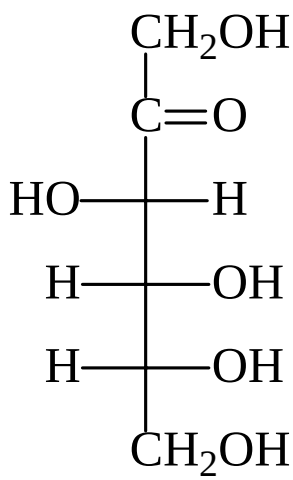
- D-glucose, D-galactose, and D-fructose are all structural isomers (diastereomers).
- D-glucose and D-galactose differ only in the projection at carbon 4 ➔ epimers



D-glucose



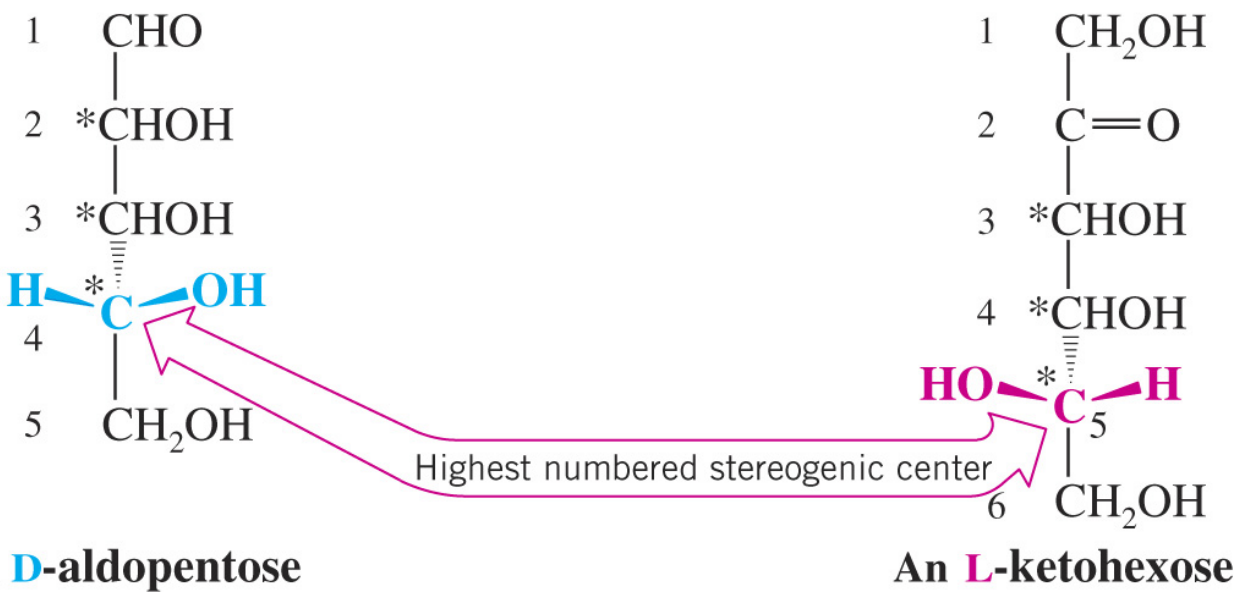
D- galactose



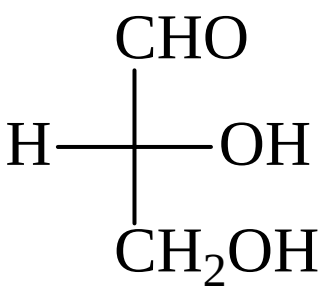
D-fructose

The D and L System

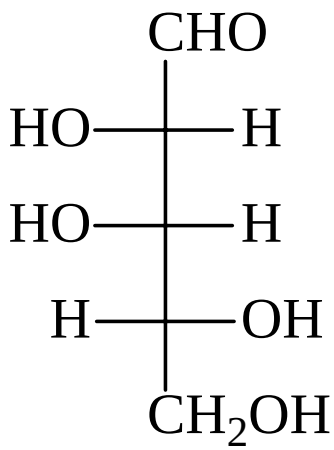
- **If the OH on the last chiral carbon is projected to the right ➔ D**
- **If the OH on the last chiral carbon is projected to the left ➔ L**



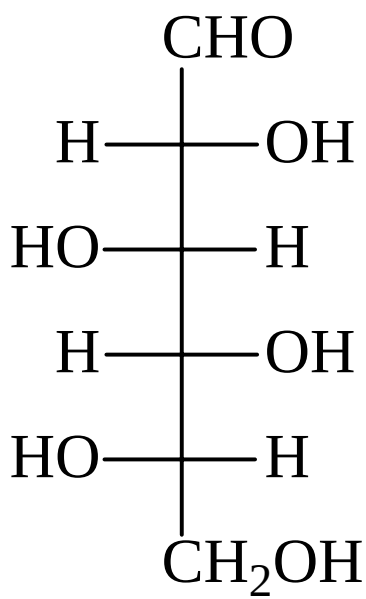
Examples



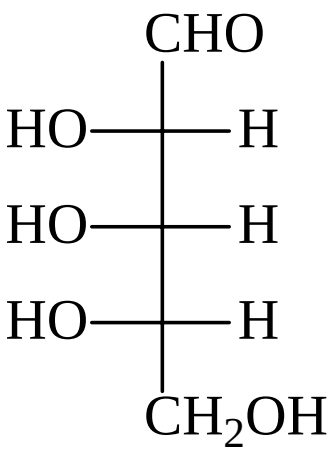
D-glyceraldehyde



D- lyxose

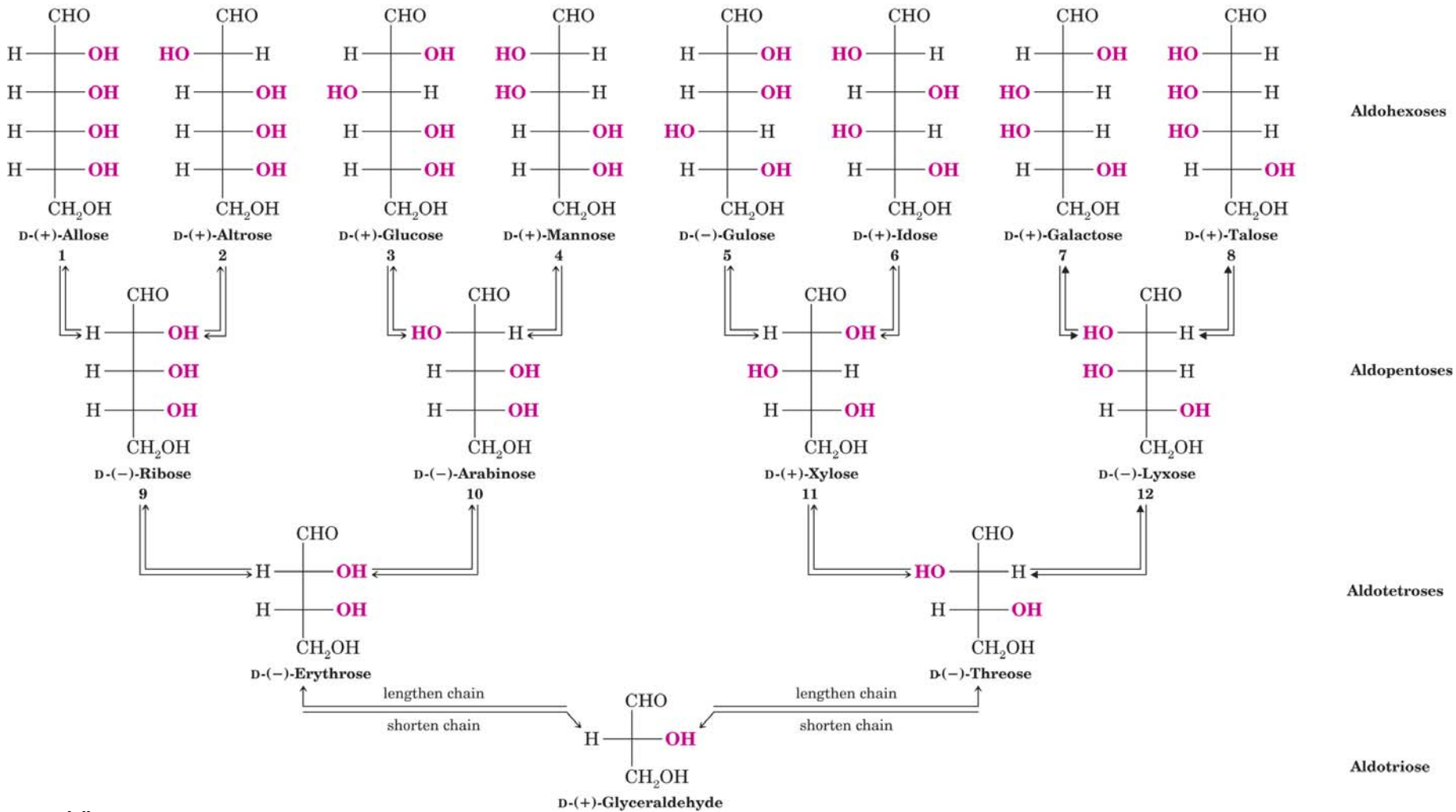


L-aldohexose



L-ripose

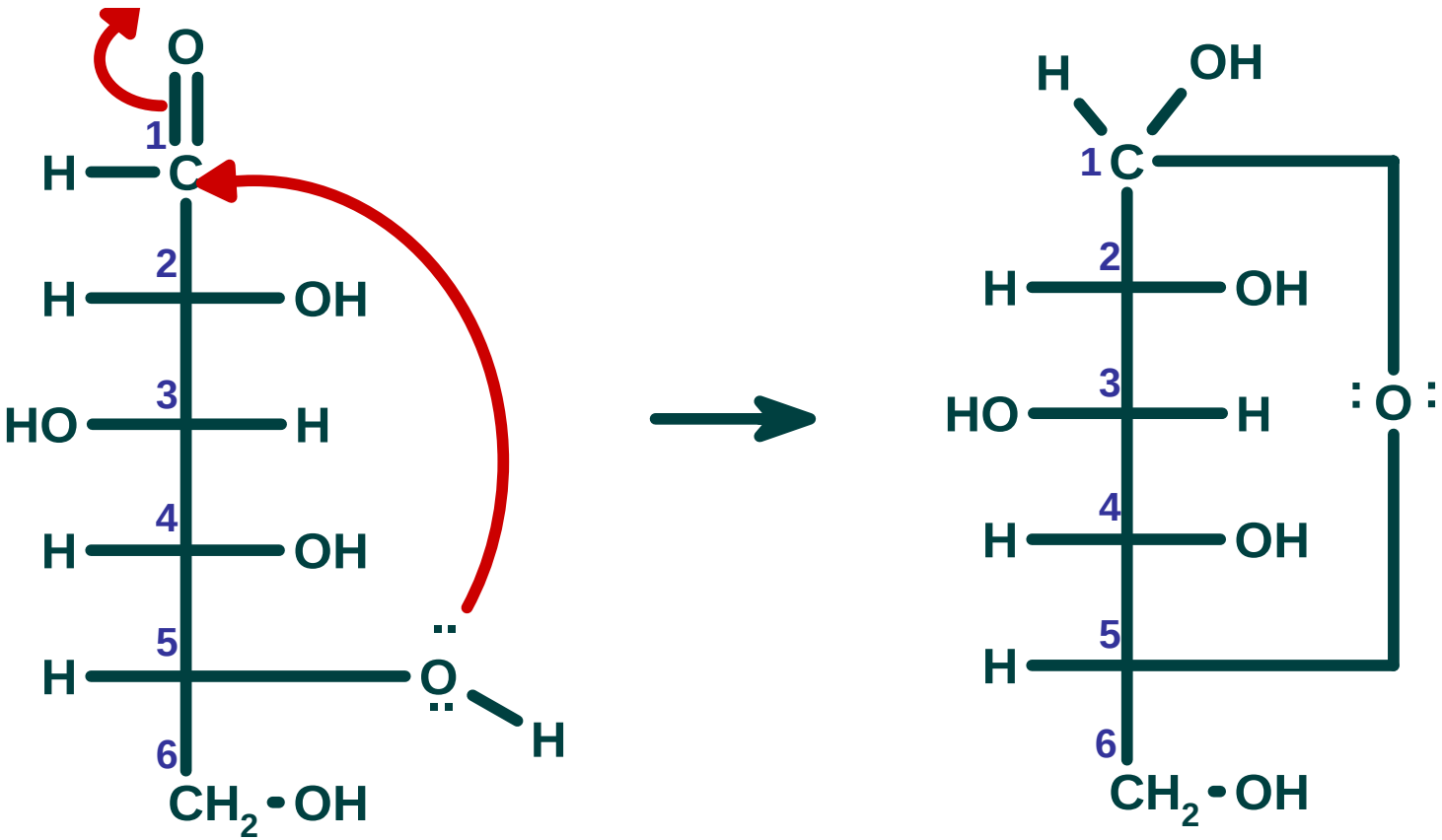
The D Family of Aldoses



Cyclization of Monosaccharides

only sugars seem to make stable hemiacetals

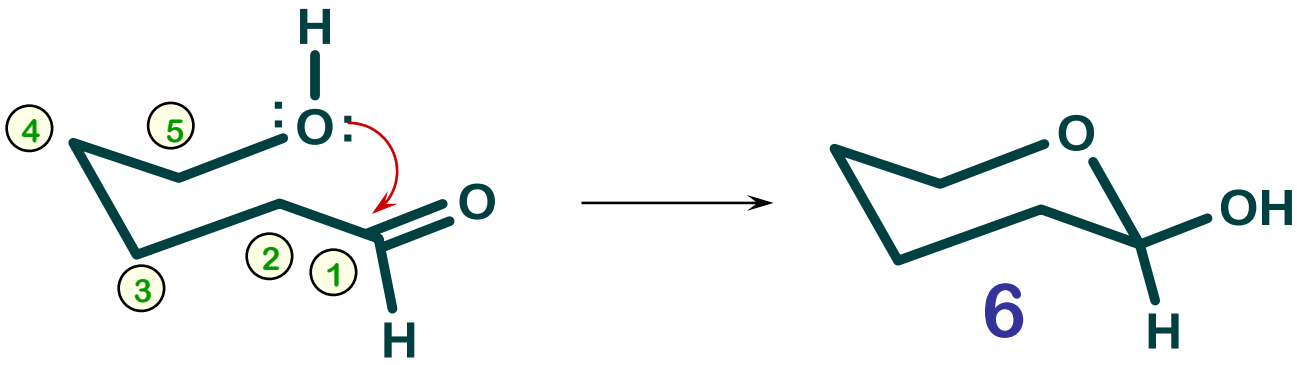
a hemiacetal



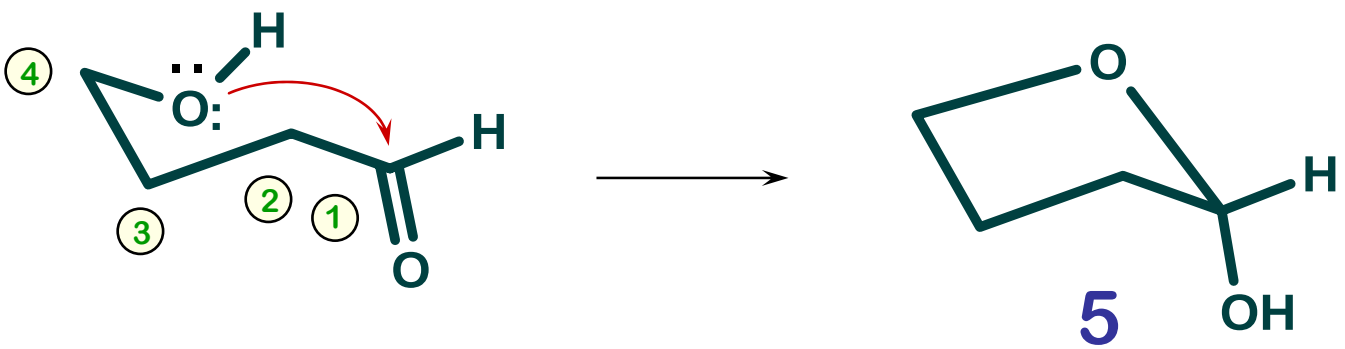
glucose

glucopyranose

FURANOSE AND PYRANOSE RINGS

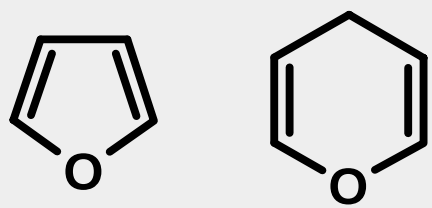


a pyranose ring



two anomers are possible in each case

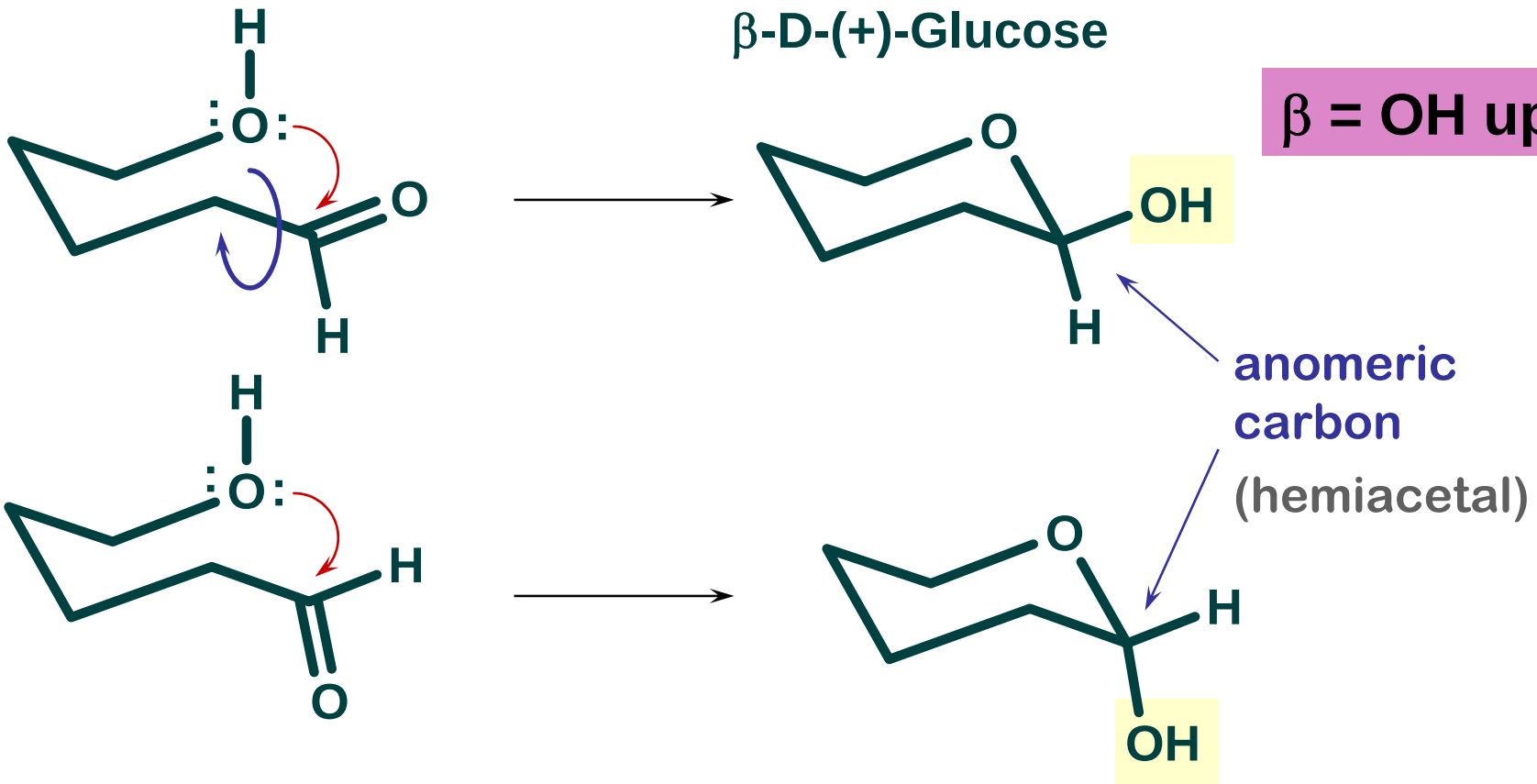
a furanose ring



furan pyran

for clarity no hydroxyl groups are shown on the chains or rings

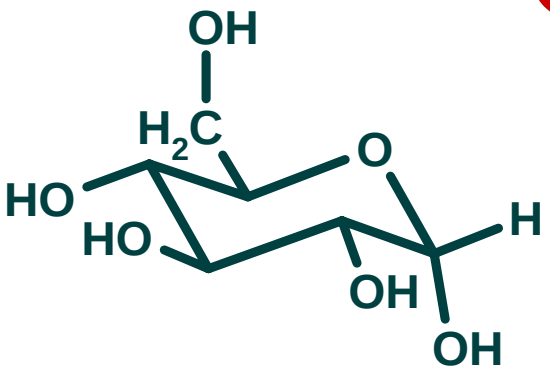
ANOMERS



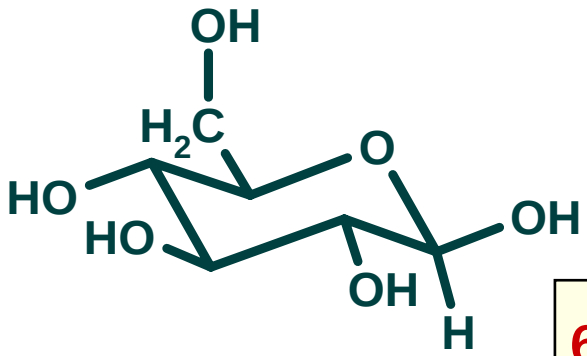
for clarity hydroxyl groups on the chain are not shown

anomers differ in configuration at the anomeric carbon # 1

Glucose



hemiacetals



34%

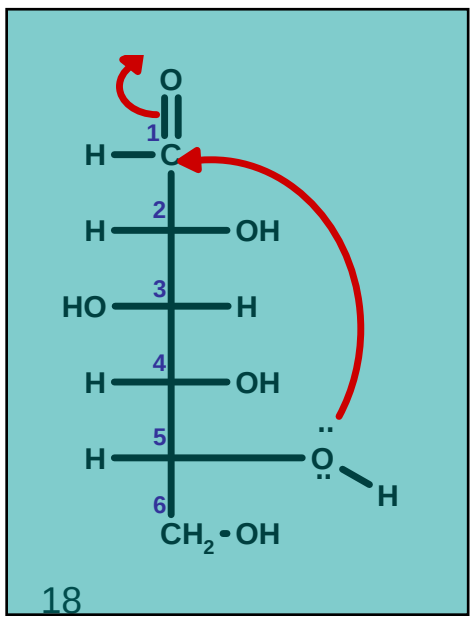
66%

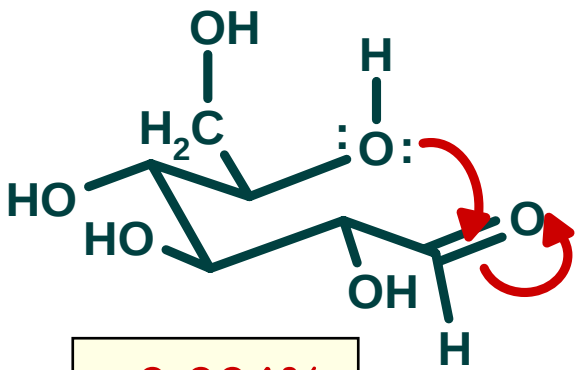
α-D-(+)-Glucose

[α] = + 112.2°

β-D-(+)-Glucose

[α] = + 18.7°





< 0.001%

open chain

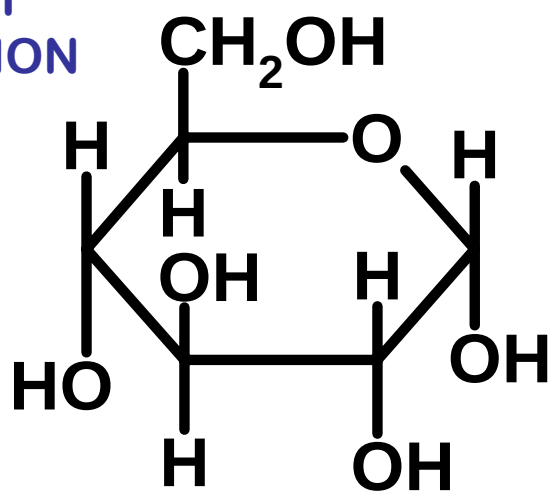
Equilibrium mixture:

[α] = + 52.7°

HAWORTH PROJECTIONS

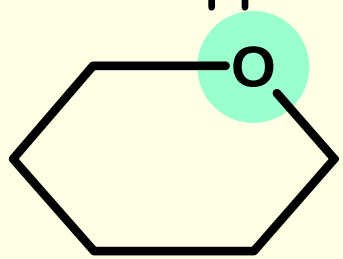
It is convenient to view the cyclic sugars (glucopyranoses) as a "Haworth Projection", where the ring is flattened.

HAWORTH PROJECTION



α-D-(+)-glucopyranose

Standard Position

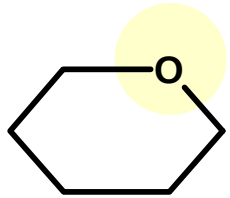


This orientation is always used for a Haworth Projection

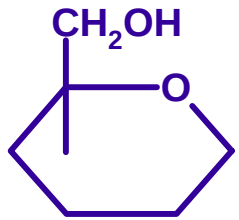
HAWORTH PROJECTIONS

HERE ARE SOME CONVENTIONS YOU MUST LEARN

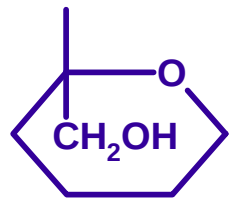
1) The ring is always oriented with the oxygen in the upper right-hand back corner.



2) The -CH_2OH group is placed
UP for a **D-sugar** and
DOWN for an **L-sugar**.

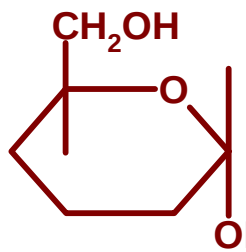


D



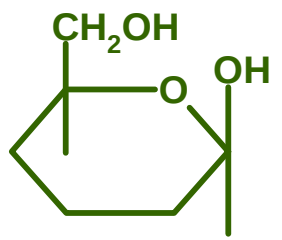
L

3) α-Sugars have
the anomeric hydroxyl group *down.*



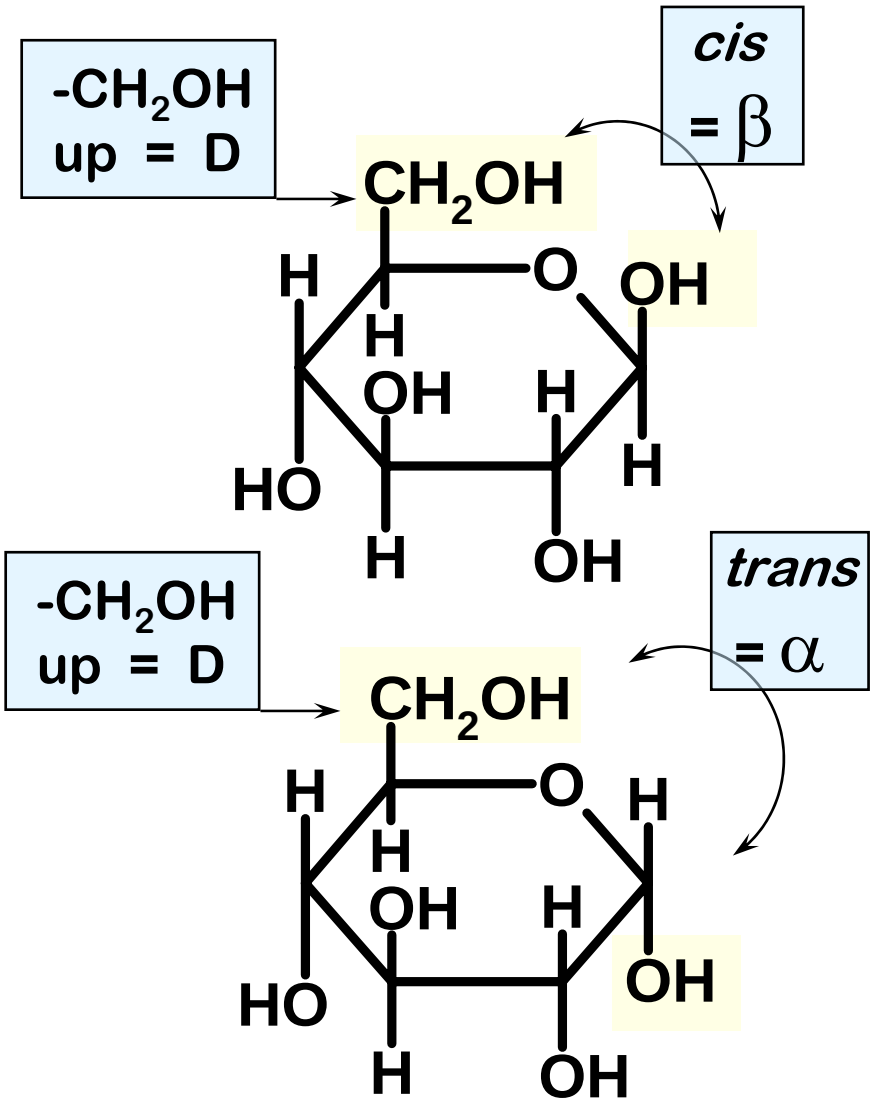
α

4) β-Sugars have
the anomeric hydroxyl group *up*



β

SOME HAWORTH PROJECTIONS



D-SUGARS

β-D

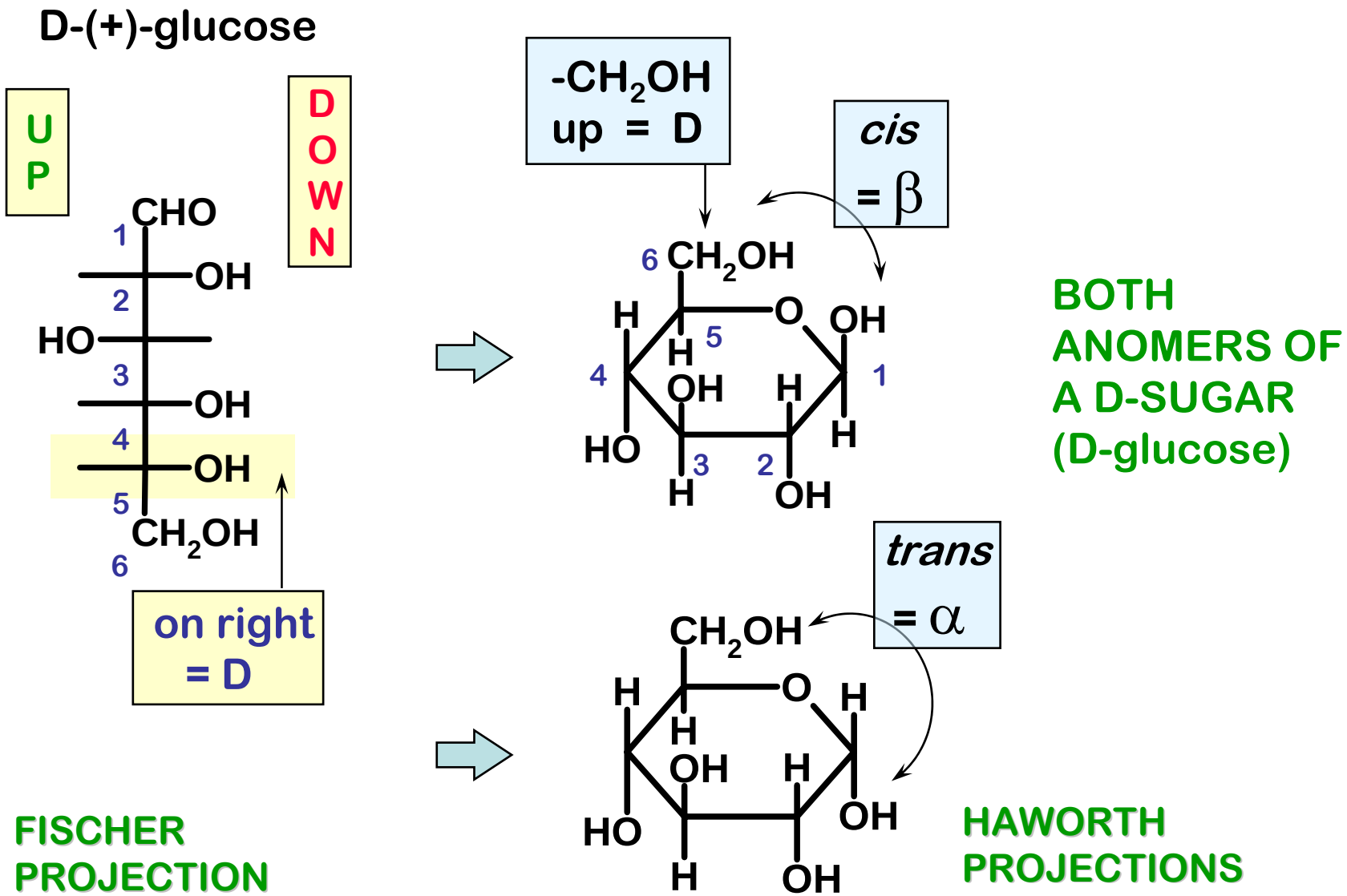
ANOMERS

α-D

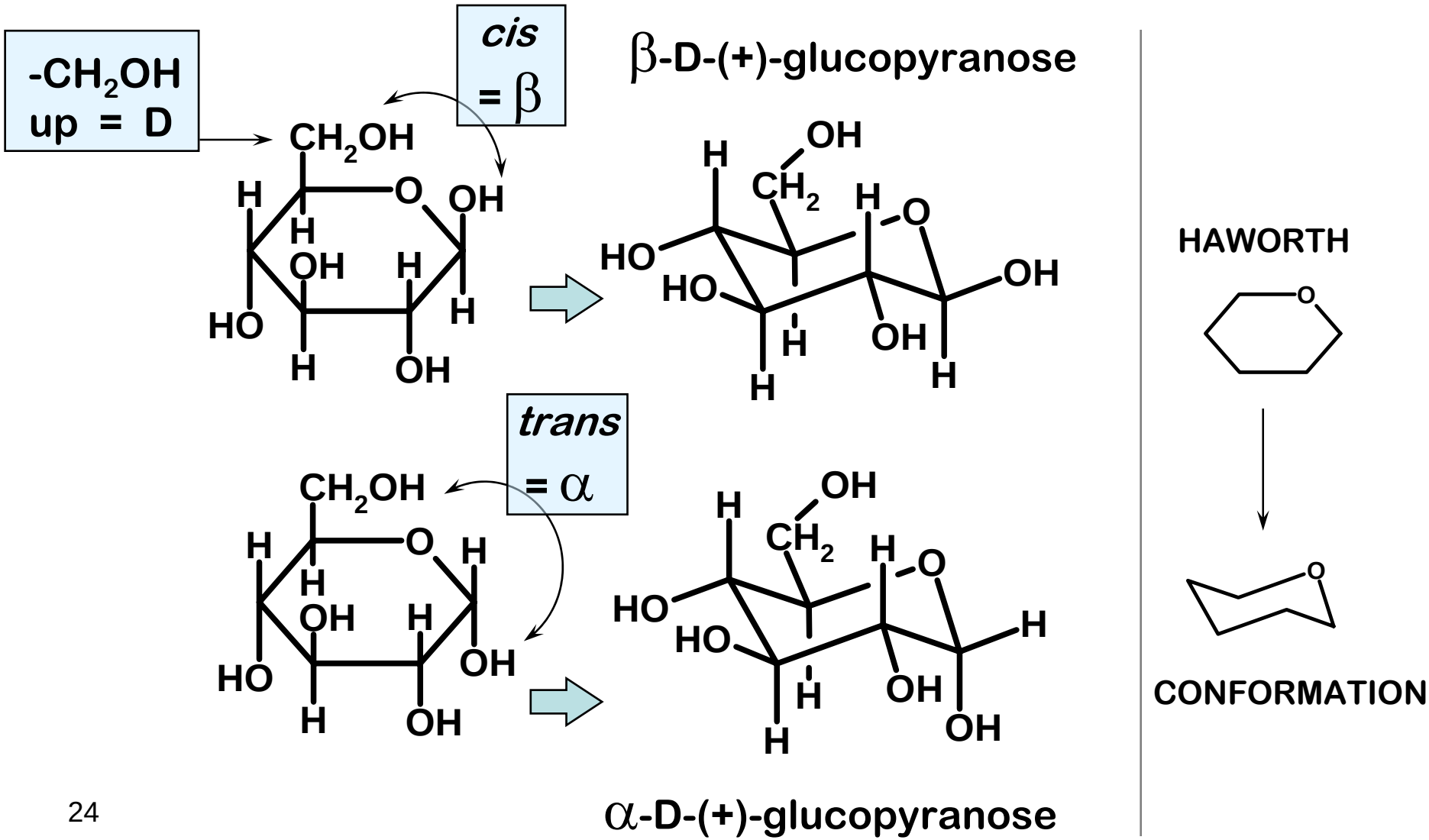
BOTH OF THESE ARE D-GLUCOSE

CONVERTING FISCHER PROJECTIONS TO HAWORTH PROJECTIONS

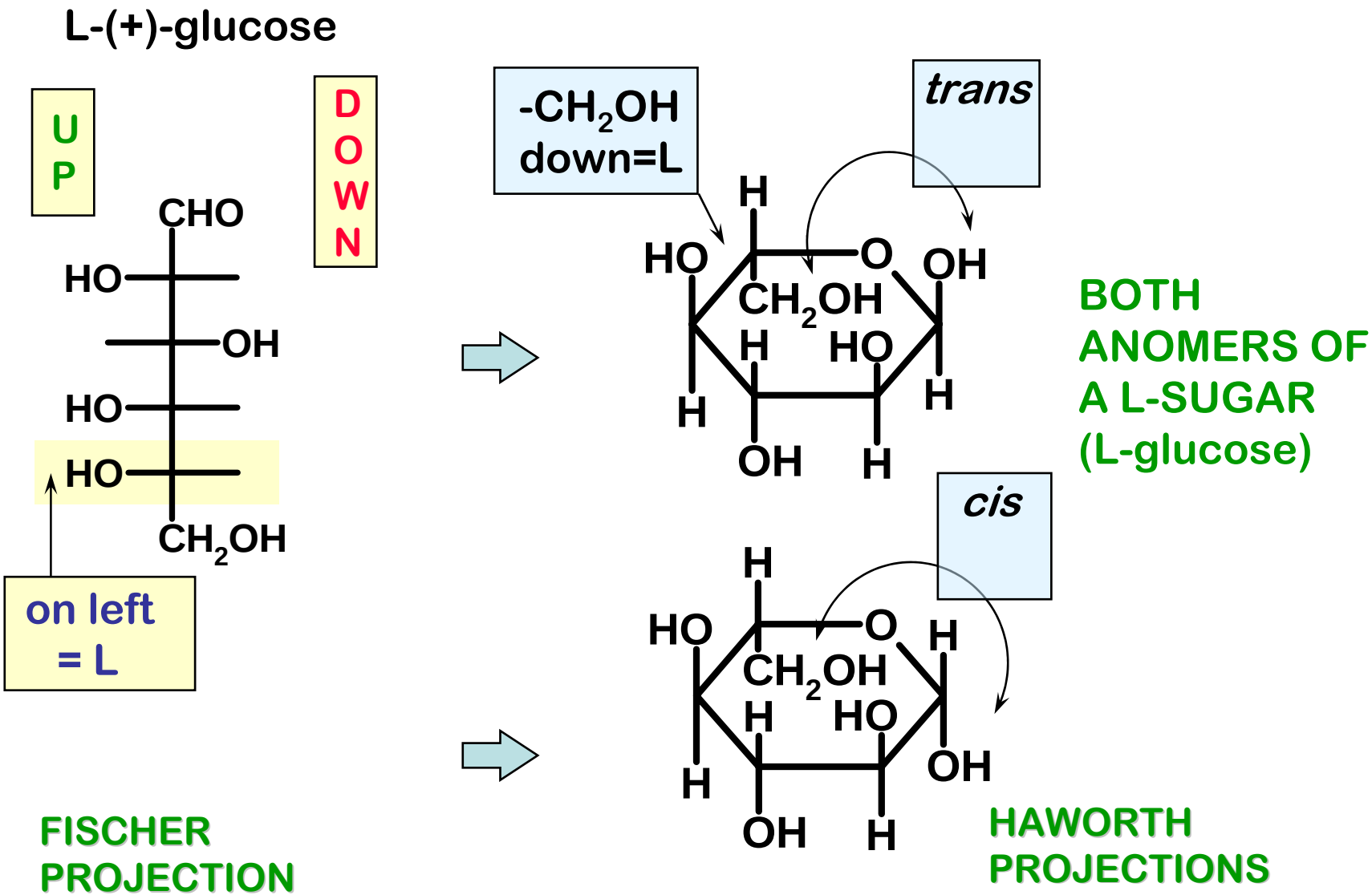
CONVERTING TO HAWORTH PROJECTIONS



CONVERTING TO ACTUAL CONFORMATIONS



HAWORTH PROJECTIONS OF L-SUGARS



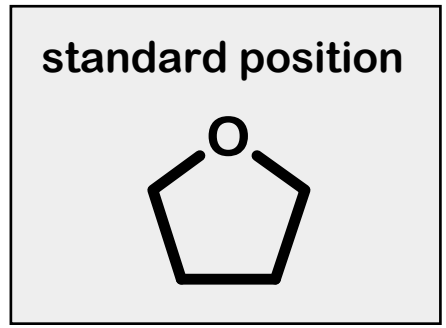
CONVERTING FISCHER TO HAWORTH PROJECTIONS

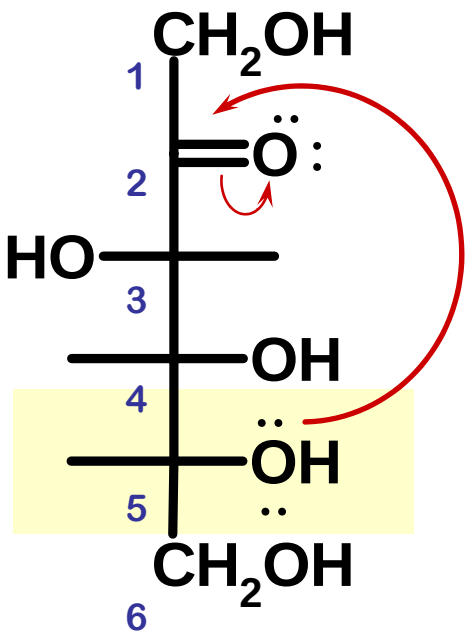
Genral rules

LEFT = UP RIGHT = DOWN β = *up* α = *down*	These rules are the same for both D- and L- sugars	The only difference when converting D- and L- sugars is : D-sugars $-CH_2OH$ = UP L-sugars $-CH_2OH$ = DOWN

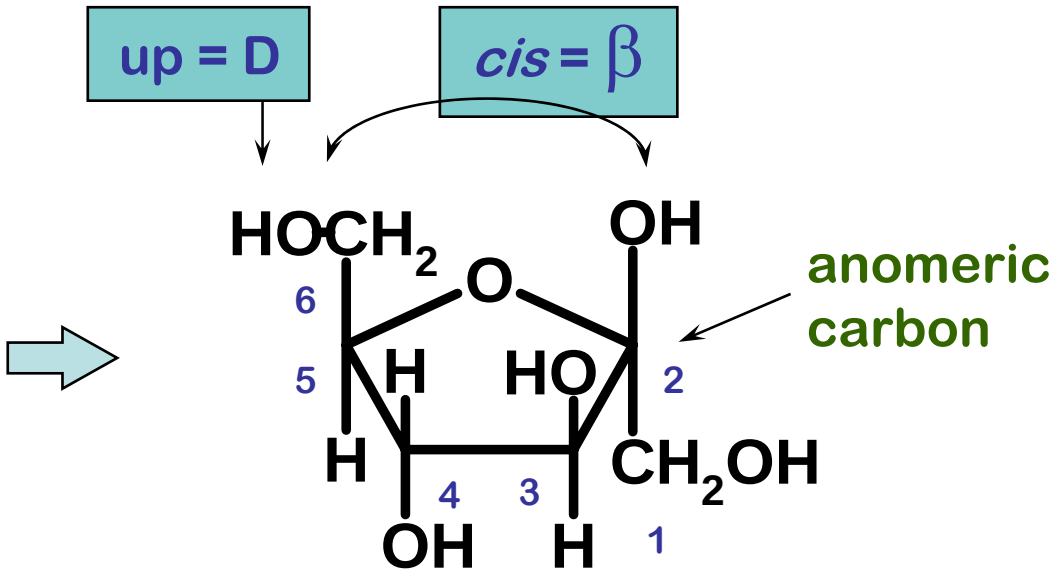
FRUCTOFURANOSES

FRUCTOSE





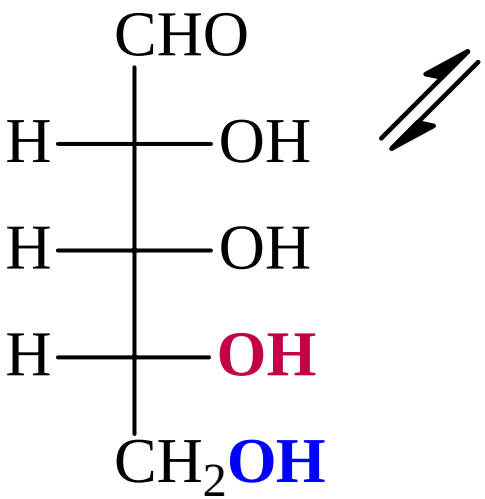
D-(-)-Fructose



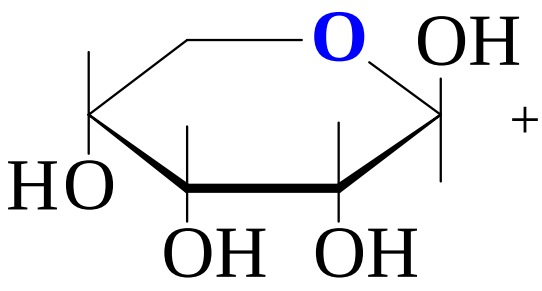
β-D-(-)-Fructofuranose

Anomeric Effect

β-anomer is the most stable anomer

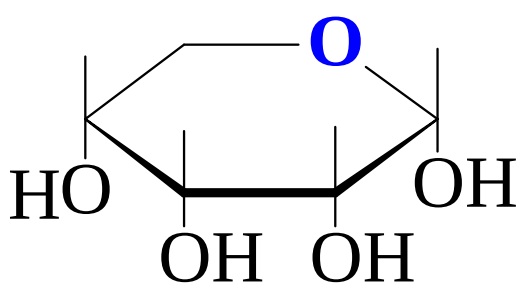


D-ribose

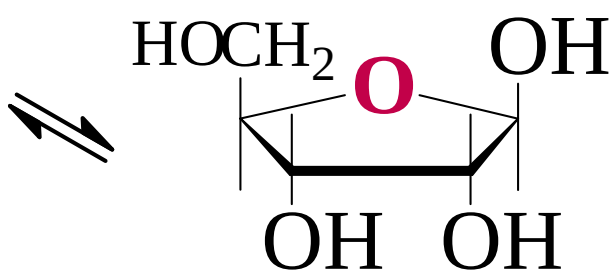


β-D-ribopyranose (56%)

+

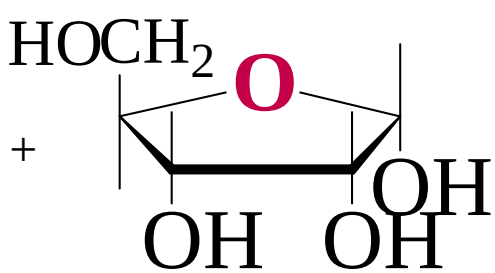


α-D-ribopyranose (20%)



β-D-ribofuranose (18%)

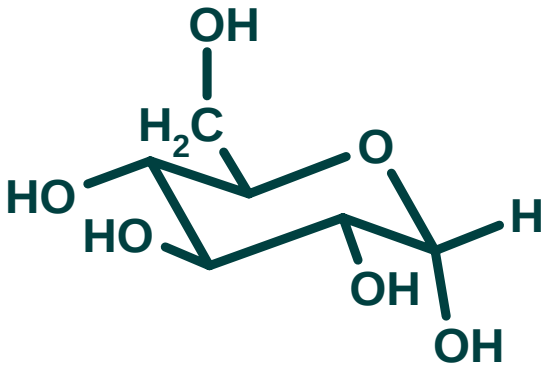
+



α-D-ribofuranose (6%)

MUTAROTATION

Mutarotation of Glucose

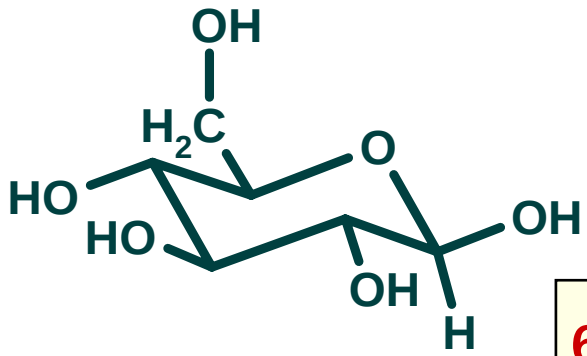


α-D-(+)-Glucose

[α] = + 112.2°

36%

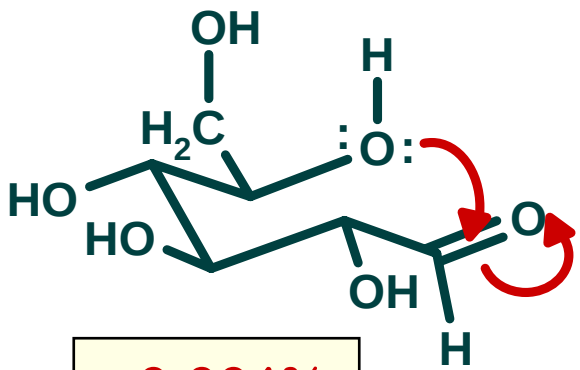
hemiacetals



β-D-(+)-Glucose

[α] = + 18.7°

64%



< 0.001%

open chain

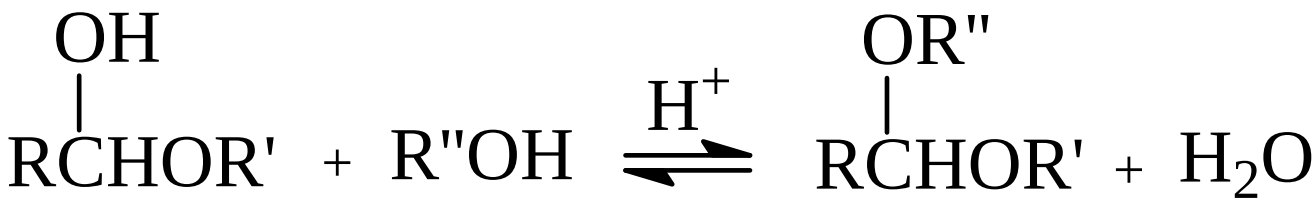
Equilibrium mixture:

[α] = + 52.7°

Glycoside Formation

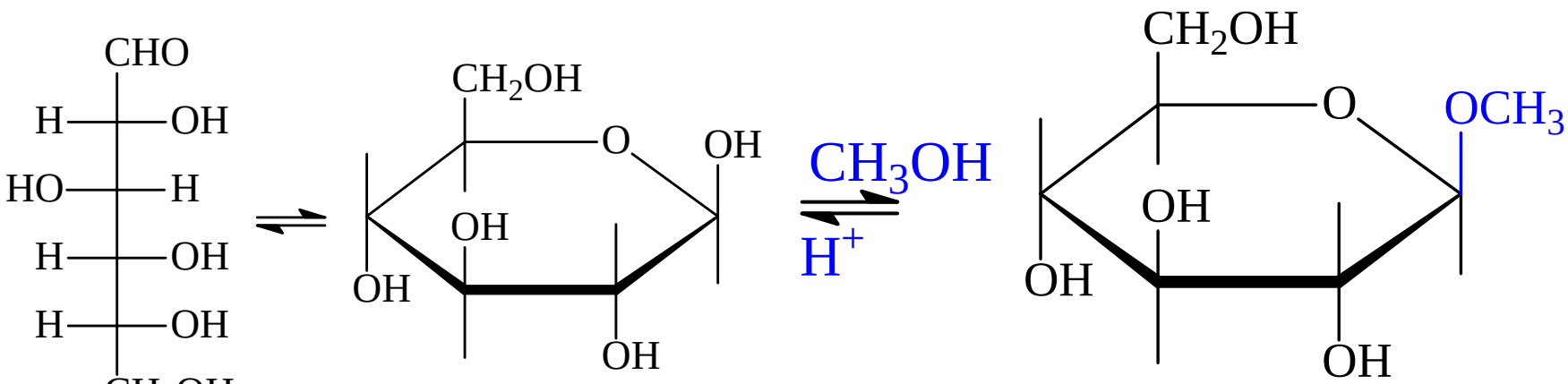
- Glycosides are acetals at the anomeric carbon of carbohydrates

Remember



a hemiacetal

An acetal

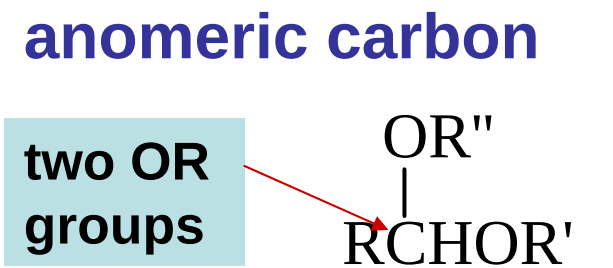


β –D-glucopyranose

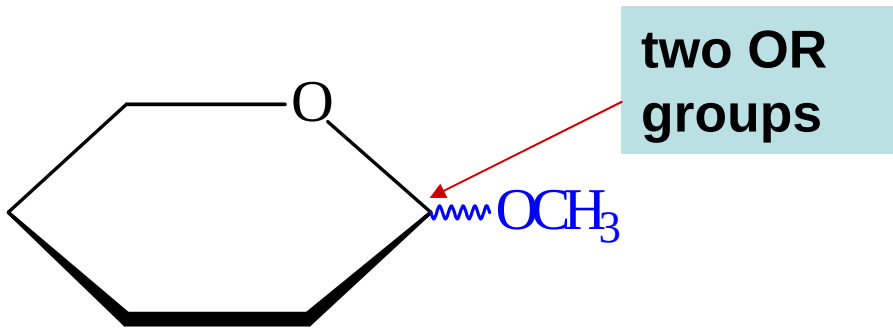
Methyl β –D-glucopyranoside

Glycosides

Glycoside has two or groups attached to the anomeric carbon

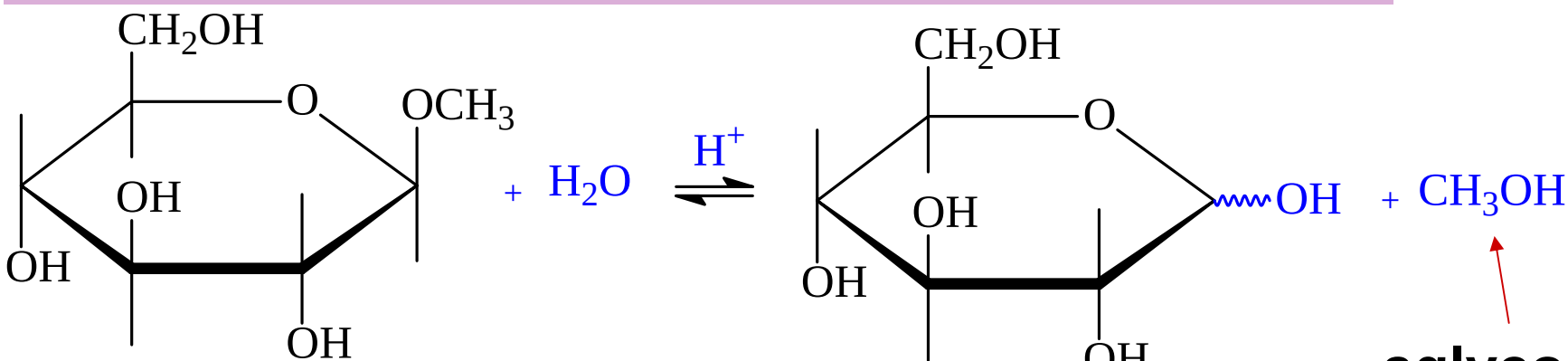


An acetal



A glycoside

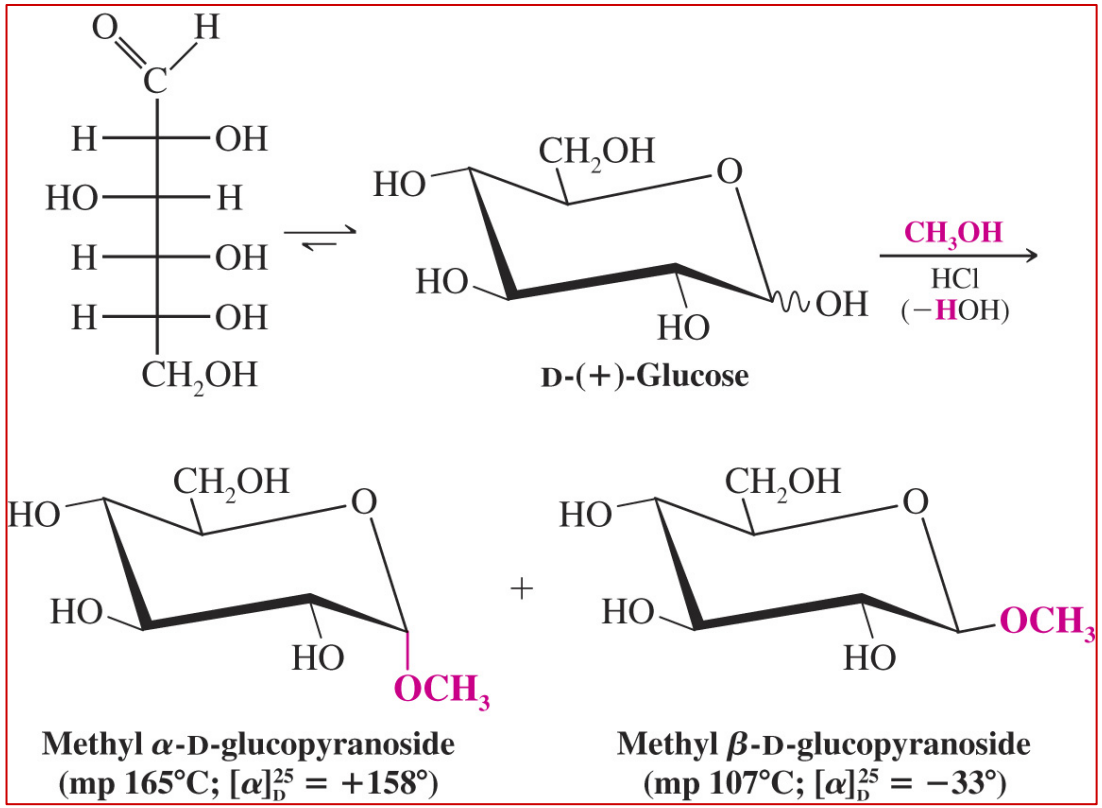
Glycosides can be hydrolyzed in aqueous acid



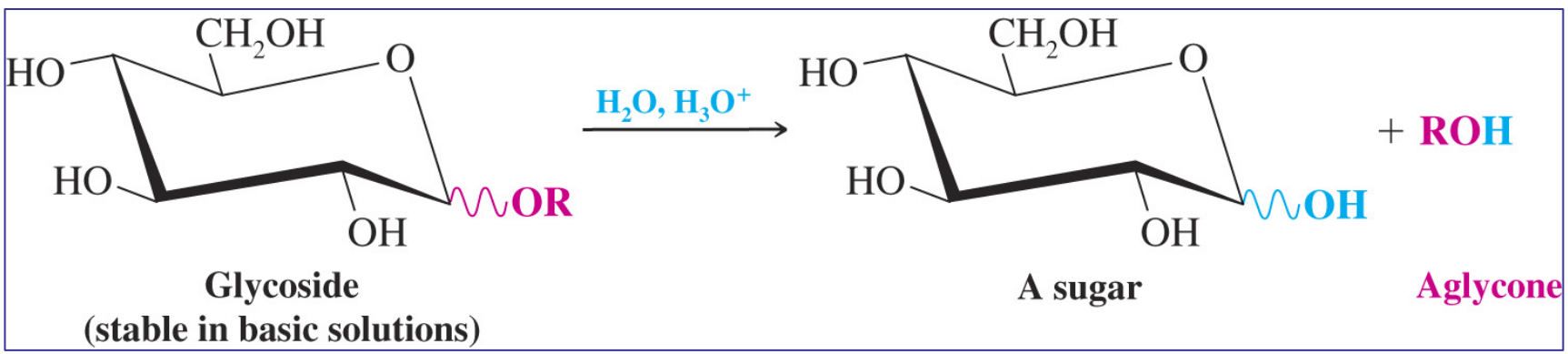
Methyl β –D-glucopyranoside

D-glucopyranose

Glycoside formation

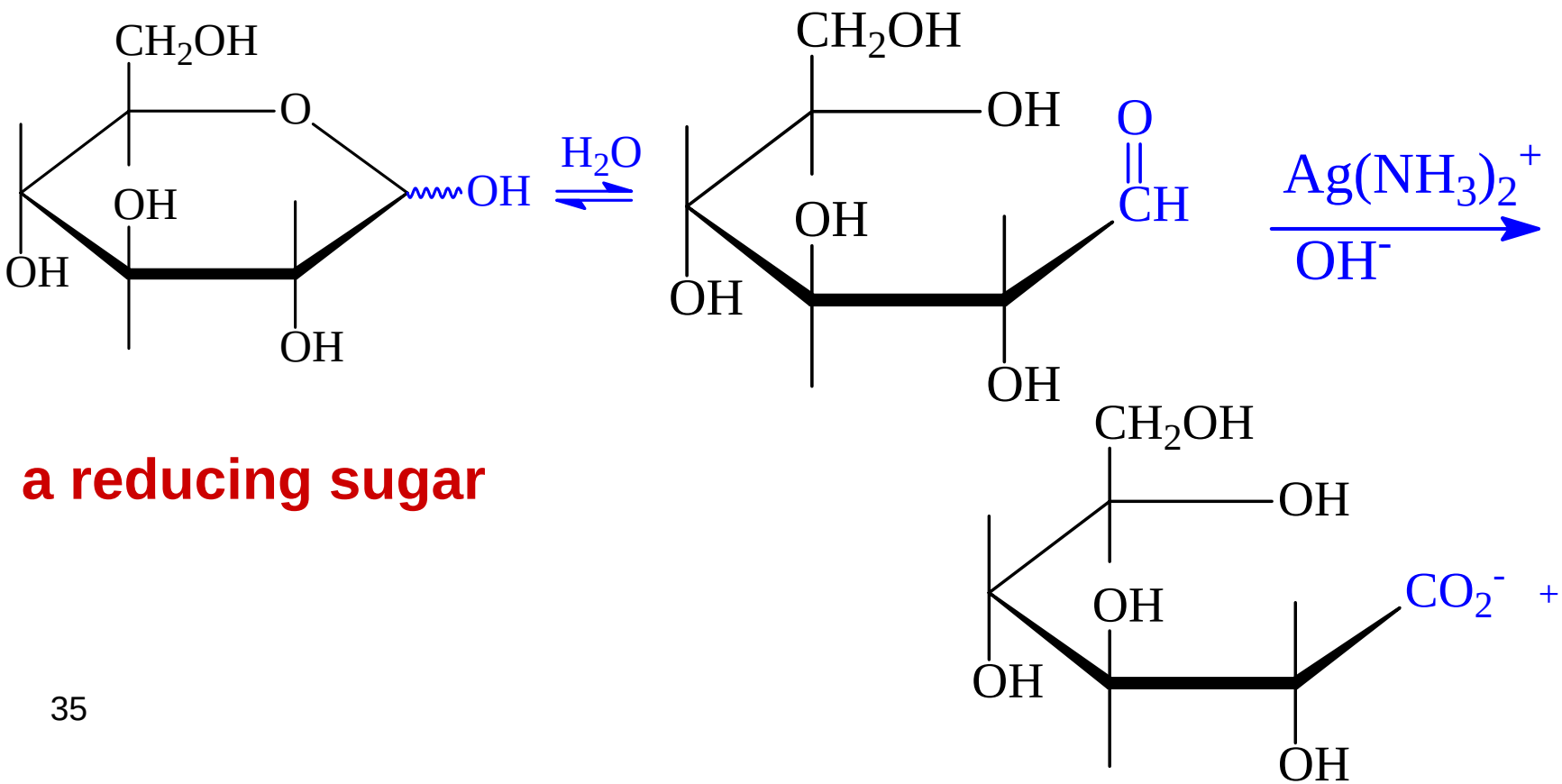


Hydrolysis of glycosides



Oxidation of Monosaccharides

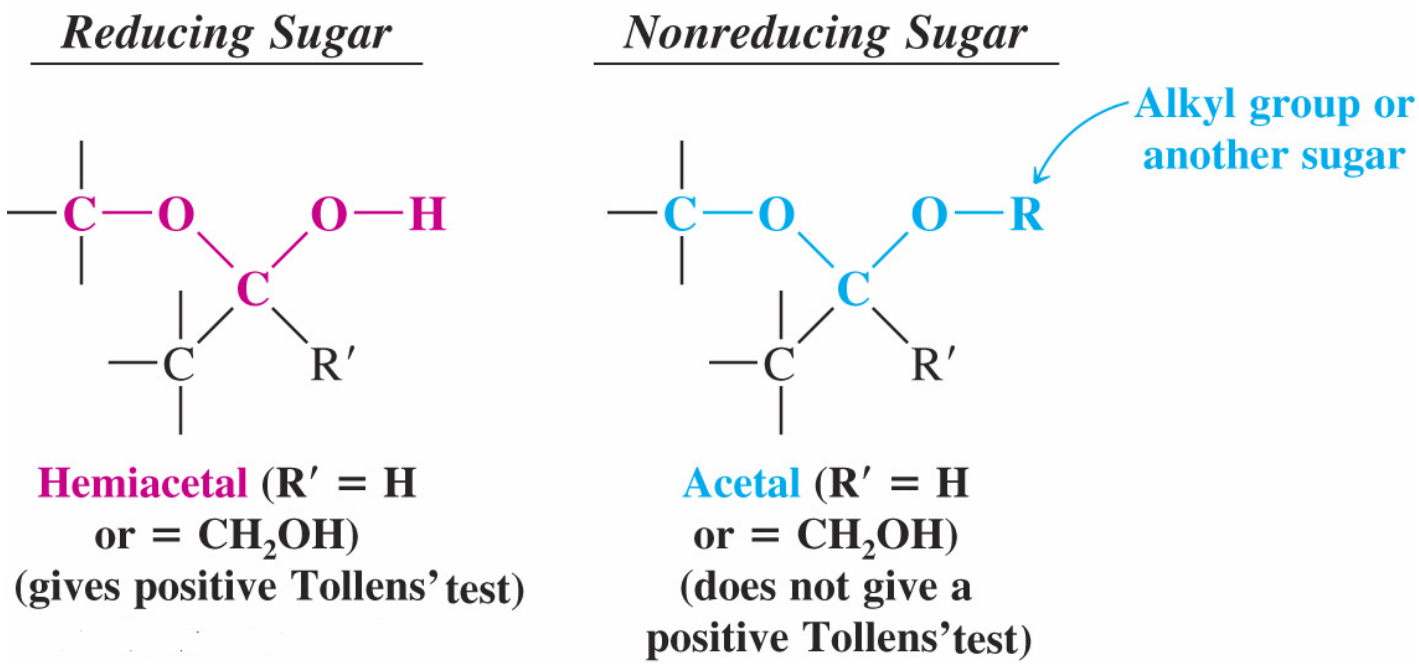
- Aldoses and ketoses are easily oxidized when treated with Tollens' reagent



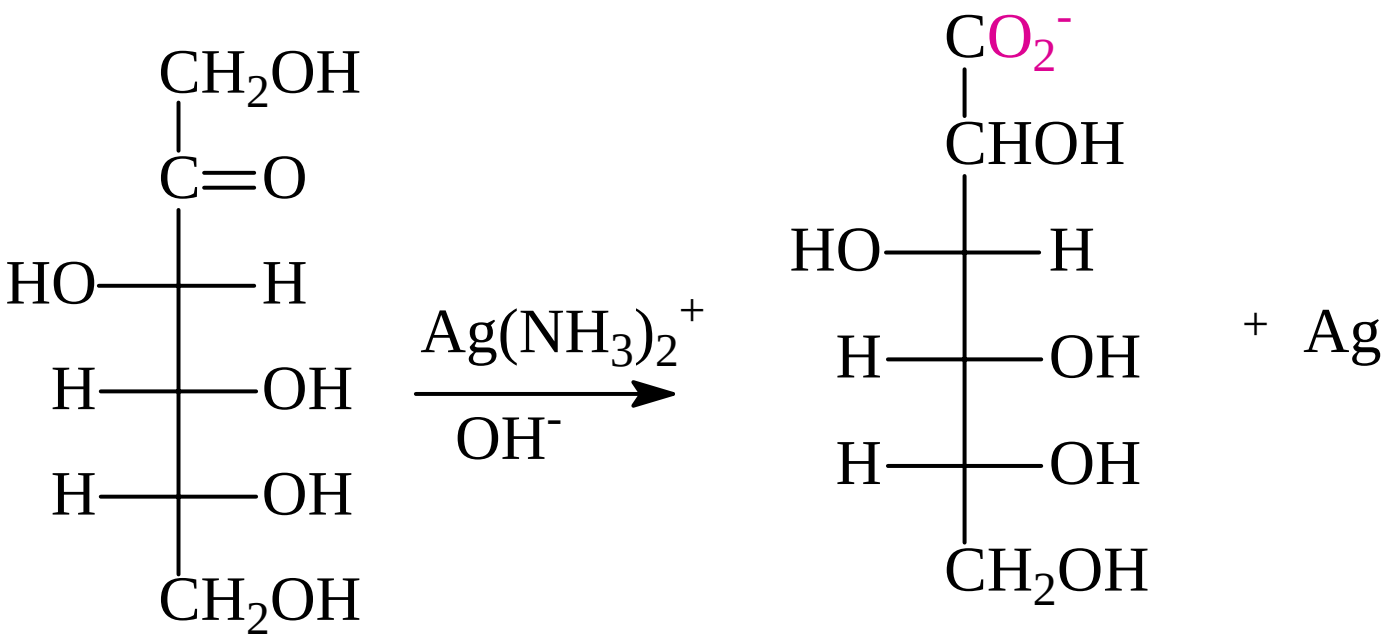
a reducing sugar

Reducing Sugars

- Carbohydrates with hemiacetal linkages are *reducing sugars* because they react with Tollens' reagent

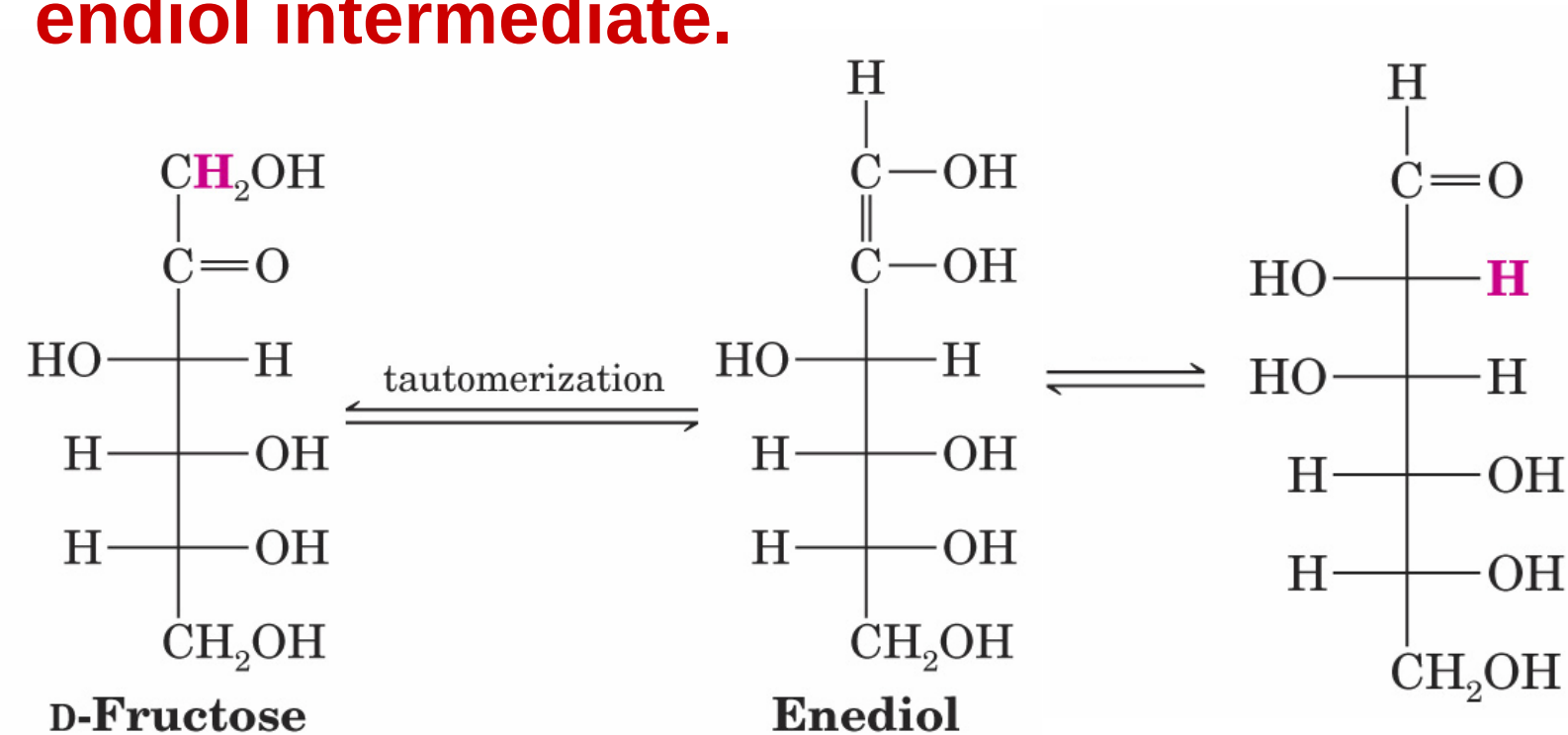


Ketoses are also reducing sugars



D-fructose

Fructose is oxidized readily because it is in equlibrium with aldehydes through an endiol intermediate.

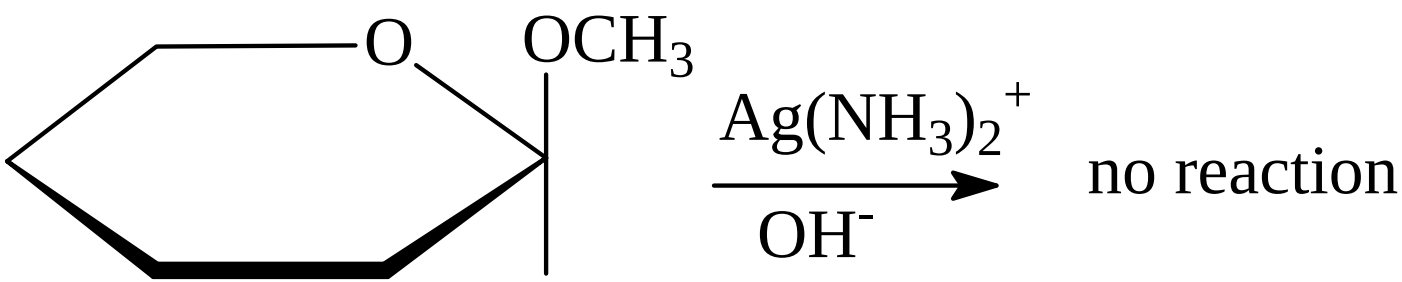


A ketone

An aldose

Glycosides are nonreducing sugars

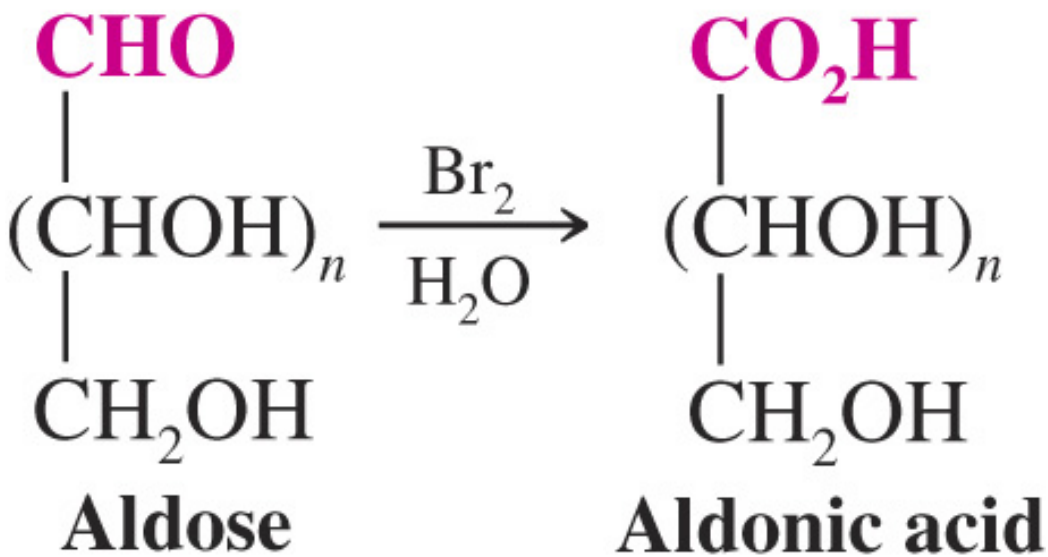
- Glycosides are not in equilibrium with aldehydes ➔ nonreducing sugars



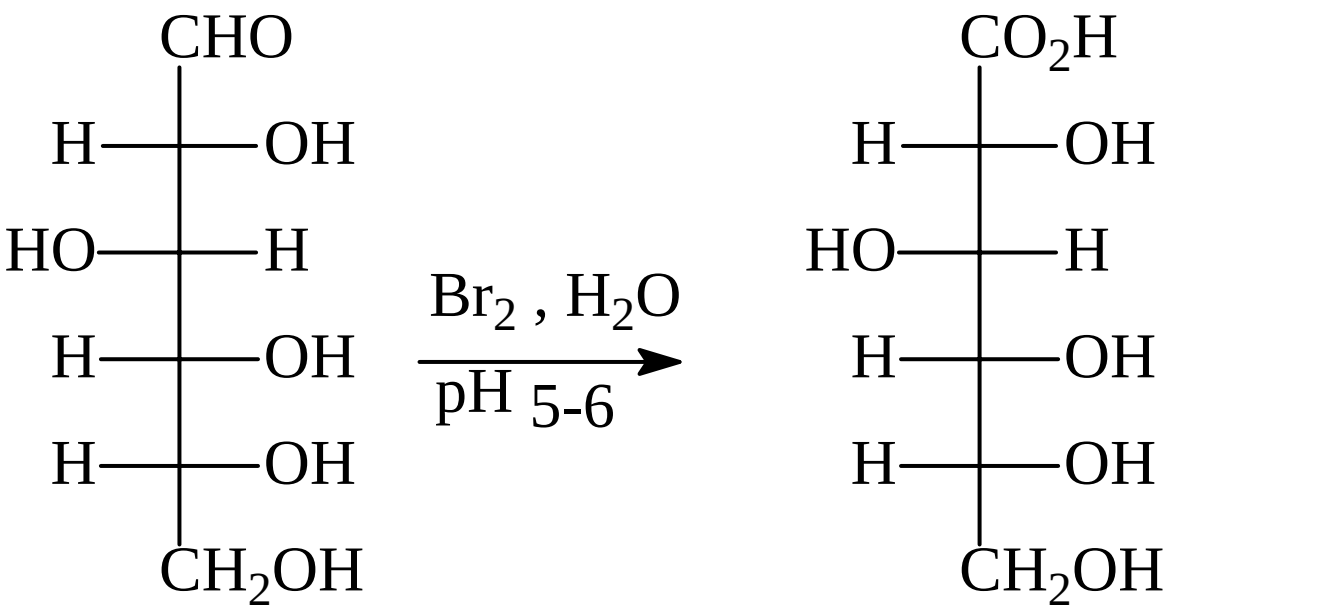
A glycoside

Aldonic Acids

- Bromine in water selectively oxidizes the aldehyde group of an aldose to the corresponding carboxylic acid



Example



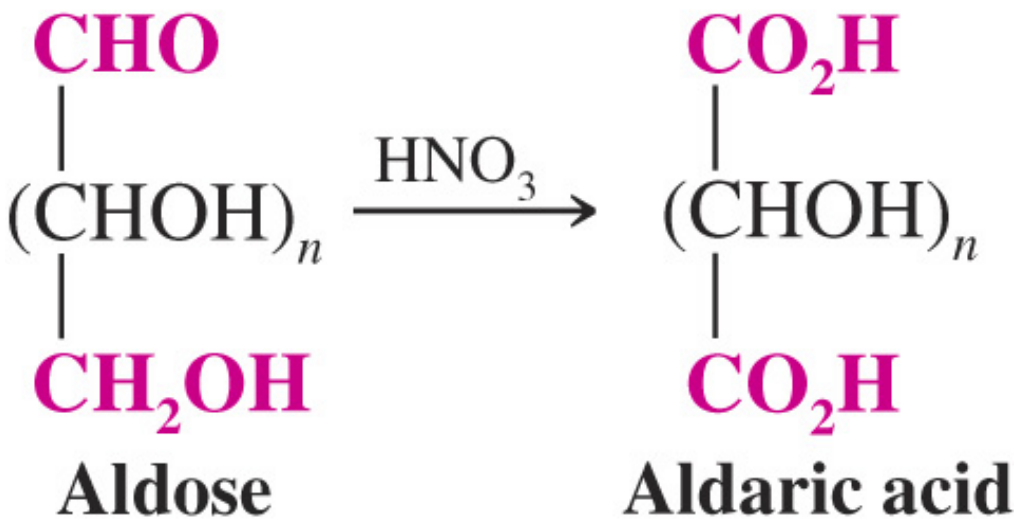
D- glucose

D-gluconic acid

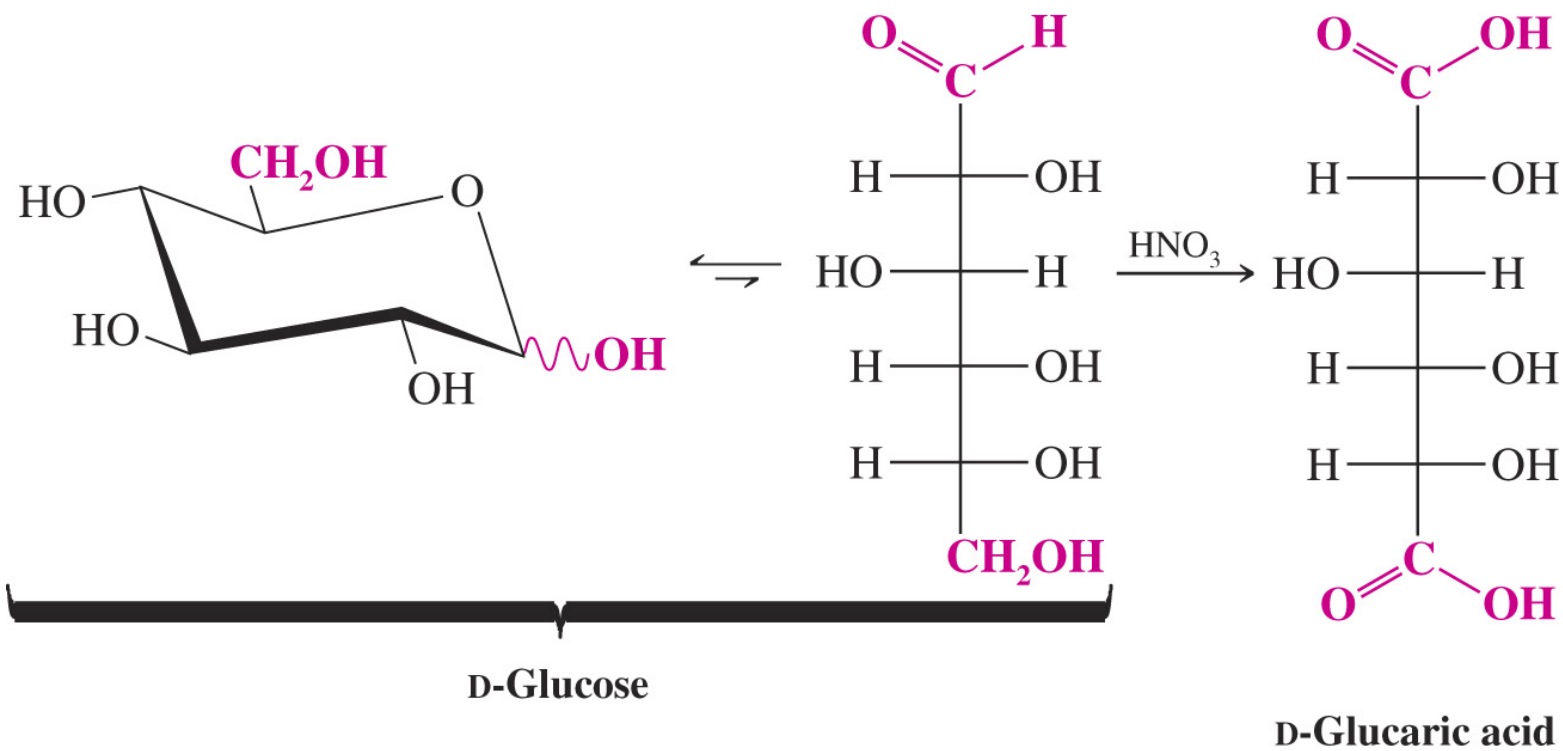
An aldonic acid

Aldaric Acids

Dilute nitric acid oxidizes both the aldehyde and primary hydroxyl groups of an aldose to an aldaric acid



Example

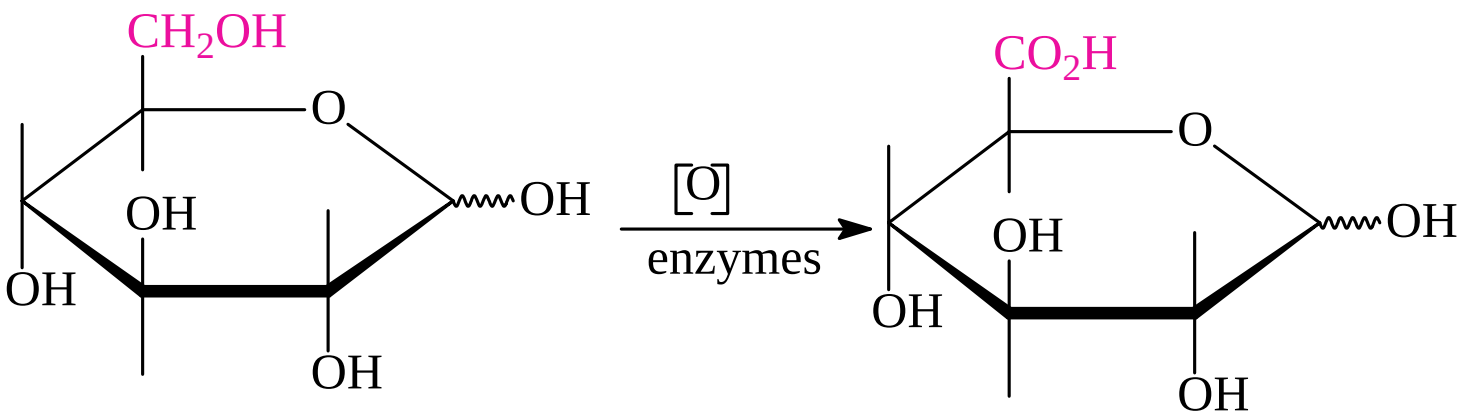


D-Glucose

D-Glucaric acid

Uronic Acids

In biological systems, the terminal CH_2OH group can be oxidized without oxidation of the aldehyde group to uronic acid



D-glucose

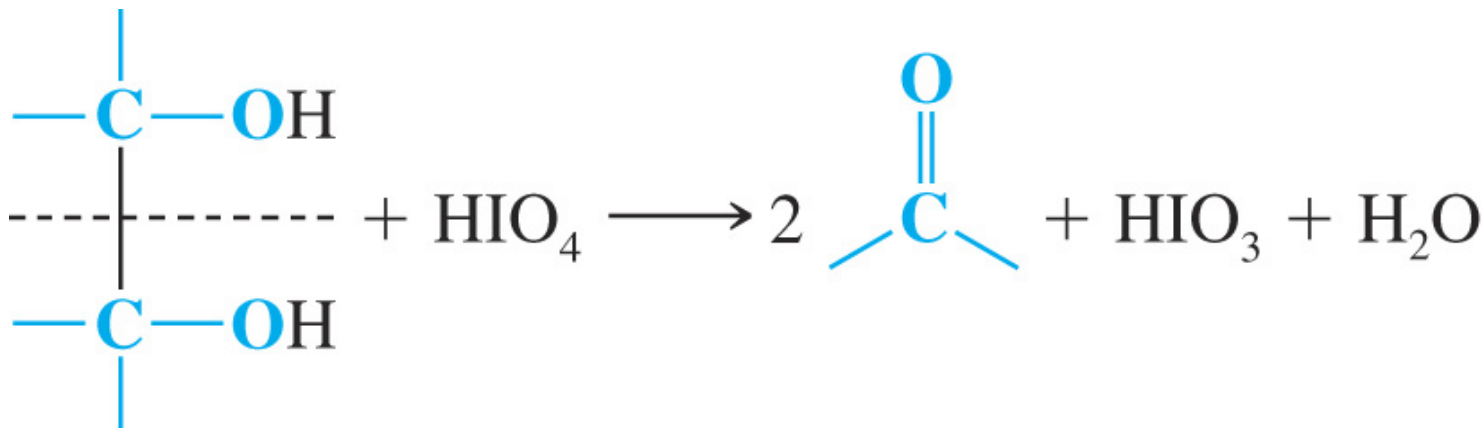
D-glucoronic acid

a uronic acid

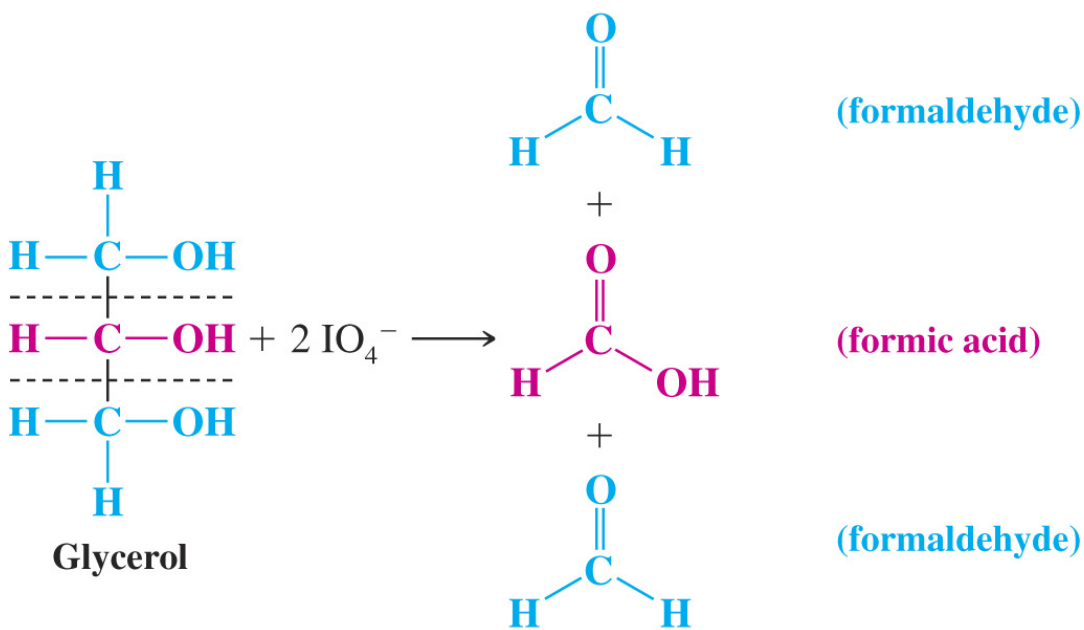
Periodic Acid Oxidation: Oxidative Cleavage of Polyhydroxy Compounds

Compounds with hydroxyl groups on adjacent carbons undergo cleavage of carbon-carbon bonds between the hydroxyl groups

The products are aldehydes, ketones or carboxylic acids

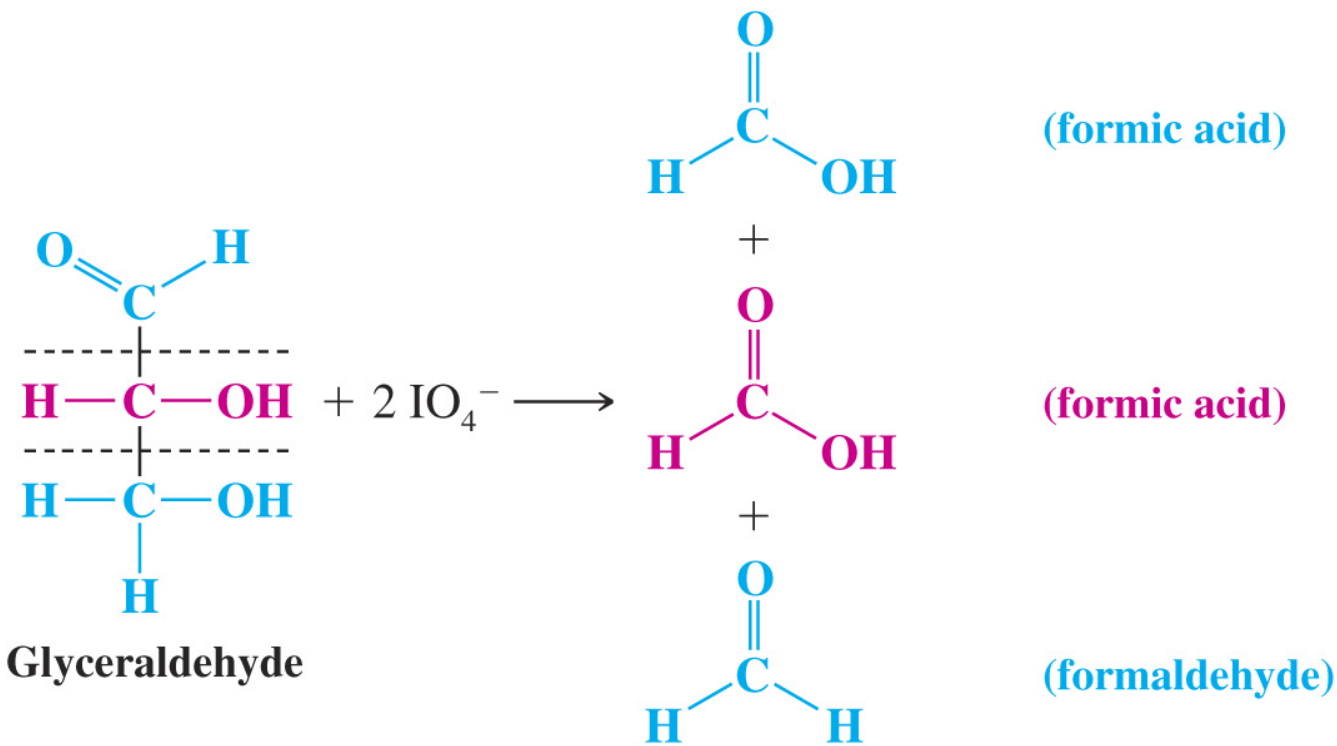


- **The carbonyl group is oxidized to a carboxyl group, while the hydroxyl group is oxidized to an aldehyde or ketone.**
- With three or more contiguous hydroxyl groups, the internal carbons become formic acid

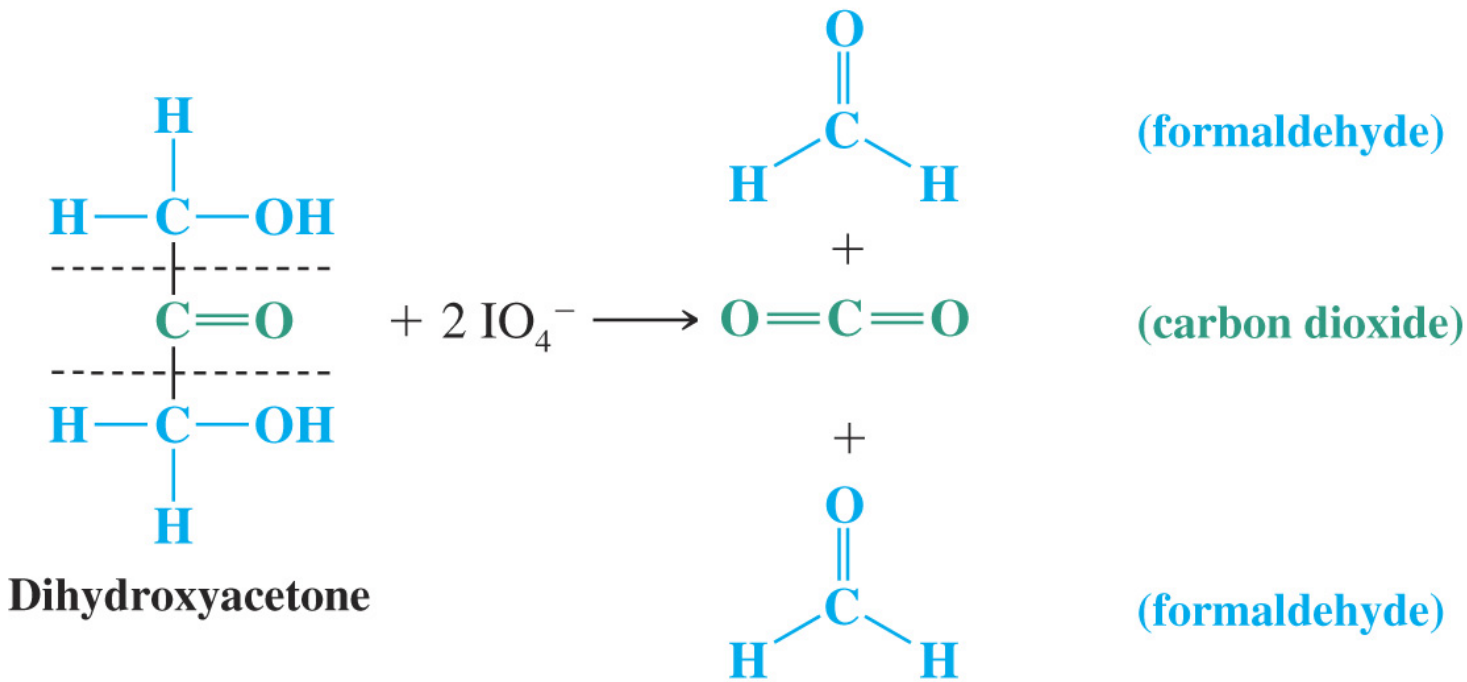


Cleavage also takes place when a hydroxyl group is adjacent to an aldehyde or ketone group

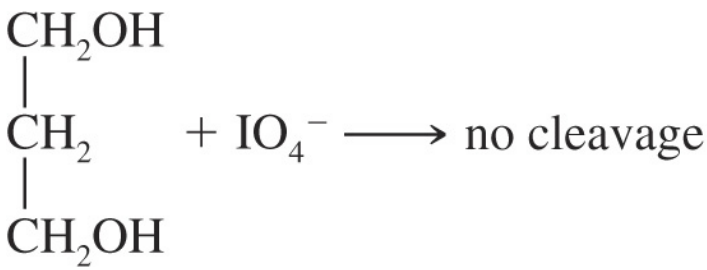
- An aldehyde is oxidized to formic acid; a ketone is oxidized to carbon dioxide

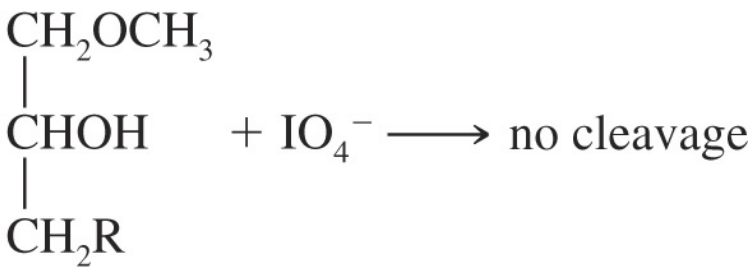


Glyceraldehyde


H
H—C—OH
C=O
H—C—OH
H
Dihydroxyacetone
+ 2 IO_4^-
O
C
H
H
(formaldehyde)
+
O=C=O
(carbon dioxide)
+
O
C
H
H
(formaldehyde)

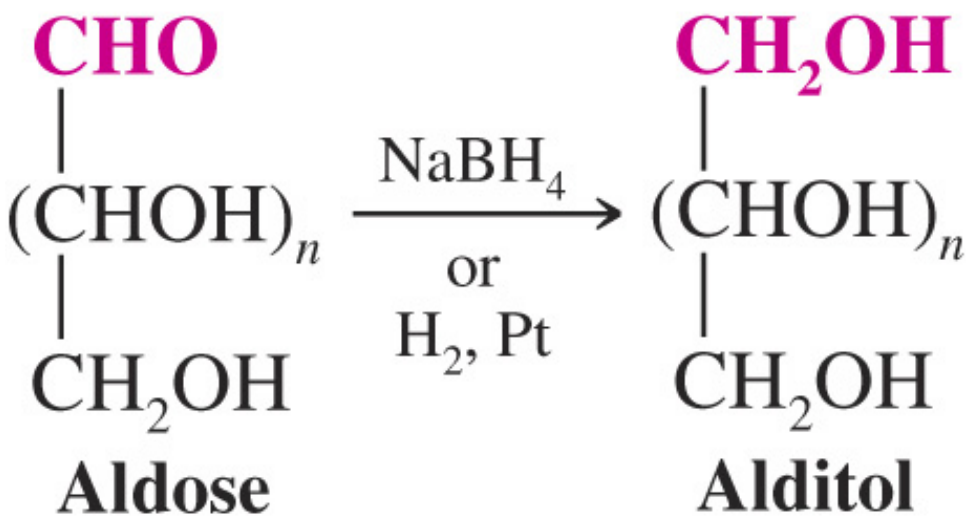
➔No cleavage results if there are intervening carbons that do not bear hydroxyl or carbonyl groups



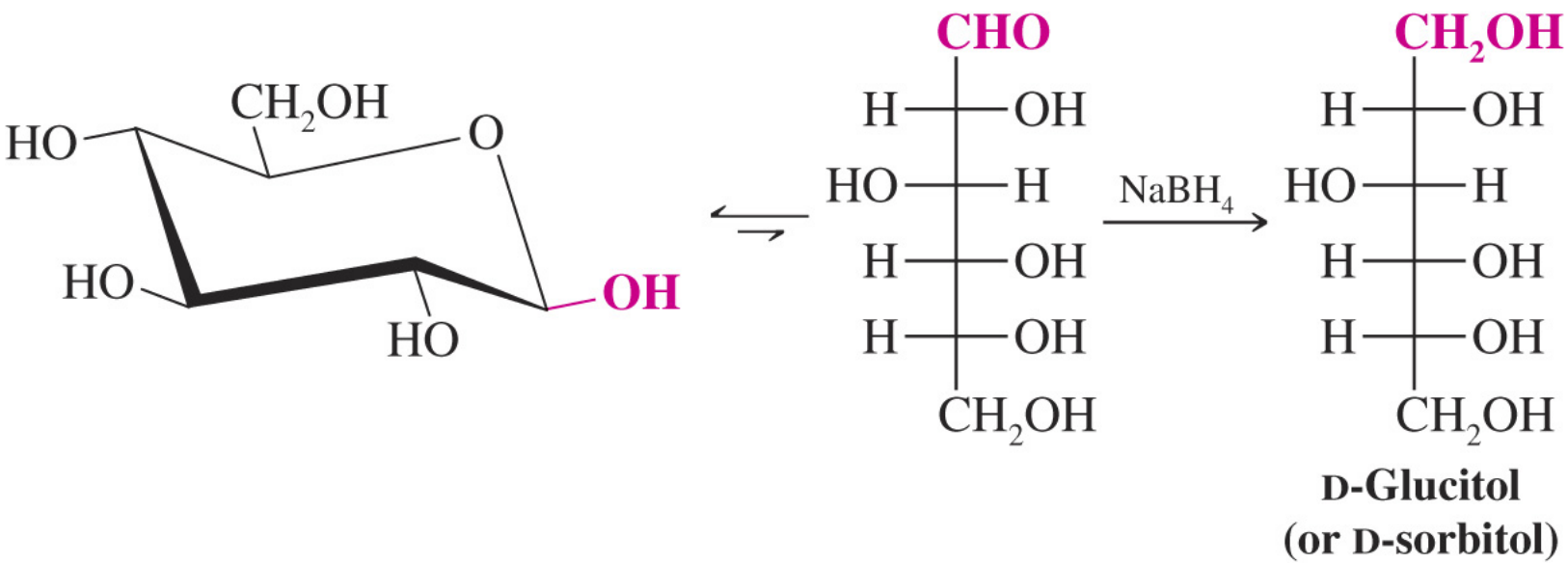


Reduction of Monosaccharides

- Aldoses and ketoses can be reduced to alditols



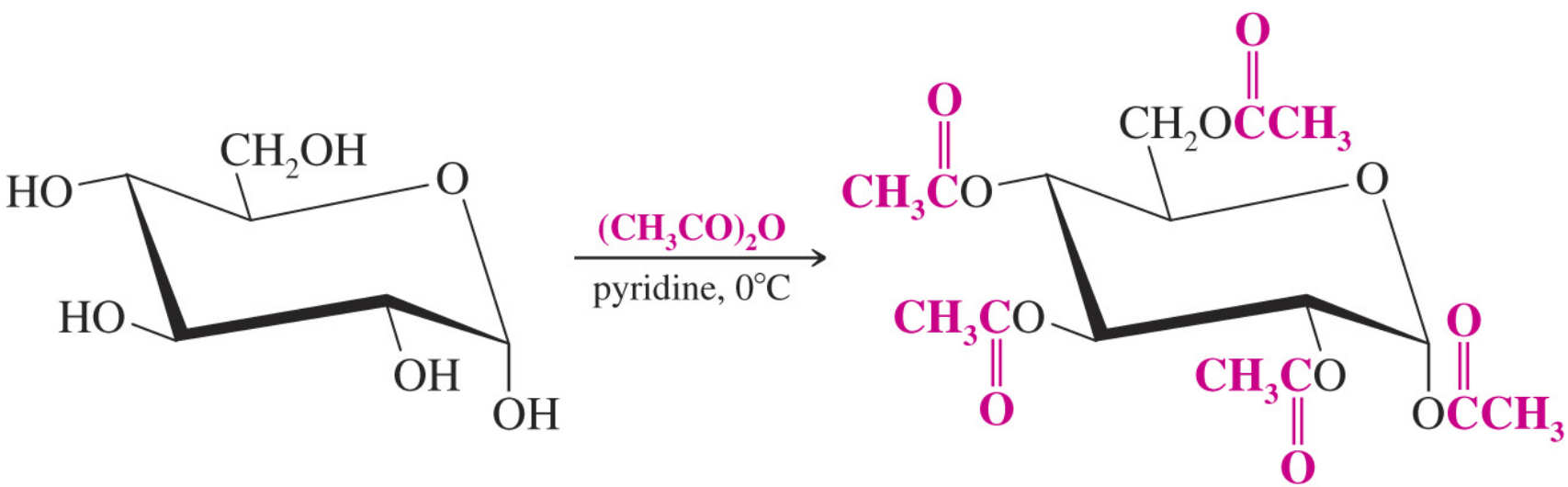
Example


HO
CH2OH
O
HO
HO
OH
CHO
H
OH
HO
H
H
OH
H
OH
CH2OH
NaBH4
CH2OH
H
OH
HO
H
H
OH
H
OH
CH2OH
D-Glucitol
(or D-sorbitol)

Reaction at the Hydroxyl Groups

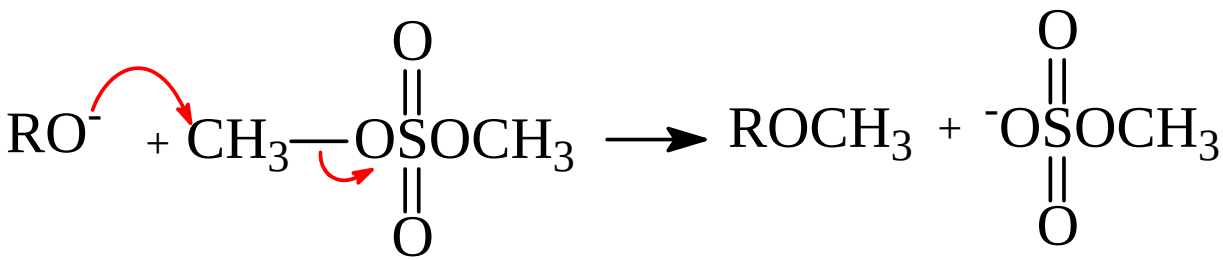
Acetate Formation

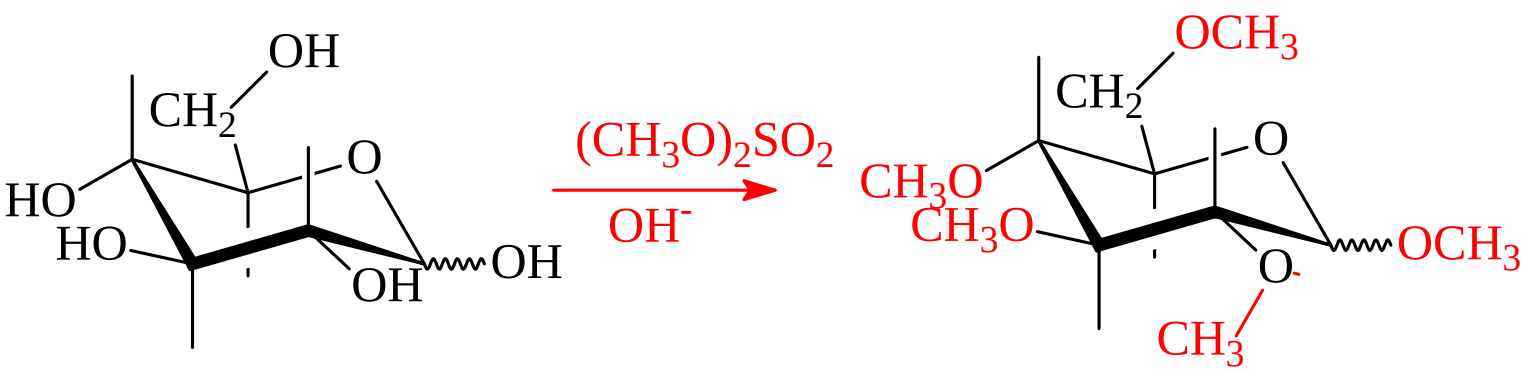
Carbohydrates react with acetic anhydride in the presence of weak base to convert all hydroxyl groups to acetate esters



Ether Formation

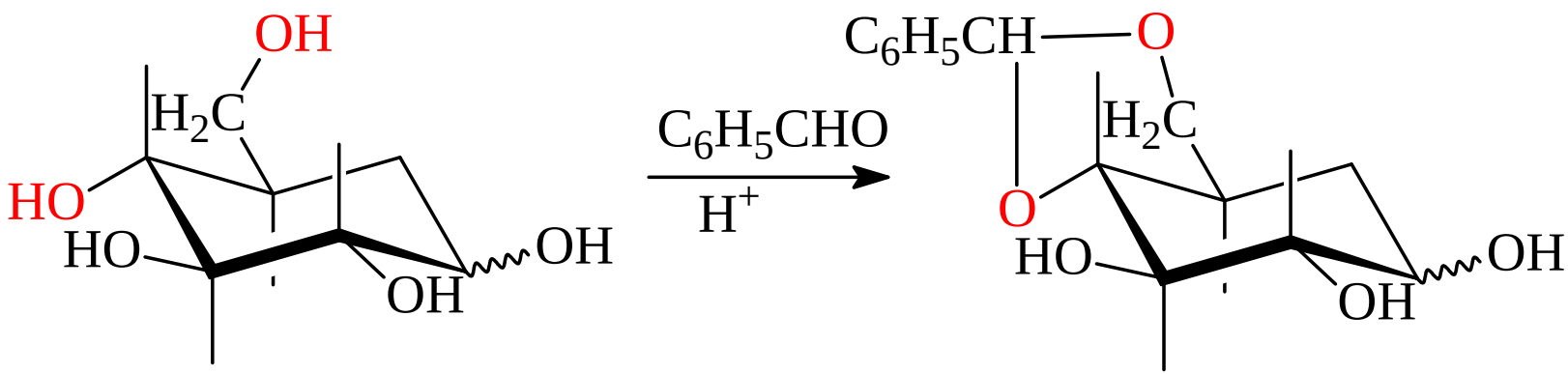
Reaction of monosaccharides with excess dimethylsulfate and NaOH produces multi methyl ether.





Cyclic Acetal Formation

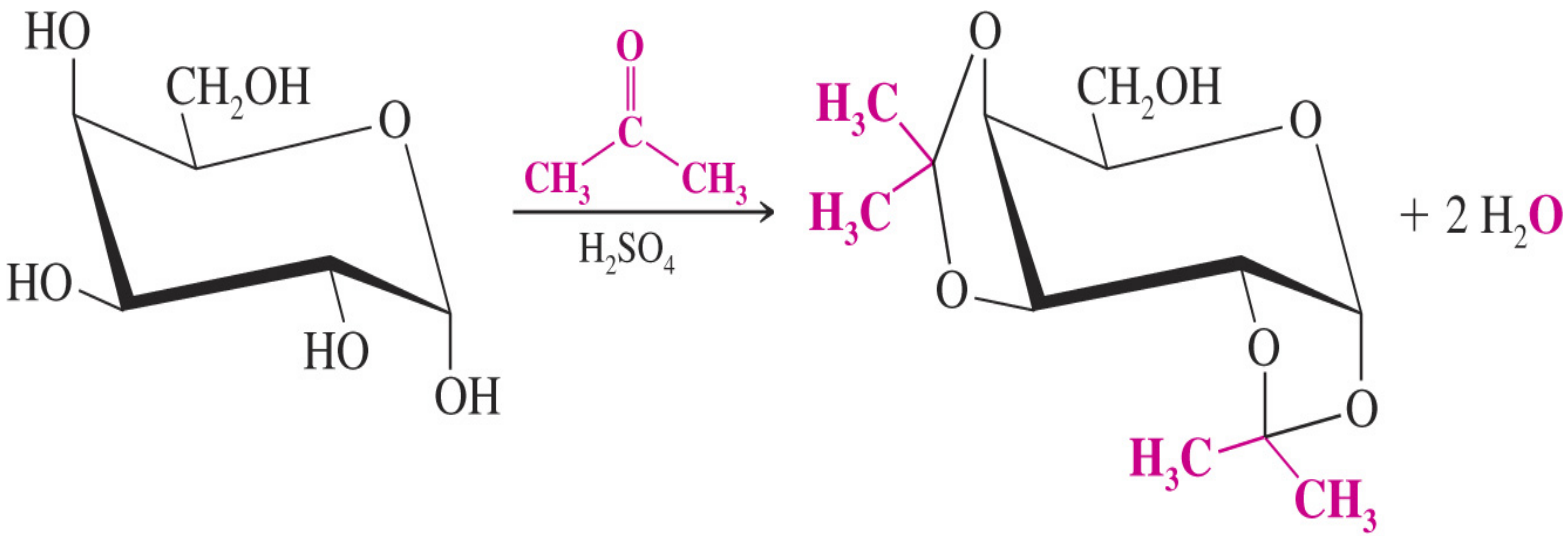
Carbohydrates form cyclic acetals with benzaldehyde selectively between 1,3-diol.



Cyclic acetal

Cyclic Ketal Formation

Carbohydrates form cyclic ketals with acetone selectively between cis-vicinal hydroxyl groups.

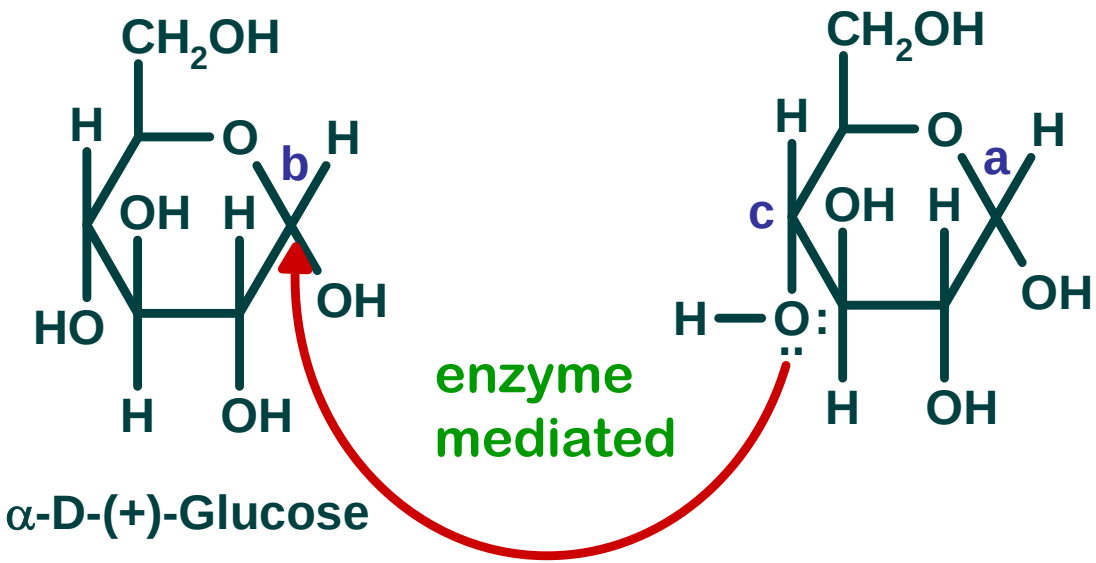


Disaccharides

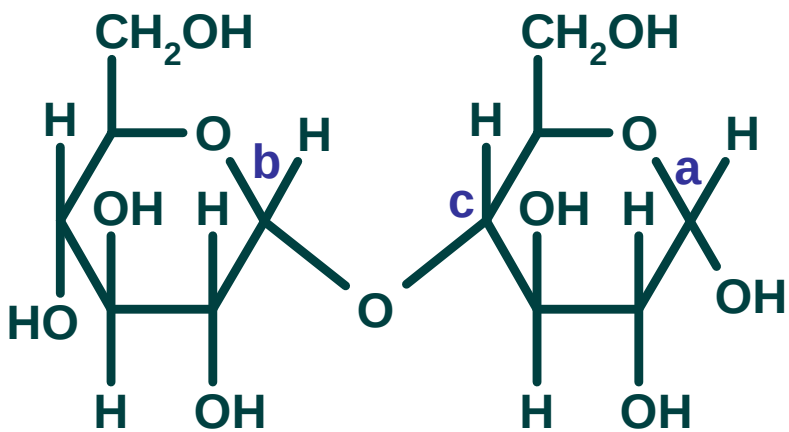
A disaccharide is a carbohydrate compound of two units of monosaccharides joined together by glycoside link from carbon 1 of one unit to an OH of the other unit

Maltose

Contain two units of D-glucopyranose



1,4'-αGlycosidic Linkage

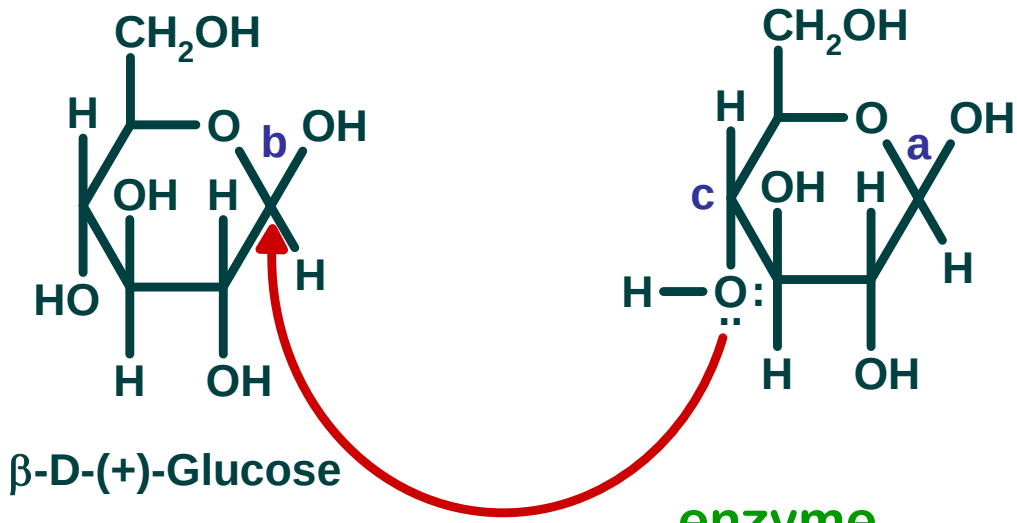


Maltose

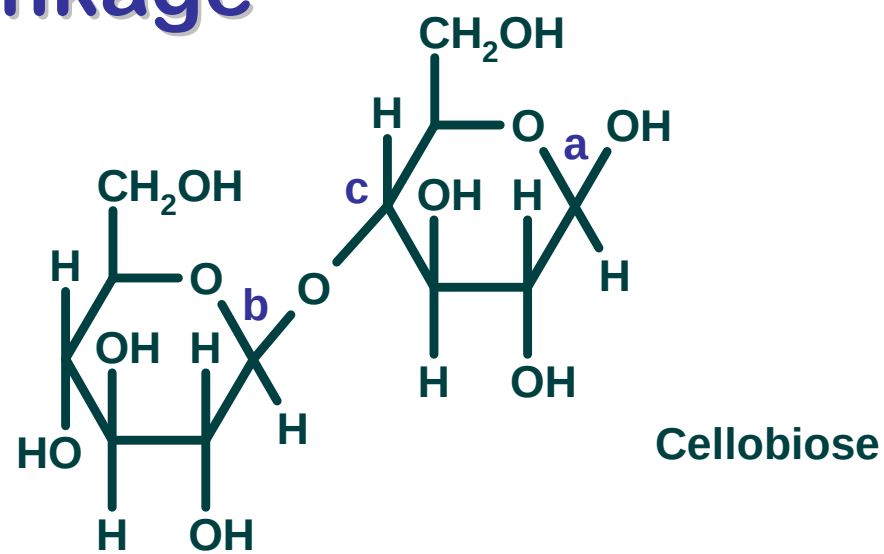
Humans can digest α-1,4

Cellobiose

Two glucose units



1,4'-β Glycosidic Linkage



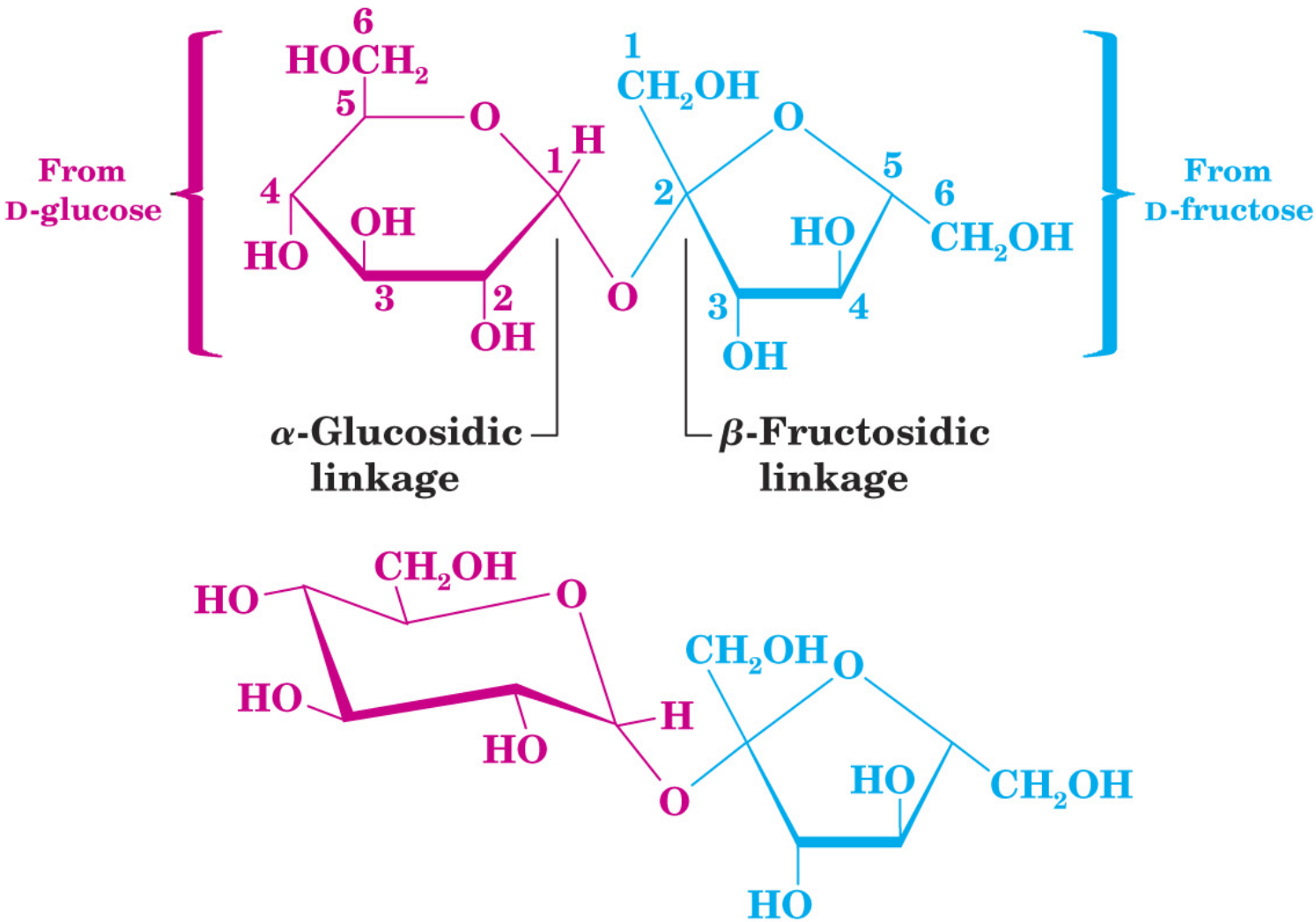
If continued, you get cellulose.

Humans can't digest β-1,4

Sucrose (Table sugar)

Sucrose is a disaccharide formed from D-glucose and D-fructose

- **The glycosidic linkage is between C1 of glucose and C2 of fructose (both anomeric carbon atoms).**
- **Sucrose is a nonreducing sugar because of its acetal linkage**



β-D-fructofuranosyl α-D-glucopyranoside

1,2`link

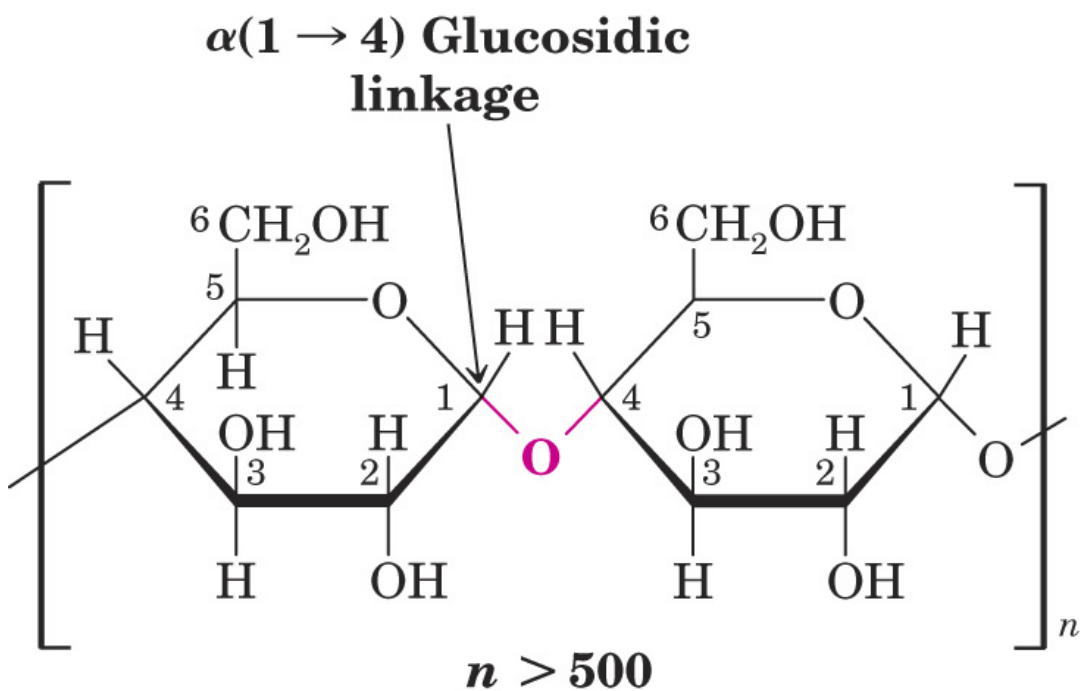
Polysaccharides

- A polysaccharide is a compound in which the molecule contain many units of monosaccharide joined together by glycoside link.
- Two important polysaccharides are starch and cellulose

Starch

- The two forms of starch are amylose and amylopectin
- Amylose consists typically of more than 1000 D-glucopyranoside units connected by α linkages between C1 of one unit and C4 of the next

1,4`α link



Amylopectin

- Amylopectin is similar to amylose but has branching points every 20-25 glucose units
  - –Branches occur between C1 of one glucose unit and C6 of another