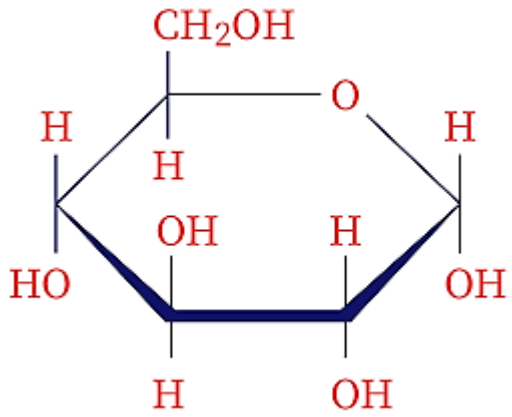
Chemistry of
Carbohydrates



Passang Tshering Lepcha
Assistant Professor
Department of Chemistry
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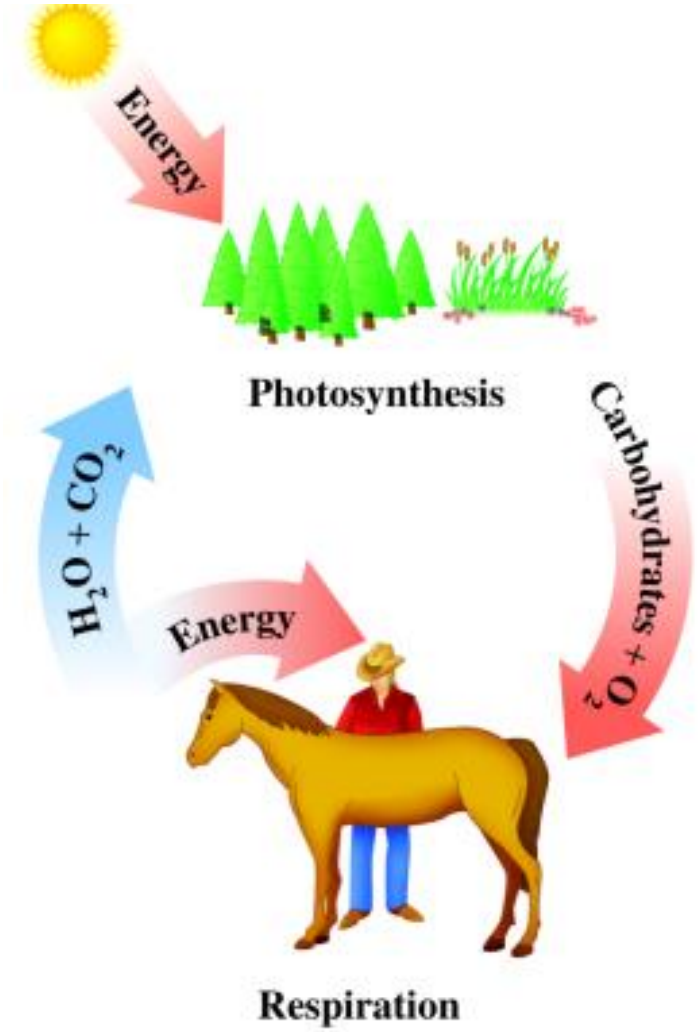
Carbohydrates



- Produced by photosynthesis in plants.
- The major source of energy from our diet.
- Composed of the elements C, H, and O.

$C_n(H_2O)_n$

$$6CO_2 + 6H_2O + \text{energy} \underset{\text{Respiration}}{\overset{\text{Photosynthesis}}{\rightleftharpoons}} C_6H_{12}O_6 + 6O_2$$

glucose

Carbohydrates

- The most abundant organic compounds in nature (50% of the earth's biomass).

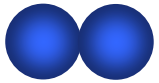
- 3/4 of the weight of plants

- 65% of the foods in our diet.

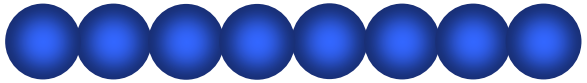
Classification of Carbohydrates

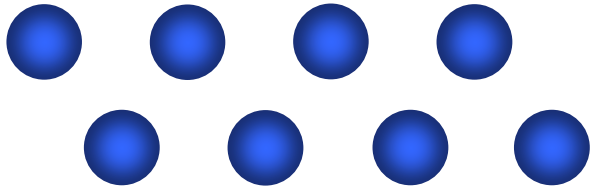
1. Monosaccharide + H_2O $\xrightarrow{H^+ \text{ or enzyme}}$ no hydrolysis

2. Disaccharide + H_2O $\xrightarrow{H^+ \text{ or enzyme}}$ two monosaccharide units



3. Polysaccharide + many H_2O $\xrightarrow{H^+ \text{ or enzyme}}$ many monosaccharide units





Monosaccharides (Simple Sugar)

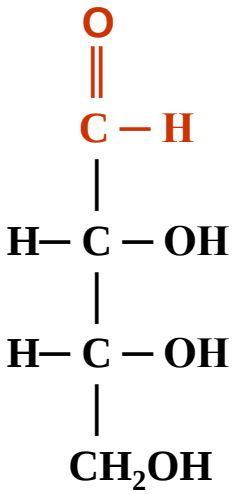
A carbohydrate that cannot be split or hydrolyzed into smaller carbohydrates.

Monosaccharides are carbohydrates with:

- The simplest carbohydrates
- 3-9 carbon atoms
- A carbonyl group (aldehyde or ketone)
- Several hydroxyl groups

$C_n(H_2O)_n$

$C_nH_{2n}O_n$

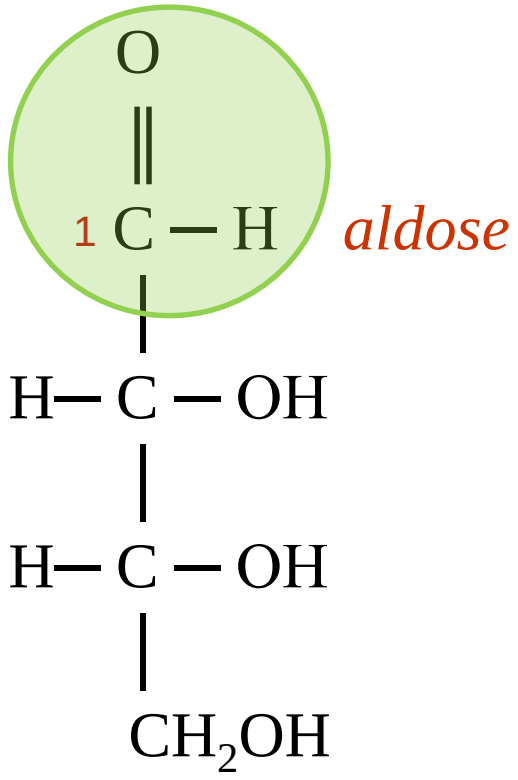


Monosaccharides - Aldose

Aldose is monosaccharide:

- With an aldehyde group and many hydroxyl (-OH) groups.

- *triose* (3C atoms)
- *tetrose* (4C atoms)
- *pentose* (5 C atoms)
- *hexose* (6 C atoms)



“Aldo-” + suffix(ose)

an aldotetrose

(Erythose)

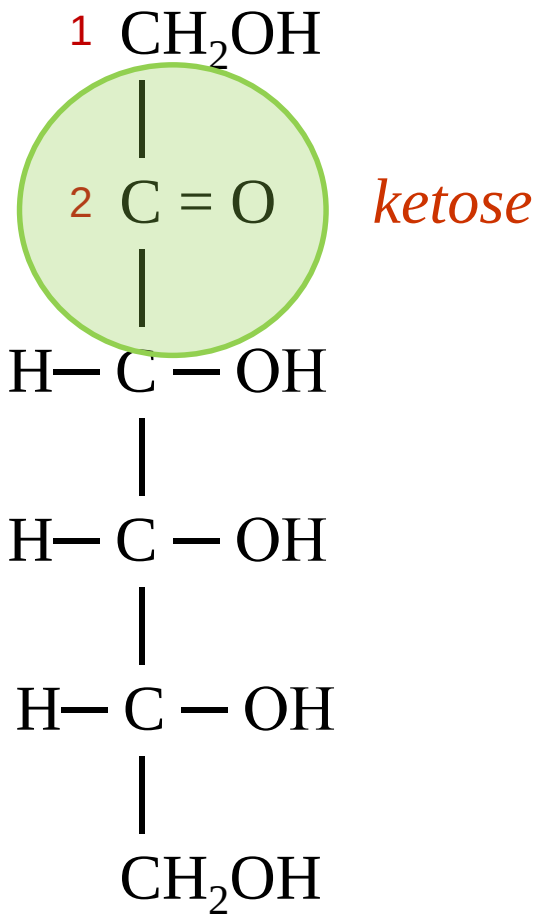
Monosaccharides - Ketose

Ketose is monosaccharide:

- With a ketone group and many hydroxyl (-OH) groups.

- *triose* (3C atoms)
- *tetrose* (4C atoms)
- *pentose* (5 C atoms)
- *hexose* (6 C atoms)

“Keto-” + suffix(ose)

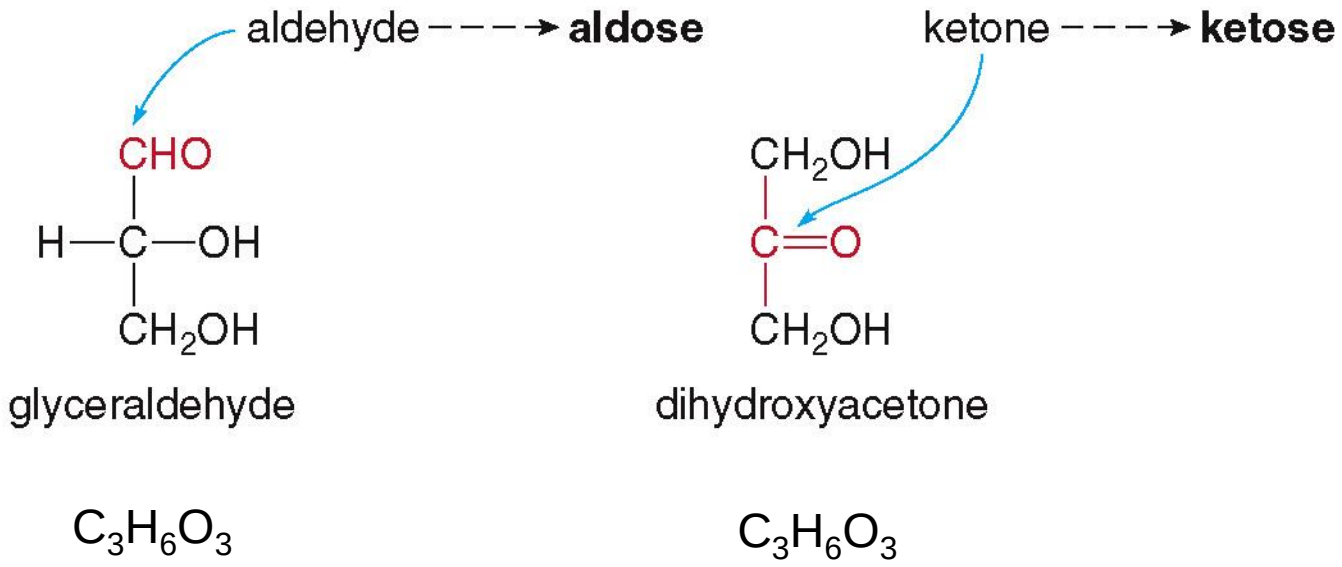


a ketohexose

(Fructose)

Monosaccharides (Simple Sugar)

- The simplest aldose is glyceraldehyde.
- The simplest ketose is dihydroxyacetone.



$C_3H_6O_3$ $C_3H_6O_3$

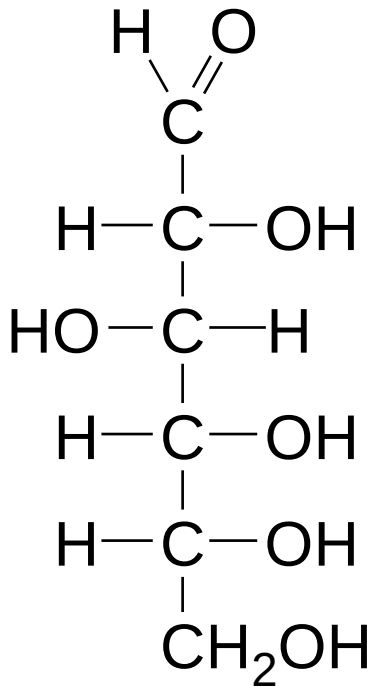
Constitutional Isomers

Some important Monosaccharides

Glucose (Dextrose)

($C_6H_{12}O_6$, aldohexose) – Blood sugar

- The most abundant monosaccharide
- Is found in fruits, vegetables, corn syrup, and honey.
- Is found in disaccharides such as sucrose, lactose, and maltose.
- Makes up polysaccharides such as starch, cellulose, and glycogen.



Some important Monosaccharides

Glucose (Dextrose)

- Normal blood glucose levels are 70-110 mg/dL.

- Excess glucose is stored as the polysaccharide glycogen.

- Insulin (a protein produced in the pancreas) regulates blood glucose levels by stimulating the uptake of glucose into tissues or the formation of glycogen.

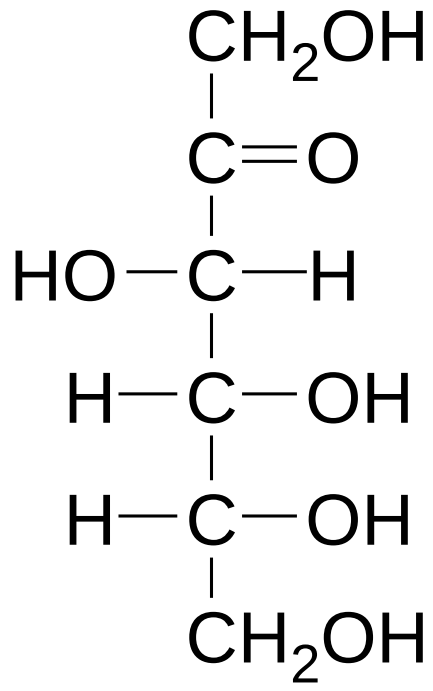
- Patients with diabetes produce insufficient insulin to adequately regulate blood sugar levels, so they must monitor their diet and/or inject insulin daily.

Some important Monosaccharides

Fructose

($C_6H_{12}O_6$, ketohexose),

- Is the sweetest of the carbohydrates.
- Is found in fruit juices and honey **(fruit sugar).**
- In bloodstream, it is converted to its isomer, glucose.
- Is bonded to glucose in sucrose (a disaccharide known as table sugar)**.**

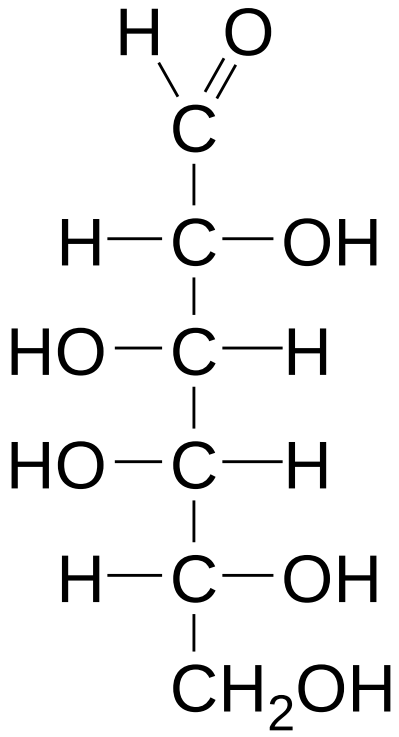


Some important Monosaccharides

Galactose

($C_6H_{12}O_6$, aldohexose),

- Has a similar structure to glucose except for the –OH on Carbon 4.
- Cannot find in the free form in nature.
- Exist in the cellular membranes of the brain and nervous system.
- Combines with glucose in lactose (a disaccharide and a sugar in milk).



Disease - Galactosemia

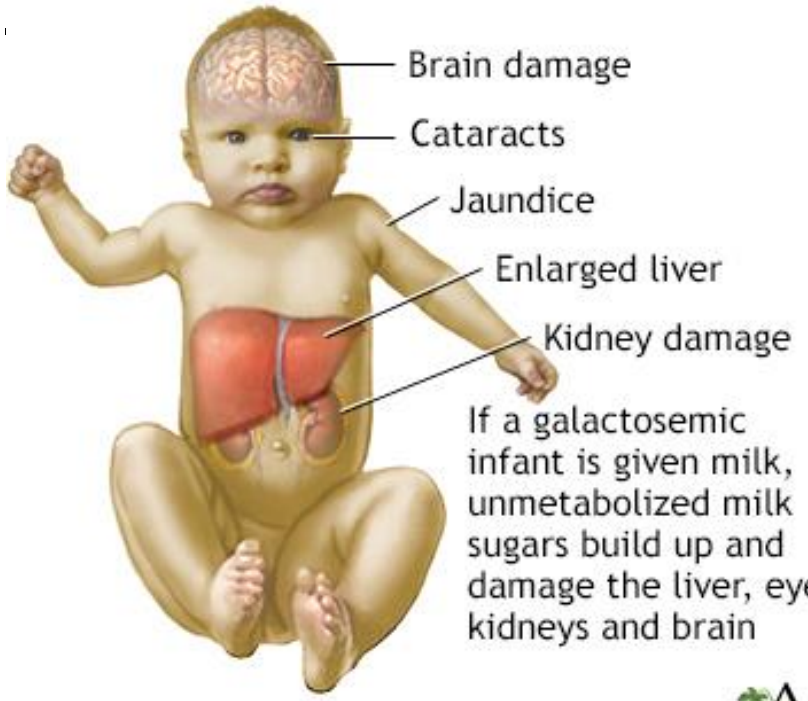
Galactosemia

missing the enzyme that convert galactose to glucose

Accumulation of galactose in the blood and tissues.

⇩

Mental retardation and cataract

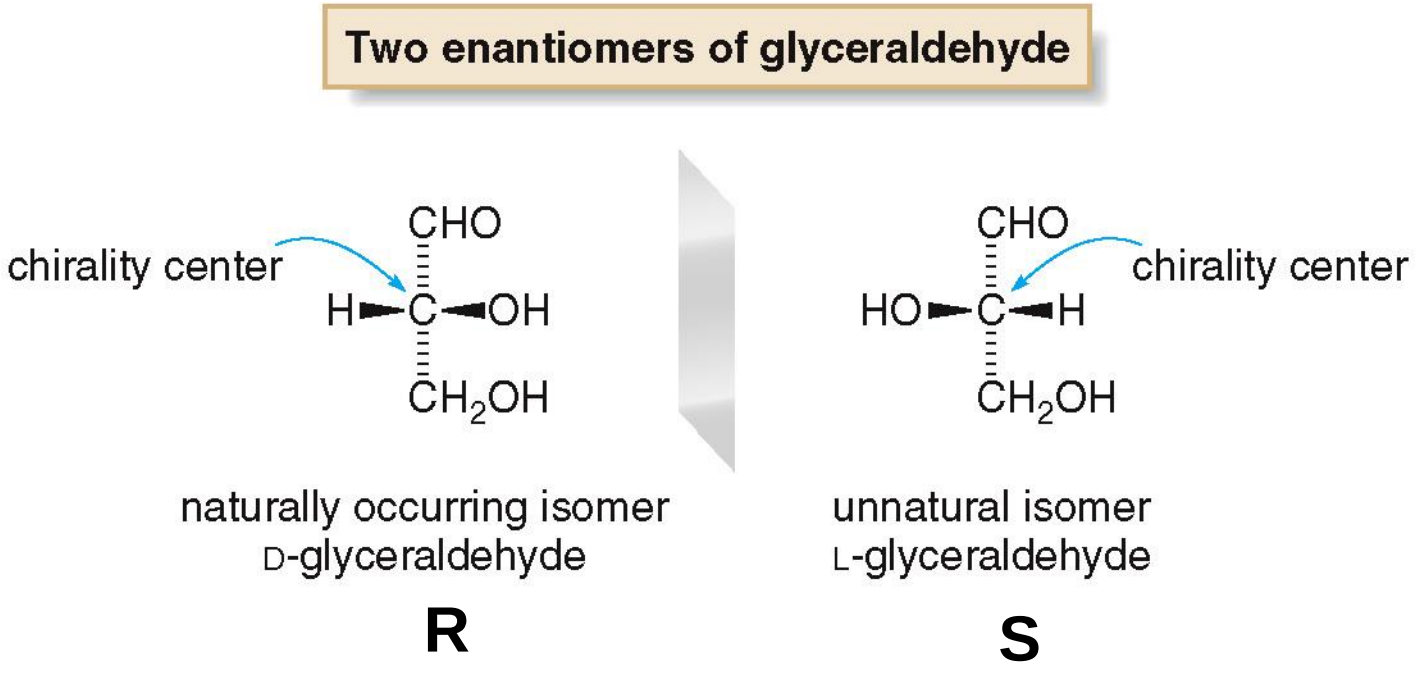


Solution: removing the galactose from food: no milk.

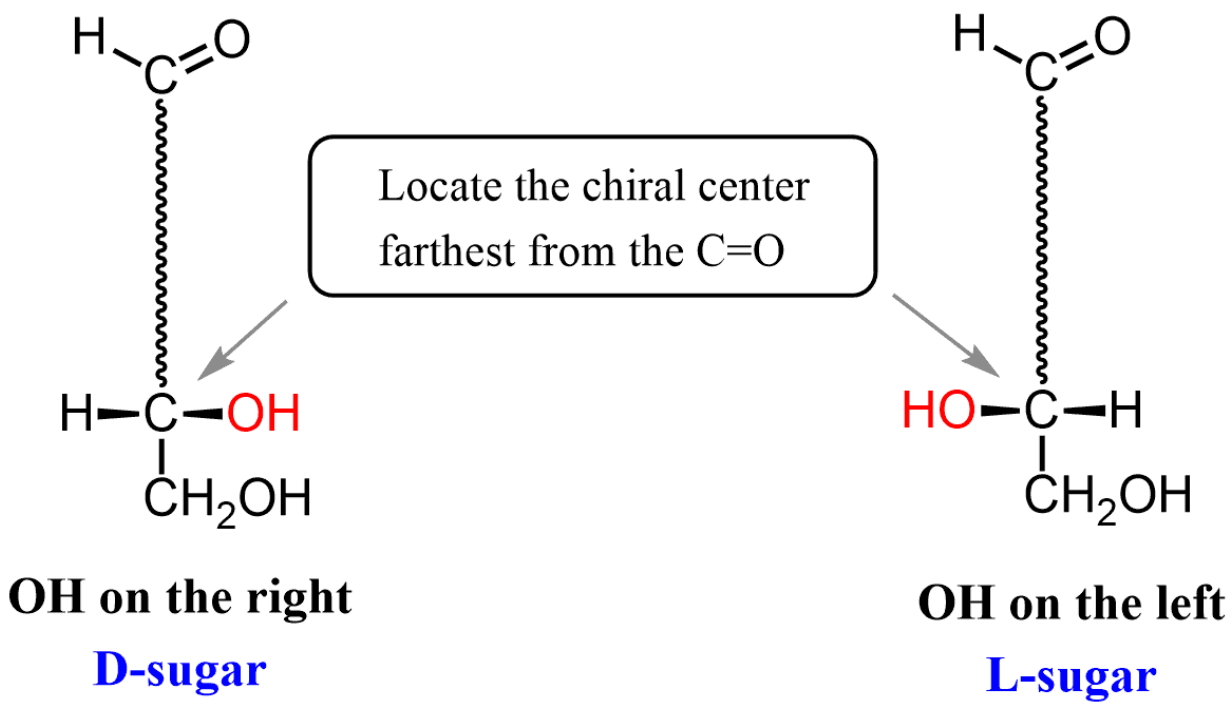
Chirality(Stereochemistry)

All carbohydrates have 1 or more chirality centers.

Glyceraldehyde, the simplest aldose, has one chirality center, and has two possible enantiomers.



D and L Configuration of Carbohydrates



In 1906 by a New York University chemist, M. A. Rosanoff, is often the preferred way of describing the stereochemistry of sugars. This strategy uses the **D and L notation** and is determined based on the chiral **carbon farthest from the C=O carbonyl group**

D and L are not related to the optical rotation

In **D-sugars** the **OH group** on the chiral center farthest from the carbonyl is **on the right.**

In **L-sugars** the **OH group** on the chiral center farthest from the carbonyl is **on the left.**

The D and L notation is applied **in reference to glyceraldehyde** which naturally occurs in the D form.

Fischer Projections

- Horizontal lines represent bonds projecting forward from the stereocenter.

- Vertical lines represent bonds projecting to the rear.

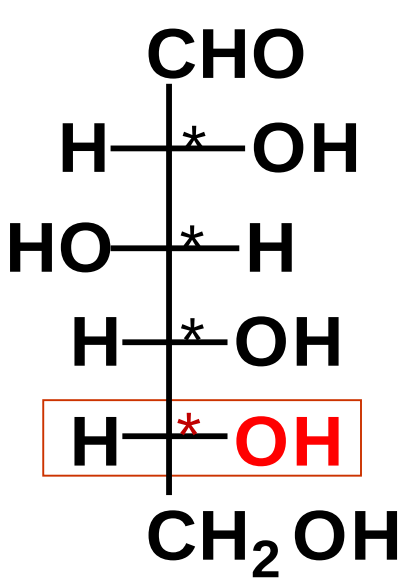
- Only the stereocenter (tetrahedral carbon) is in the plane.

3D 2D

Fischer Projections

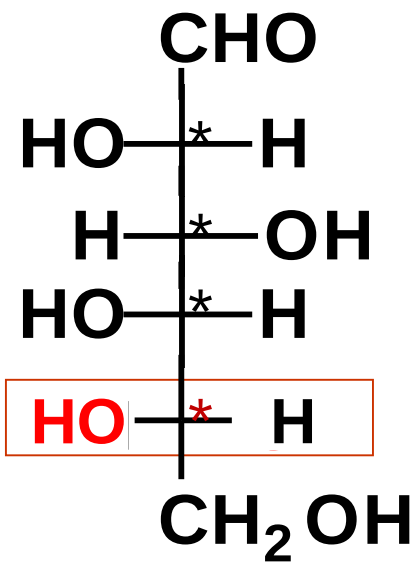
1. Carbon with four different groups bonded to it.

2. The chiral carbon furthest from the carbonyl group (-CHO).



D - glucose

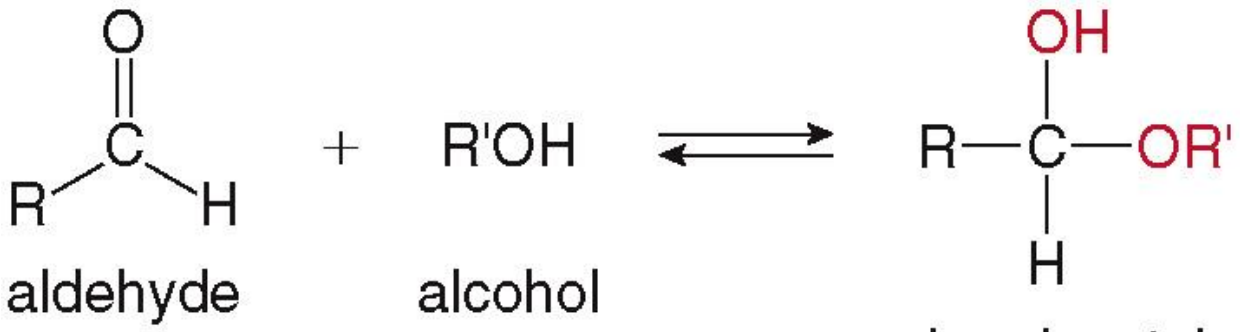
Naturally occurring enantiomer



L - glucose

Cyclic Structure – Haworth Structure

Aldehydes and ketones react with alcohols to form hemiacetals.

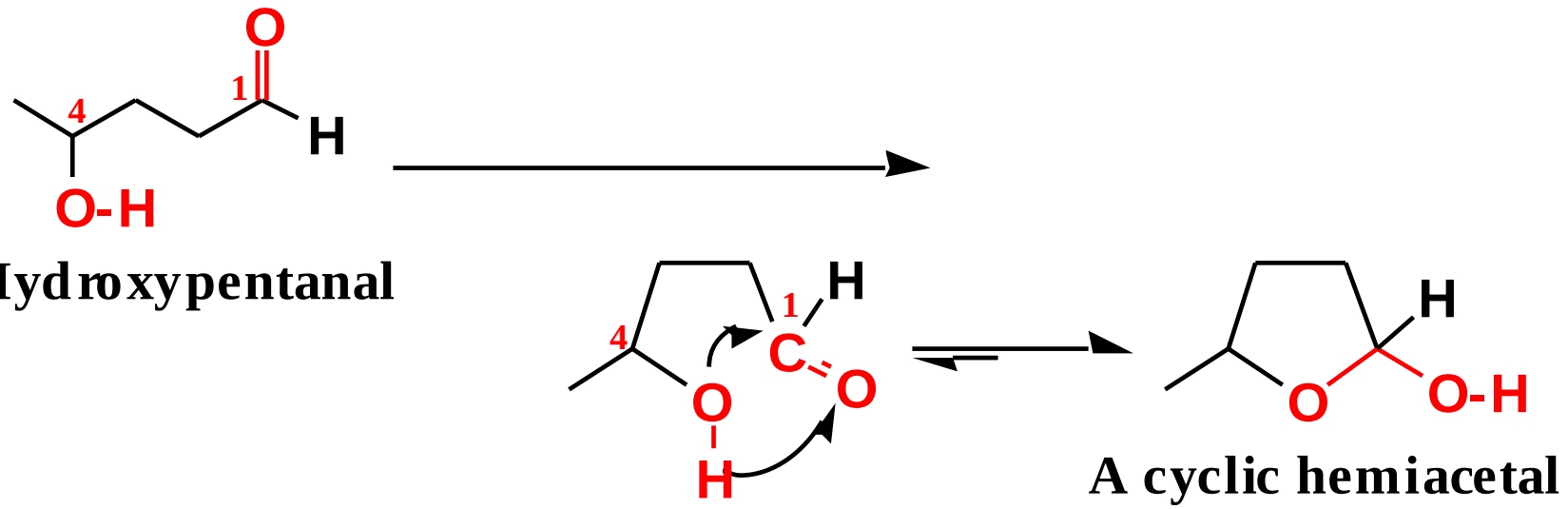


Unstable

A hemiacetal contains a hydroxyl group (OH) and an alkoxy group (OR) on the same carbon.

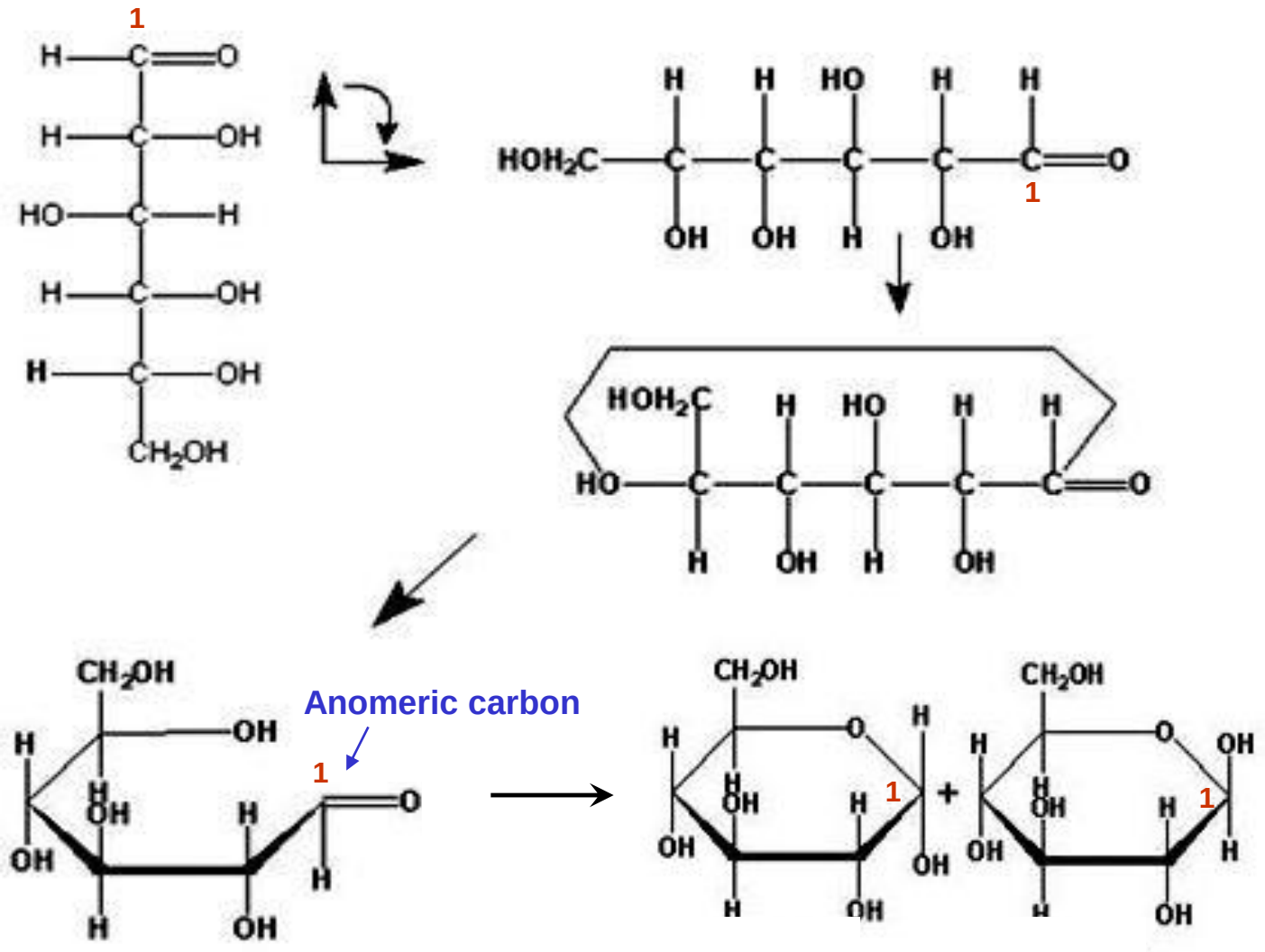
Cyclic Structure – Haworth Structure

Cyclic hemiacetals form readily when the hydroxyl and carbonyl groups are part of the same molecule.



Stable

Cyclic Structure – Haworth Structure



More stable form

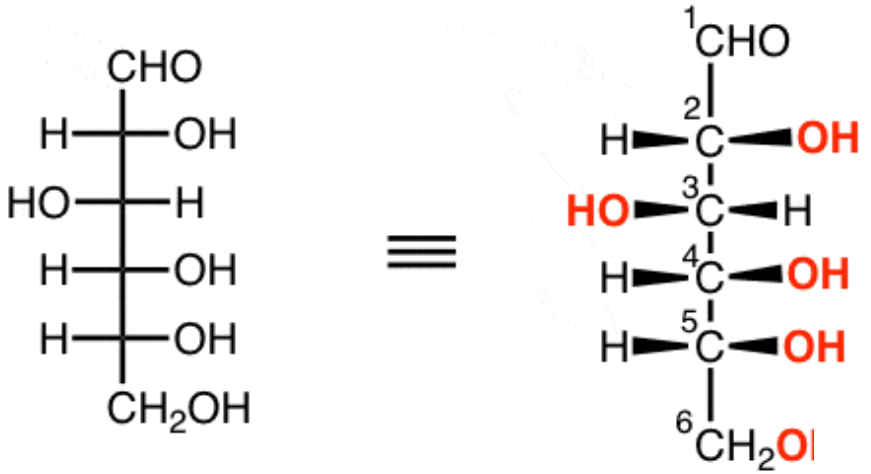
Alpha (α) Beta (β)

Anomers

Converting a Fischer to a Haworth

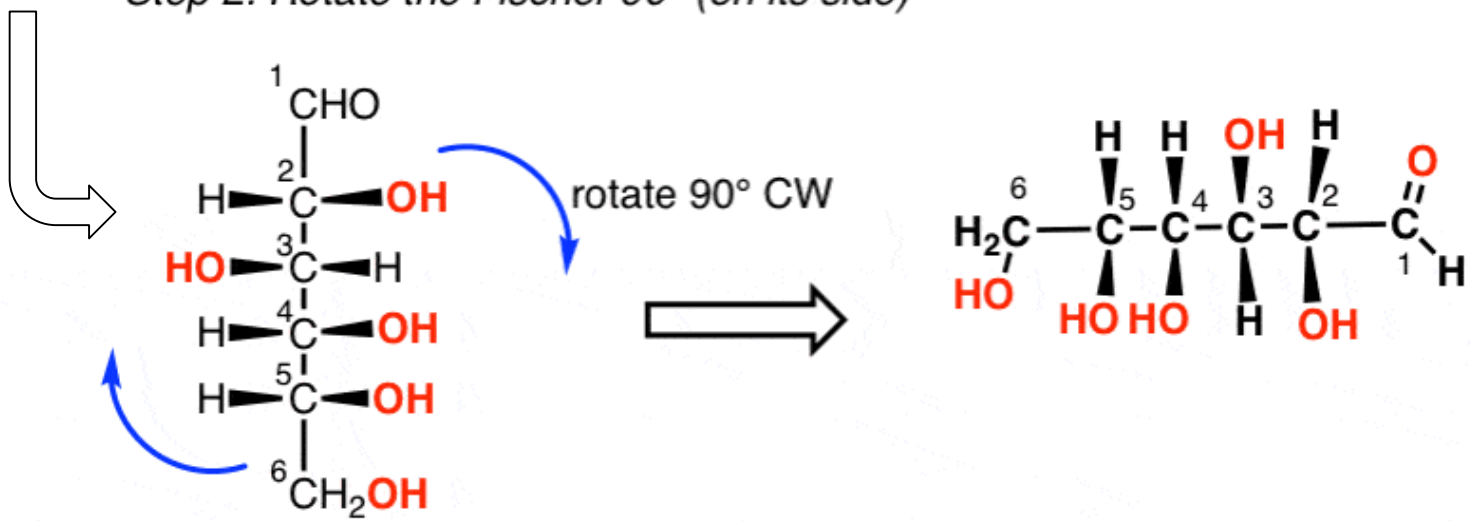
Step 1: number carbons, and draw in the Fischer stereochemistry

("the arms come out to hug you")



Converting a Fischer to a Haworth

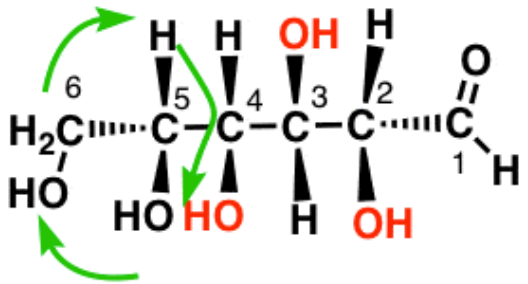
Step 2: Rotate the Fischer 90° (on its side)



Converting a Fischer to a Haworth

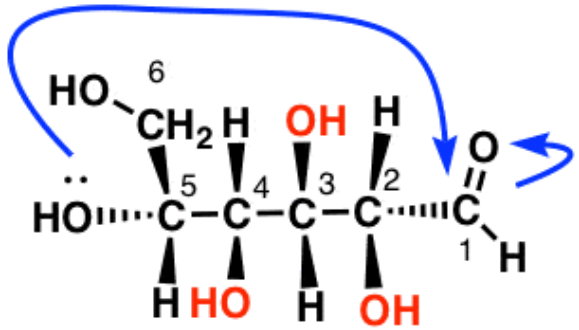
Step 3: Bond rotation on C_5

bond rotation (C_5)

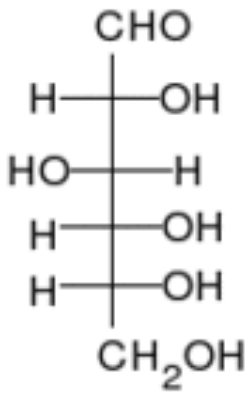


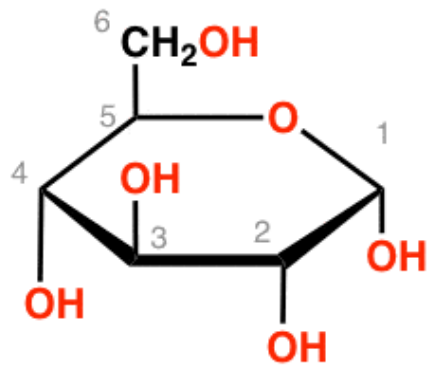
Step 4: Closure of the ring

ring closure (form O–C_1)



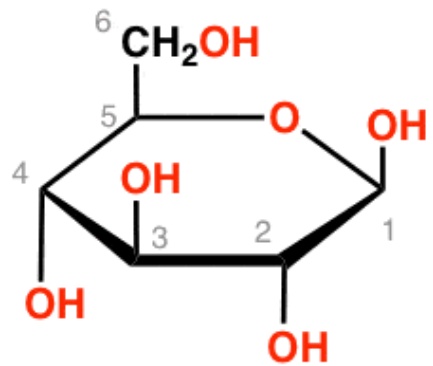
(after proton transfer)



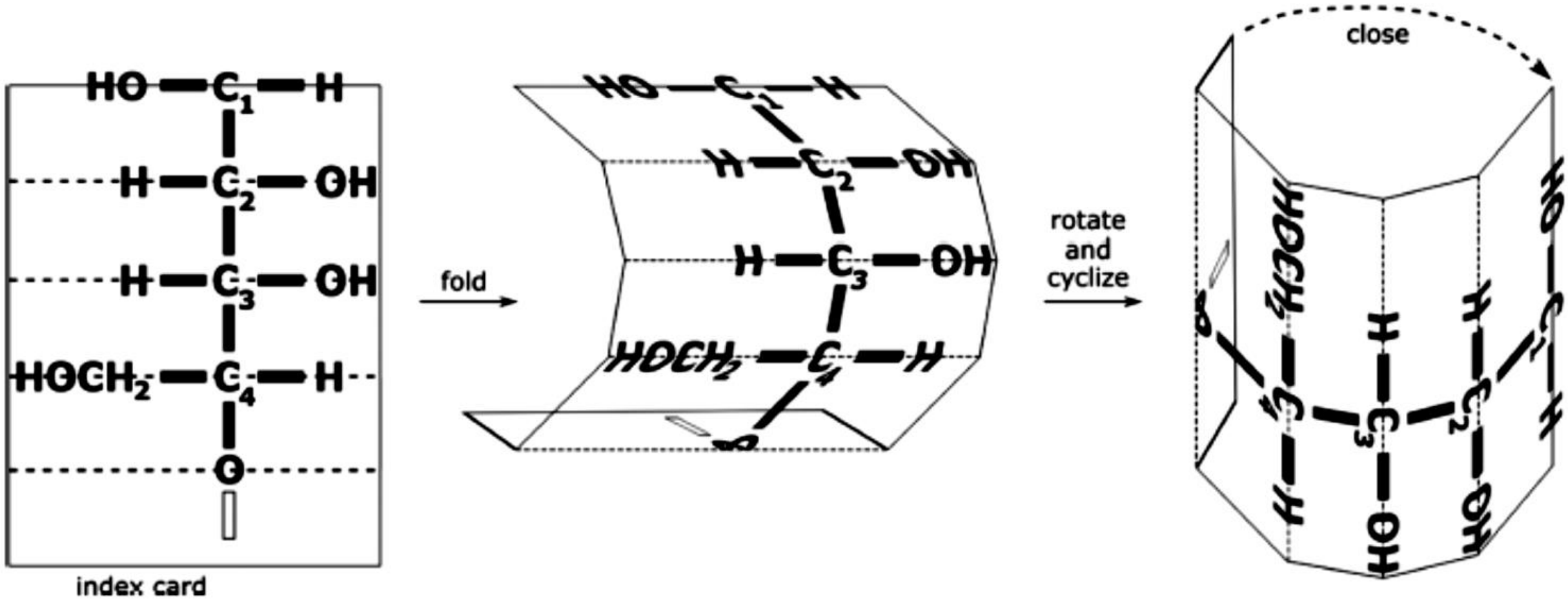


α-D-glucopyranose

or



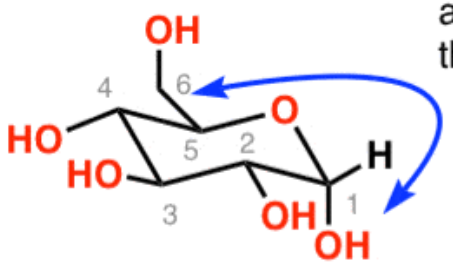
β-D-glucopyranose


index card
fold
rotate
and
cyclize
close

The two diastereomers of glucose in its "pyranose" form are called the alpha (α) and beta (β) isomers, which differ in the orientation of the OH at C-1

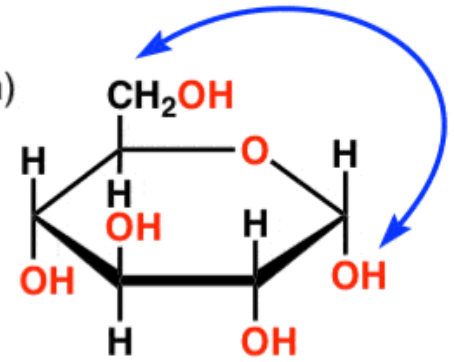
"alpha" (α) isomer:

C_5-CH_2OH (up) and C_1-OH (down) are on **opposite** faces of the ring



α-D-Glucose drawn as "chair"

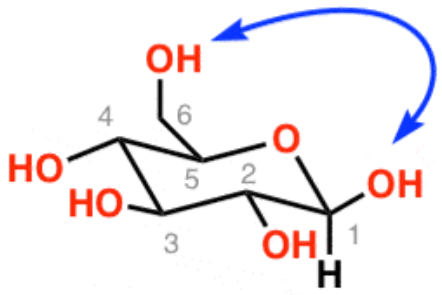
opposite face



α-D-Glucose "Haworth Projection"

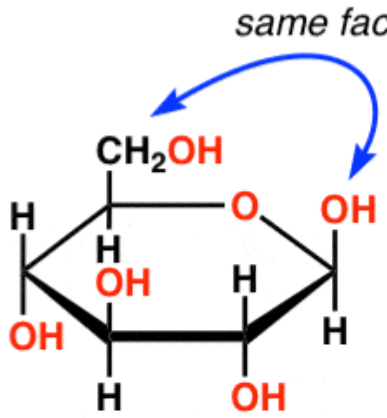
"beta" (β) isomer:

C_5-CH_2OH (up) and C_1-OH (up) are on the **same** face of the ring



β-D-Glucose drawn as "chair"

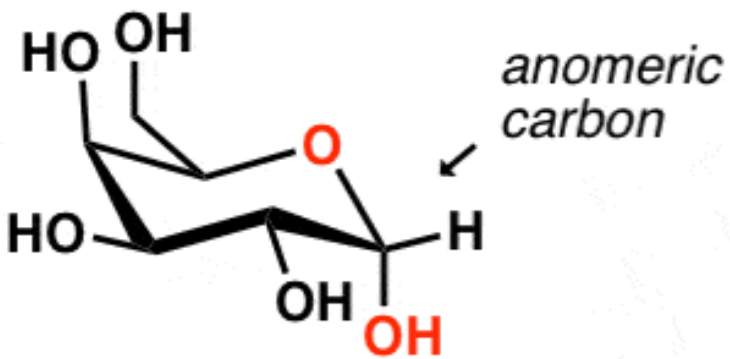
same face

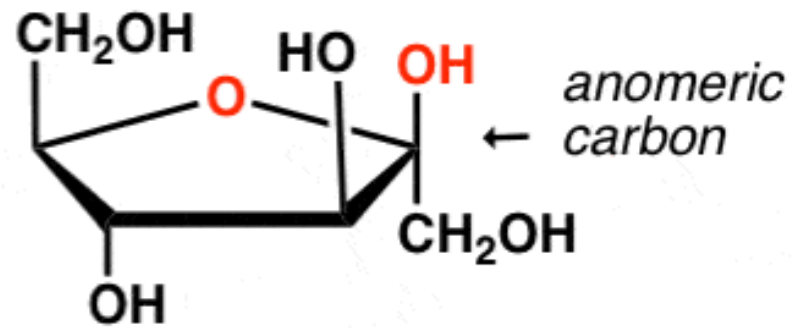


β-D-Glucose "Haworth Projection"

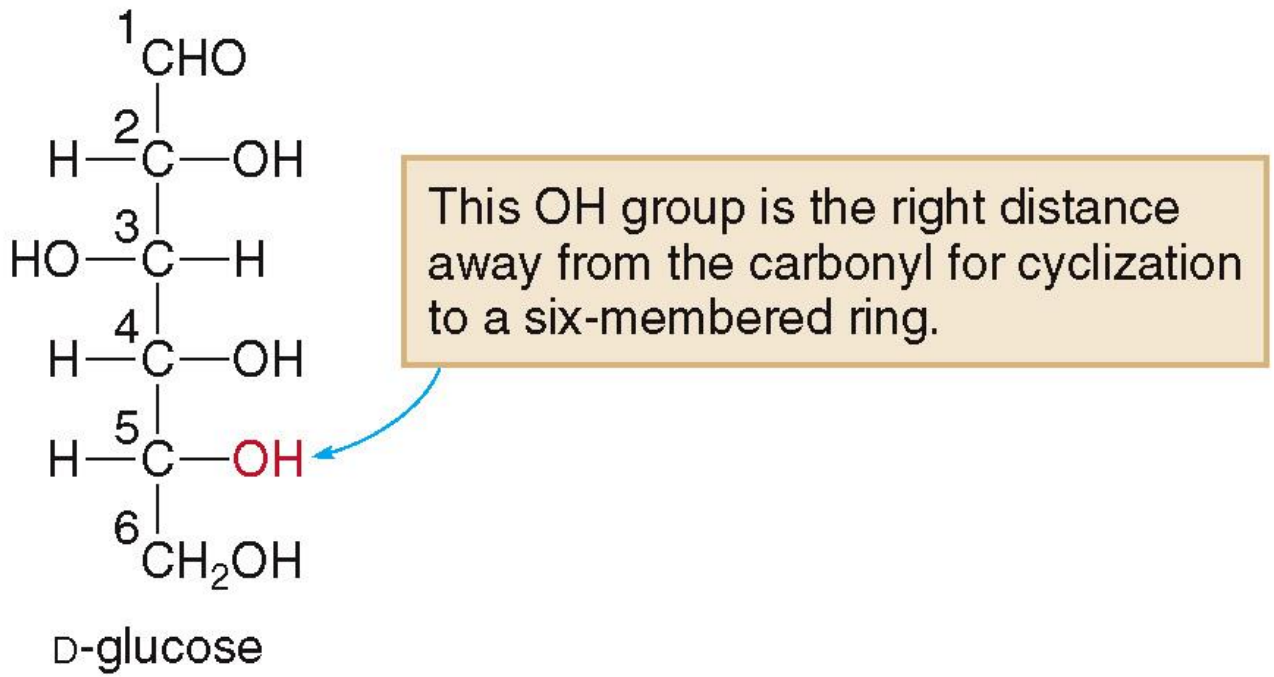
Anomeric carbon

- the hemiacetal carbon of a cyclic sugar. A chiral center which results from ring closure upon an aldehyde or ketone in an acyclic sugar



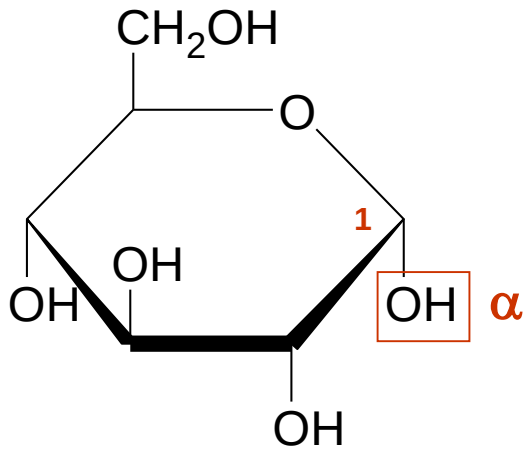


Cyclic Structure – Haworth Structure

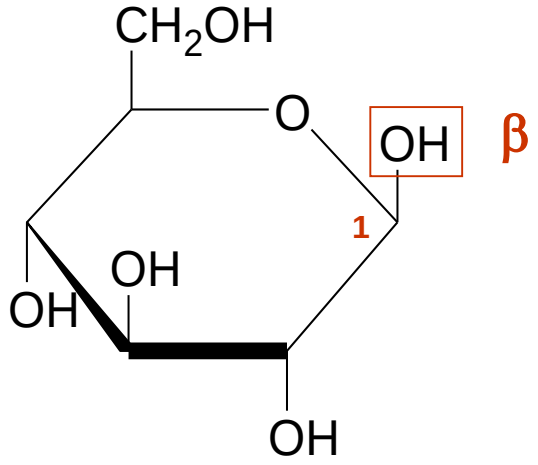


D-glucose

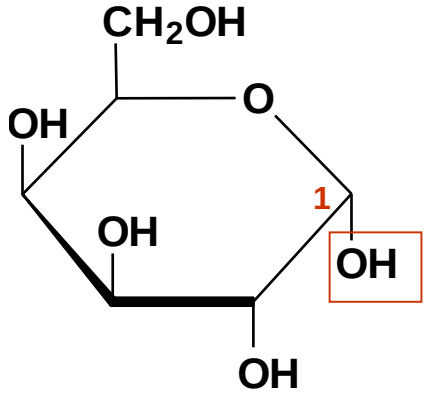
Cyclic Structure – Haworth Structure



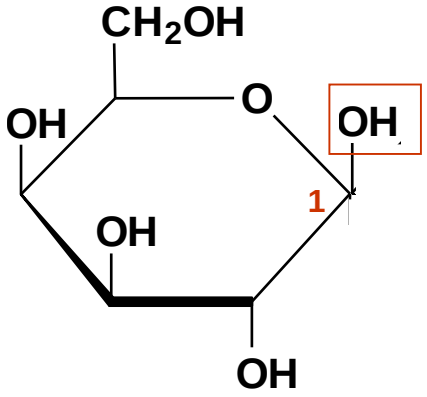
α-D-Glucose



β-D-Glucose

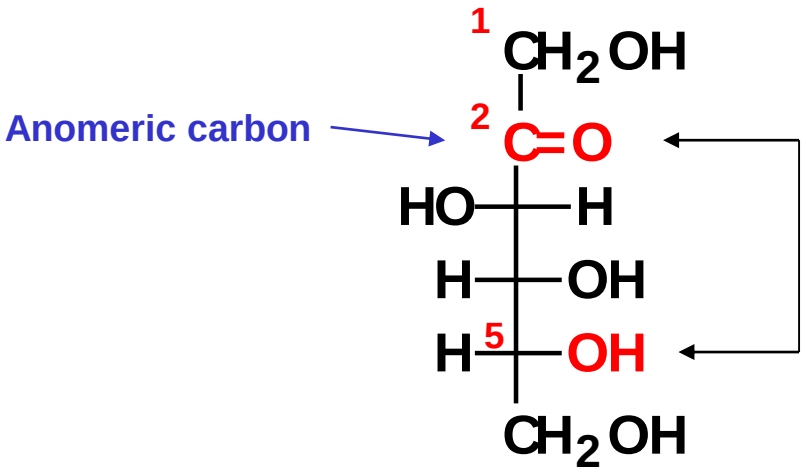


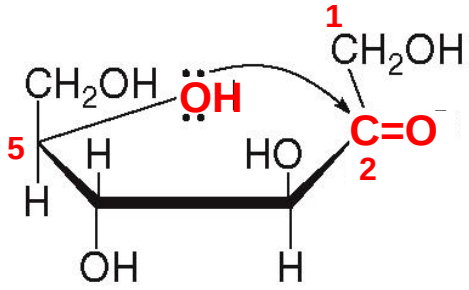
α-D-Galactose

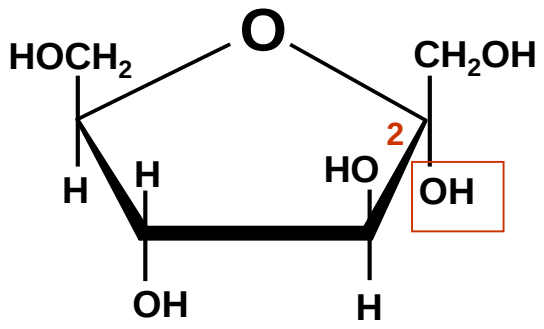


β-D-Galactose

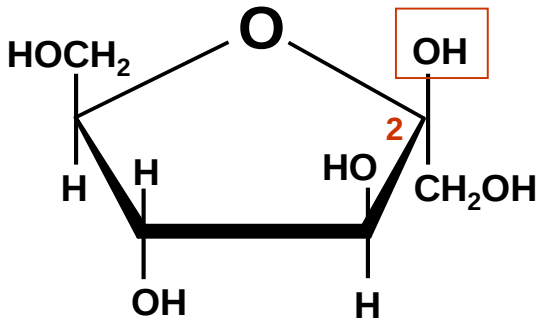
Cyclic Structure – Haworth Structure





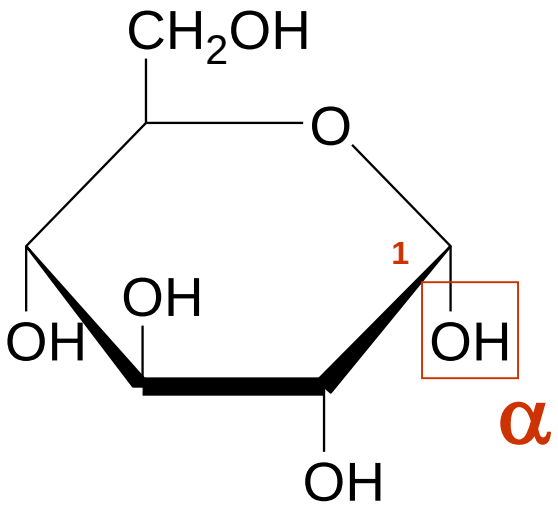


α-D-fructose

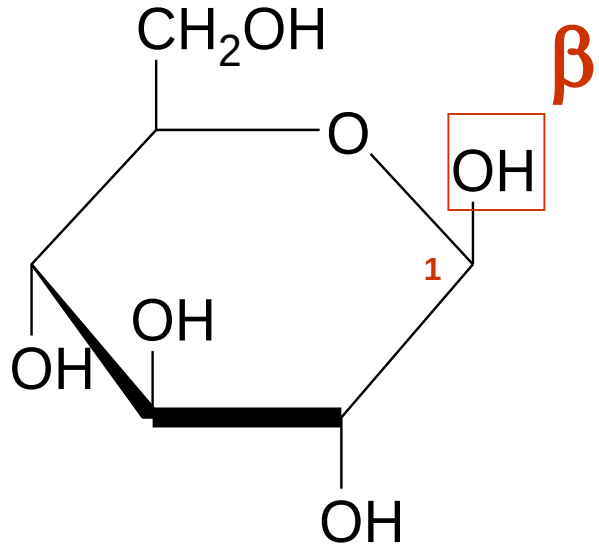


β-D-fructose

Cyclic Structure – Haworth Structure



α-D-Glucose

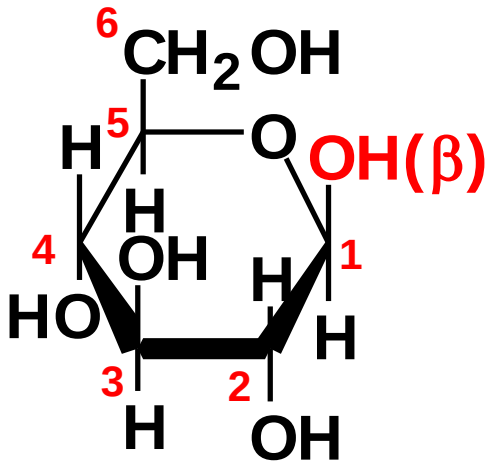


β-D-Glucose

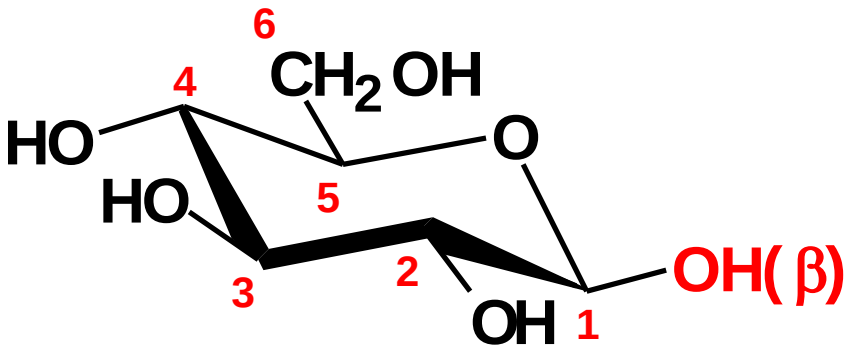
Humans have α-amylase (an enzyme) and they can digest starch products such as pasta (contain α-glucose)

Humans do not have β-amylase (an enzyme) and they cannot digest cellulose such as wood or paper (contain β-glucose)

Chair Conformation



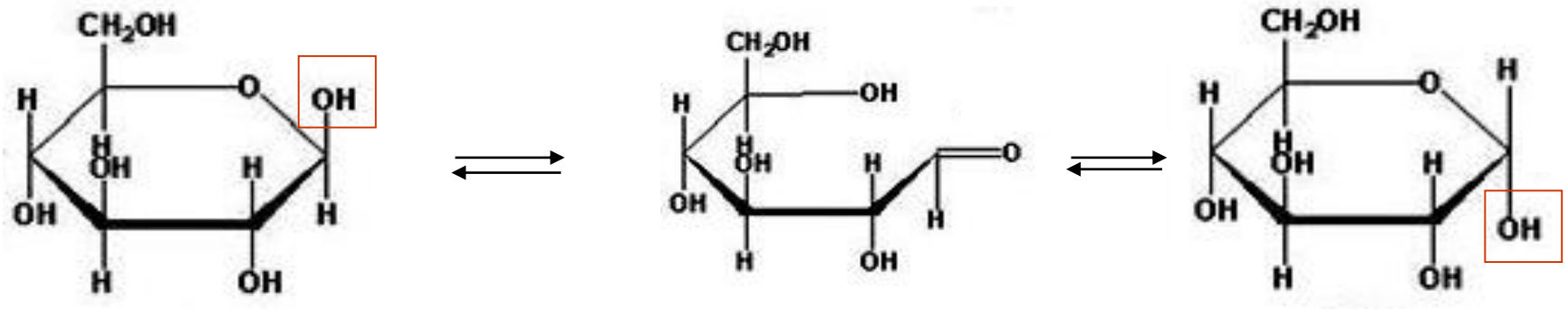
β-D-Glucose
(Haworth projection)



β-D-Glucose
(Chair conformation)

Mutarotation

Change in specific rotation that accompanies the equilibration of α and β anomers in aqueous solution.



β-D-glucose
[α]= +18.7°
64%

Open-chain form
(acyclic)
< 0.02%

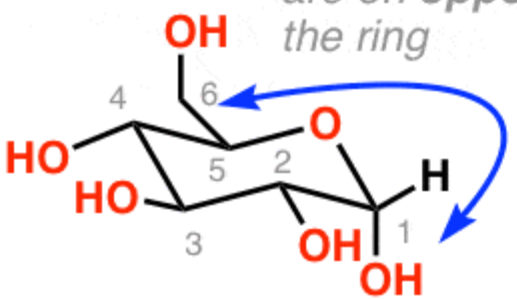
α-D-glucose
[α]= +112°
36%

Alpha (α) and beta (β) isomers ("anomers") differ in the orientation of the OH at the C-1 hemiacetal carbon

Example: D-glucose

"alpha" (α) isomer:

*C_5-CH_2OH (up) and C_1-OH (down) are on **opposite** faces of the ring*



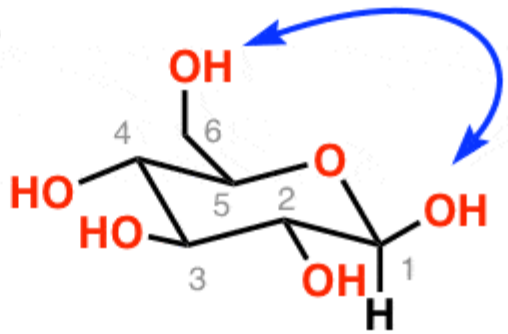
α-D-Glucose

drawn as "chair"

Specific rotation: $[\alpha]_D^{20}$ + 112°

"beta" (β) isomer:

*C_5-CH_2OH (up) and C_1-OH (up) are on the **same** face of the ring*



β-D-Glucose

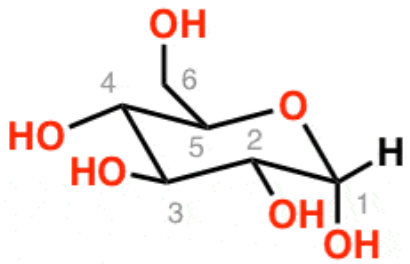
drawn as "chair"

Specific rotation: $[\alpha]_D^{20}$ + 18.7°

Note different specific rotations!

Mutarotation

When 100% pure α-D-glucopyranose is dissolved in water, the specific rotation slowly changes from +112° to + 52.5° over a few hours.



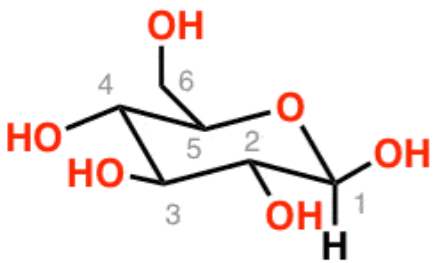
Dissolve in water →

specific rotation decreases over several hours, until reaching stable value of +52.5°

α-D-Glucose (pyranose form)

Specific rotation: $[\alpha]_D^{20}$ + 112°

Similarly, when 100% pure β-D-glucopyranose is dissolved in water, the specific rotation slowly changes from + 18.7° to + 52.5°.



Dissolve in water →

specific rotation increases over several hours, until reaching stable value of +52.5°

β-D-Glucose (pyranose form)

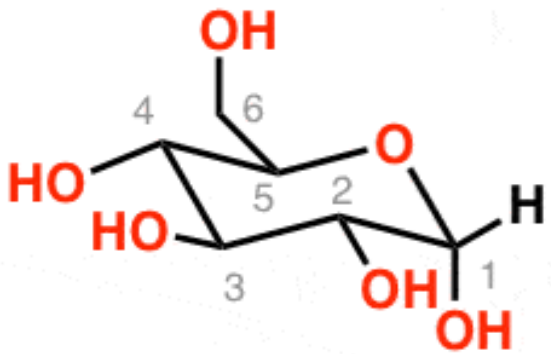
Specific rotation: $[\alpha]_D^{20}$ + 18.7°

This is called "mutarotation" (*"muta" = change, so "change of rotation"*)

Why the change in specific rotation?

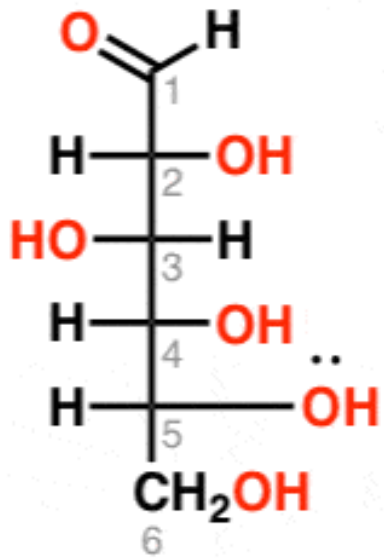
The alpha and beta anomers are each in equilibrium with the "linear" form, and therefore with each other.

"alpha" (α) isomer:



α-D-Glucose

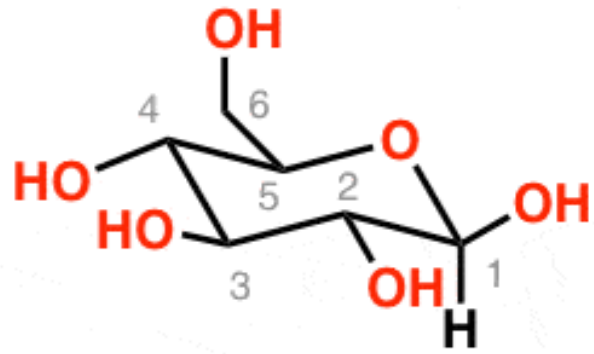
36%
(at equilibrium)



D-Glucose

("linear" form)

"beta" (β) isomer:



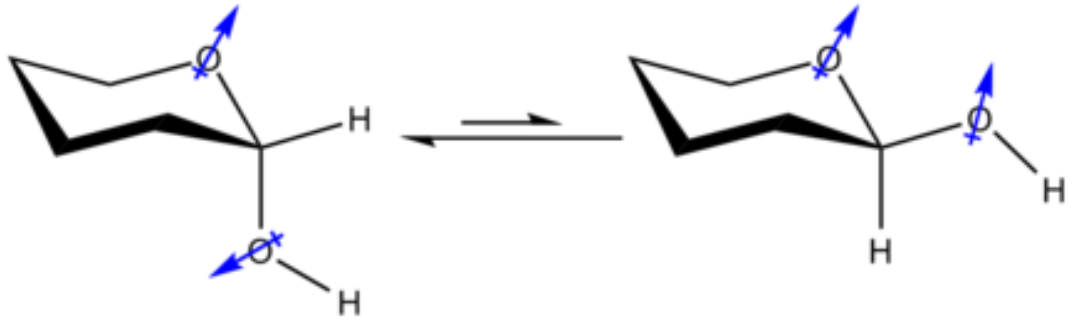
β-D-Glucose

64%
(at equilibrium)

At equilibrium the mixture consists of 36% α-D-Glucose, 64% β-D-Glucose, and traces of the linear and furanose forms.

Anomeric Effect

Hyperconjugation



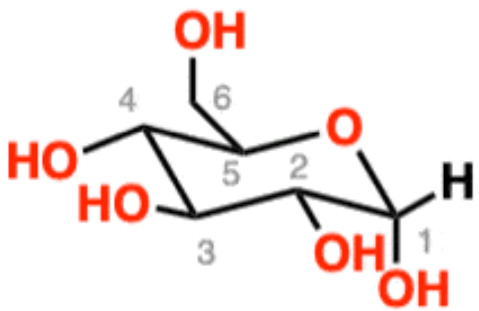
Dipole Minimization

The thermodynamic preference for polar groups bonded to C-1 (the anomeric carbon of a glycopyranosyl derivative) to take up an axial position.

Mutarotation

- When pure alpha- and beta- anomers of sugars are dissolved in a solvent, their measured specific rotations will change over time, until converging on an intermediate value.
- This change in observed specific rotation is called, "**mutarotation**".

Example: D-glucose



α-D-Glucose

"alpha" (α) isomer:

Specific rotation: $[\alpha]_D^{20}$ + 112°

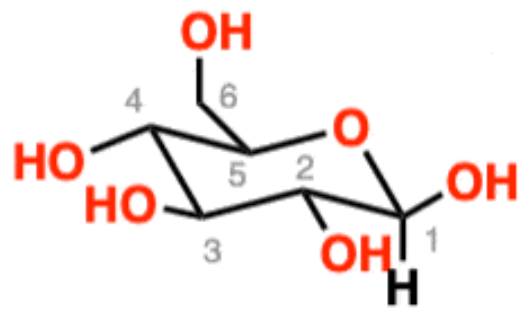
for pure form

dissolve in water →

Specific rotation changes over several hours until reaching a stable value of +52.5

← *dissolve in water*

"beta" (β) isomer:

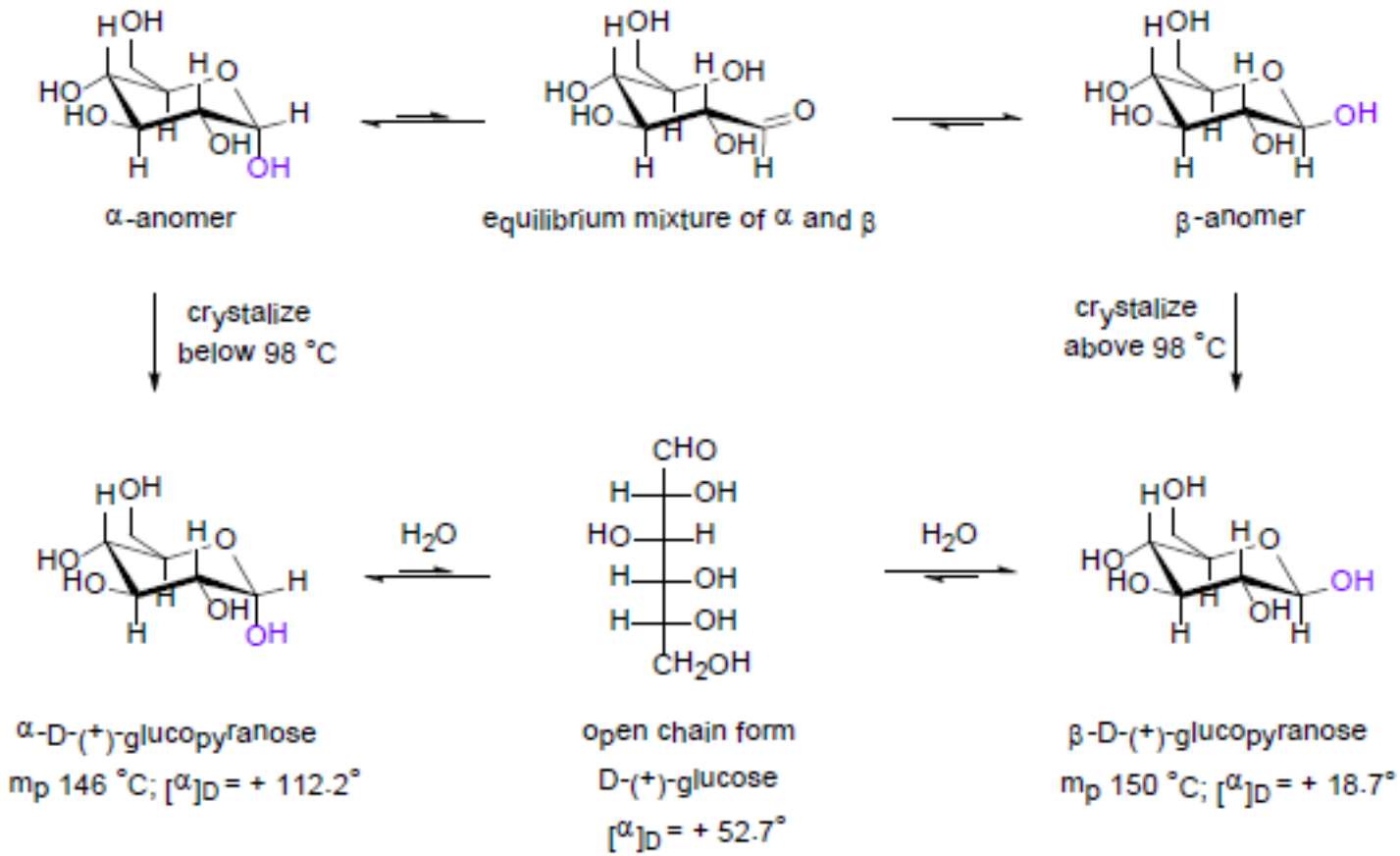


β-D-Glucose

Specific rotation: $[\alpha]_D^{20}$ + 18.7°

for pure form

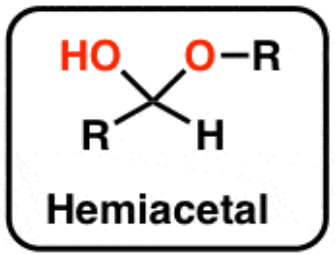
- This intermediate value reflects an **equilibrium mixture** of the alpha- and beta-anomers, which can interconvert through the intermediate **open-chain** form.


α-anomer
equilibrium mixture of α and β
β-anomer
crystalize
below 98 °C
crystalize
above 98 °C
H2O
H2O
α-D-(+)-glucopyranose
mp 146 °C; [α]D = + 112.2°
open chain form
D-(+)-glucose
[α]D = + 52.7°
β-D-(+)-glucopyranose
mp 150 °C; [α]D = + 18.7°

Any sugar* containing a hemiacetal is a reducing sugar.

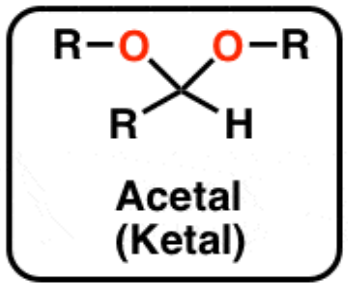
**for our purposes here, "sugar" refers to mono- and di-saccharides, not complex carbohydrates like starch, glycogen, and cellulose*

Recall the difference between hemiacetals and acetals:



Hemiacetal

- one OH group and one O-R group attached to same carbon
- in equilibrium with aldehyde/ketone

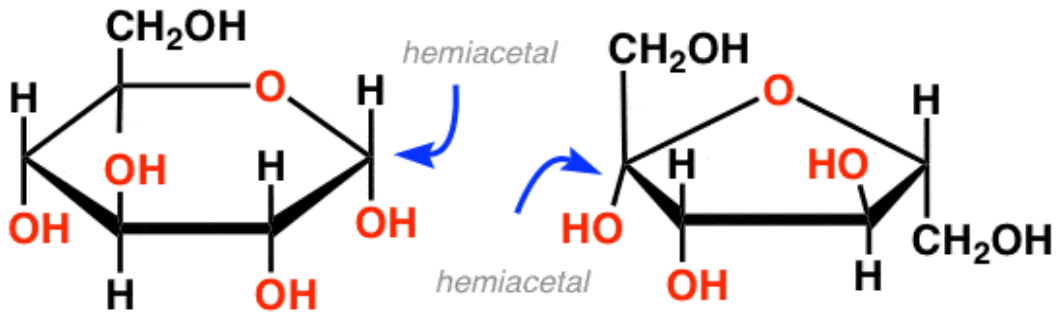


Acetal (Ketal)

- two O-R groups attached to same carbon
- not in equilibrium with aldehyde/ketone ("locked")

Sugars with a hemiacetal are in equilibrium with a ring-opened form containing an aldehyde and will react as a **reducing agent** toward certain (oxidizing) metal salts such as Cu^{2+} (Benedict's test, Fehlings aolution) and Ag^{+} (Tollens test)

Examples:



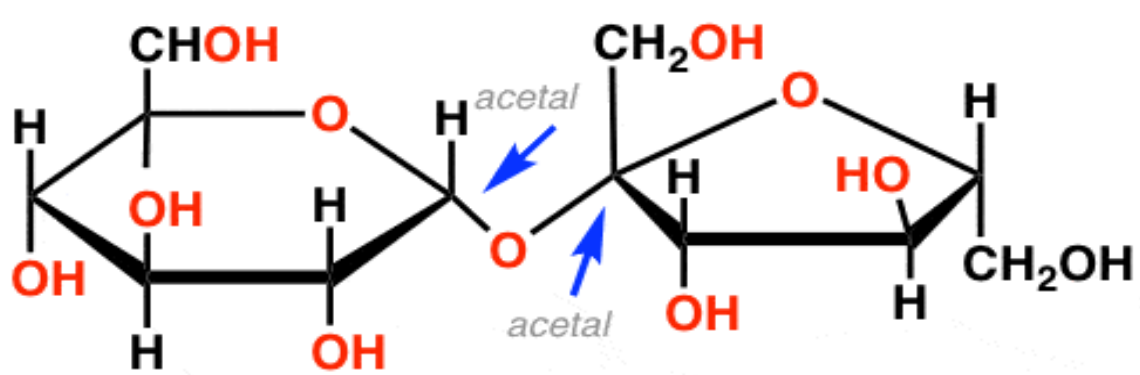
α-D-glucose **D-Fructose**

- Other monosaccharides such as galactose, mannose, ribose...
- Certain disaccharides such as lactose and maltose

A sugar without a hemiacetal is a non-reducing sugar

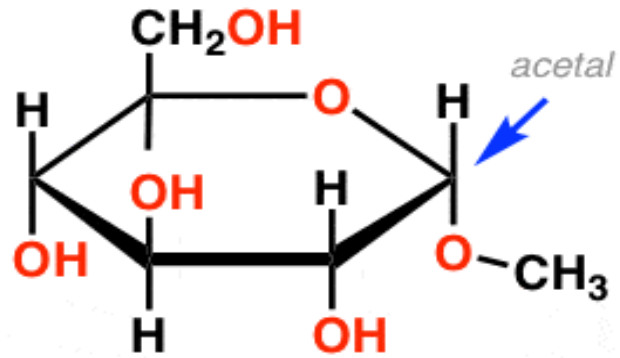
Acetals are "locked" and **not** in equilibrium with a ring-opened form with an aldehyde. They will therefore not react as a reducing agent.

Examples:



Sucrose

(a disaccharide; no hemiacetal present!)



α-D-glucose methyl glucoside

no hemiacetal

Why is this important?

An important test for quantifying blood glucose (Benedict's solution) relies on a reaction where Cu^{2+} is reduced by an aldehyde, resulting in a color change.

The "Tollens Test" For Aldehydes

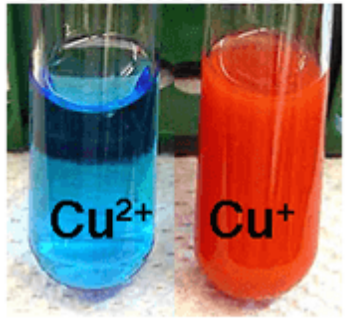
Aldehyde **Carboxylic acid**

This is a redox reaction:

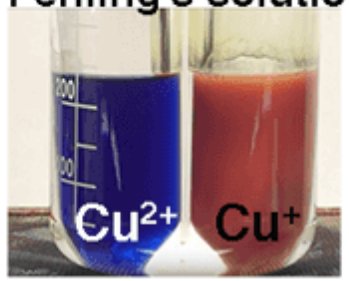
- The aldehyde is oxidized by silver(I) to the carboxylic acid
- Silver(I) is reduced by the aldehyde, forming atomic silver, which forms a mirror on the reaction flask

Three Common Tests for Aldehydes

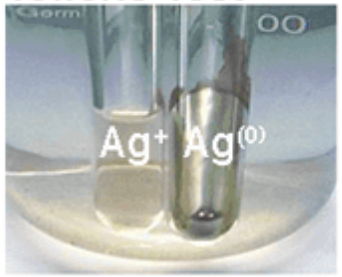
Benedict's test



Fehling's solution



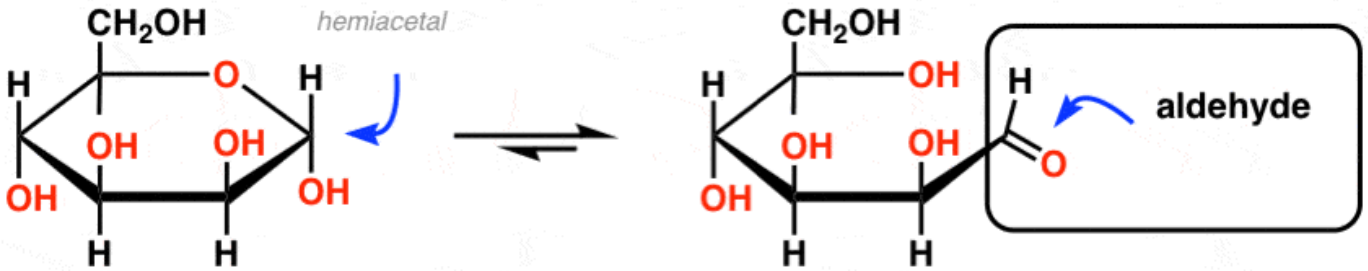
Tollens Test



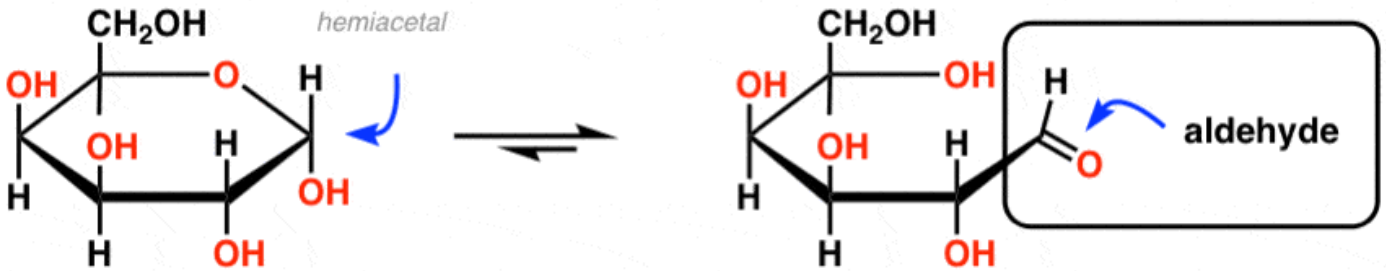
Control (blue)	Positive test (red)	Control (blue)	Positive test (red)	Control (clear)	Positive test (silver mirror)

In each case the aldehyde has been oxidized to a carboxylic acid and the metal salt (Cu^{2+} or Ag^{+}) has been reduced.

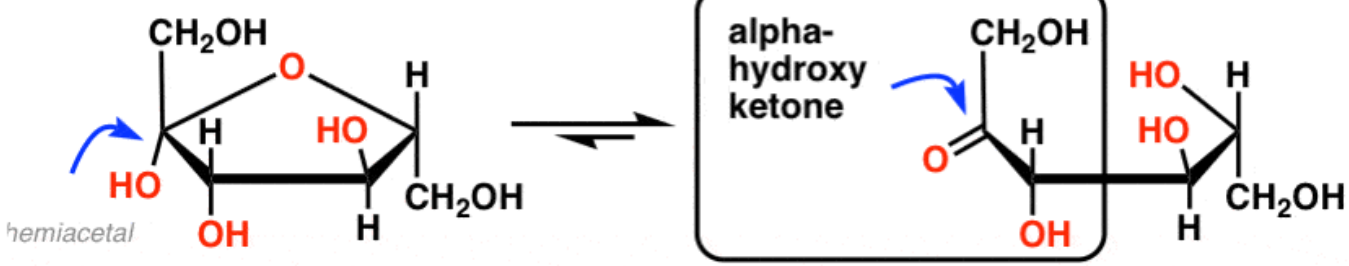
Monosaccharides with a hemiacetal are also "reducing sugars" since their open-chain form contains an aldehyde (or alpha-hydroxy ketone)



D-Mannose D-Mannose (open-chain aldehyde)



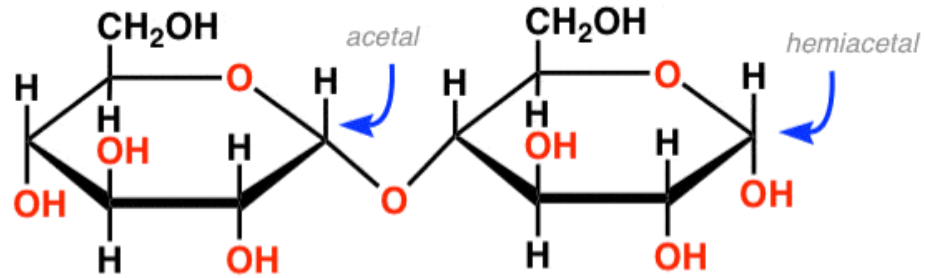
D-Galactose D-Galactose (open-chain aldehyde)



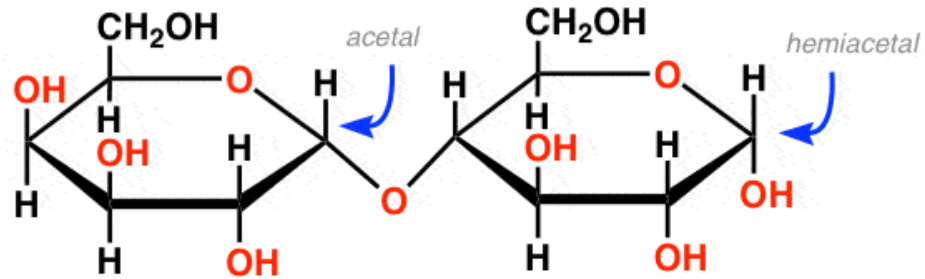
D-Fructose D-Fructose (keto form)

Lactose and Maltose are also reducing sugars and give a positive Benedict test

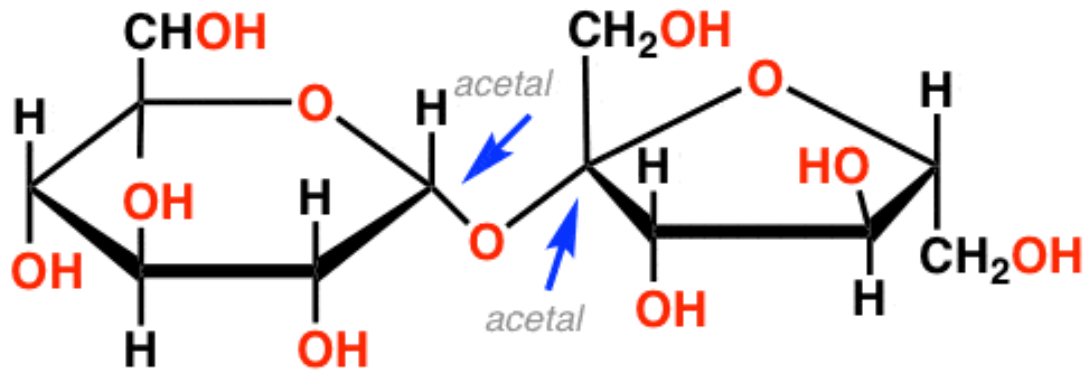
Maltose:



Lactose:

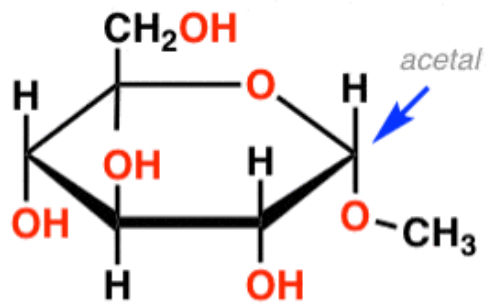


Sucrose is a non-reducing sugar



The structure lacks any hemiacetal functional groups and is therefore "locked" in its cyclic form

Another example of a non-reducing sugar: a "glucoside" of glucose

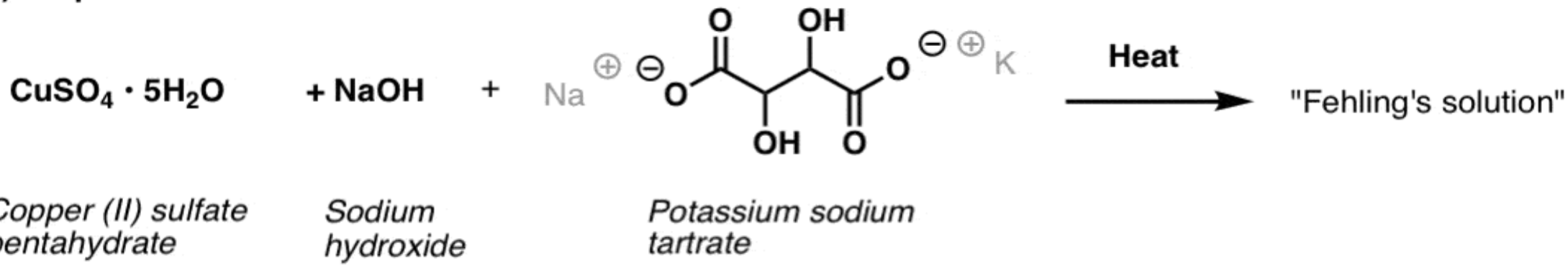


α-D-glucose methyl glucoside

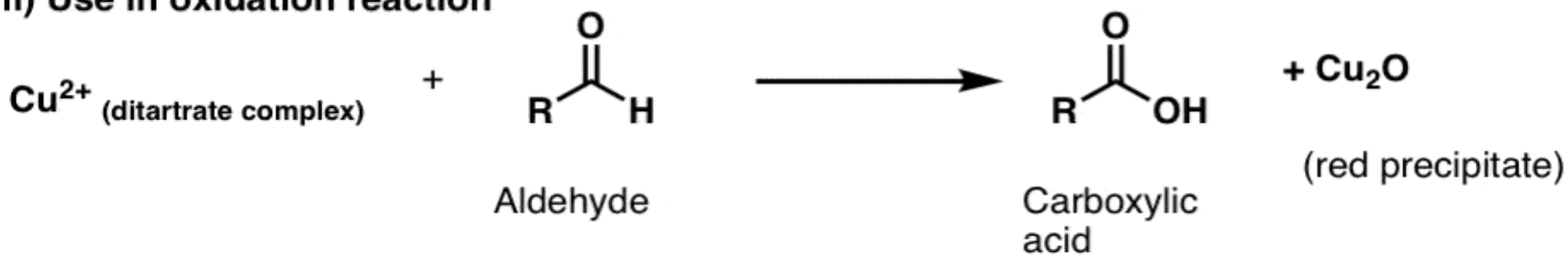
no hemiacetal

Fehling's solution

i) Preparation of the solution:



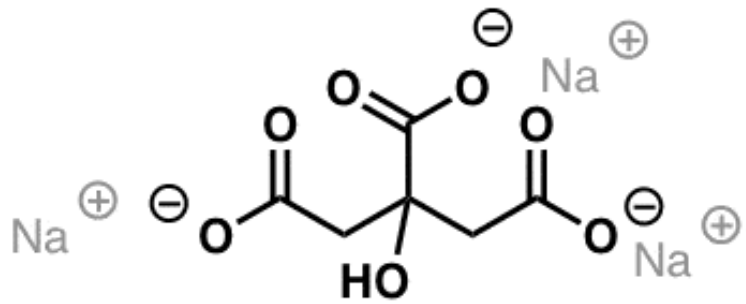
ii) Use in oxidation reaction



Benedict's Solution

(longer shelf-life than Fehling's solution)

i) Preparation of the solution:

$CuSO_4 \cdot 5H_2O$ + Na_2CO_3 + 

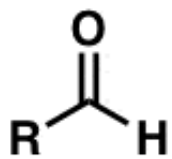
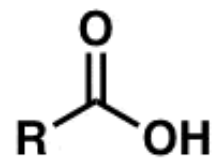
Copper sulfate

Sodium carbonate

Sodium citrate

Note: for the quantitative test, potassium thiocyanate is also added

ii) Use in oxidation reaction

Cu^{2+} **(citrate complex)** +  →  + Cu_2O

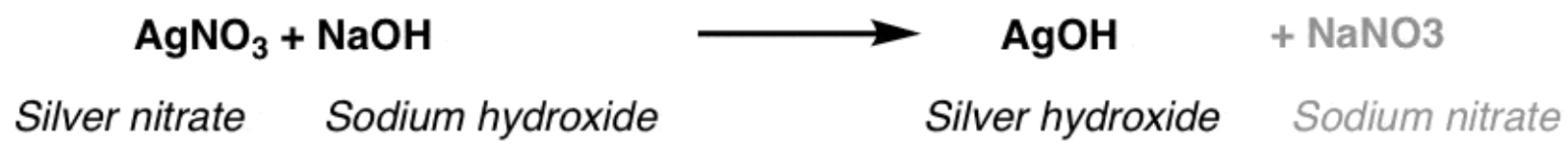
Aldehyde

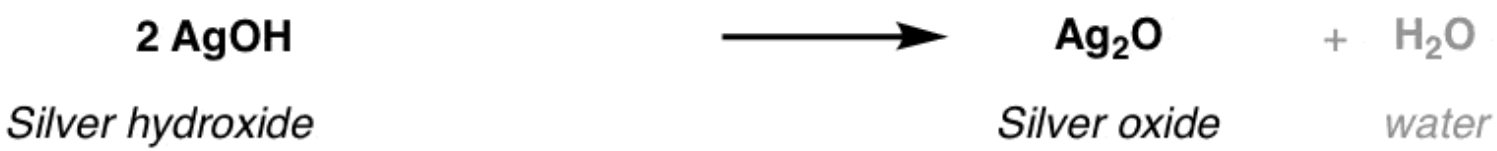
Carboxylic acid

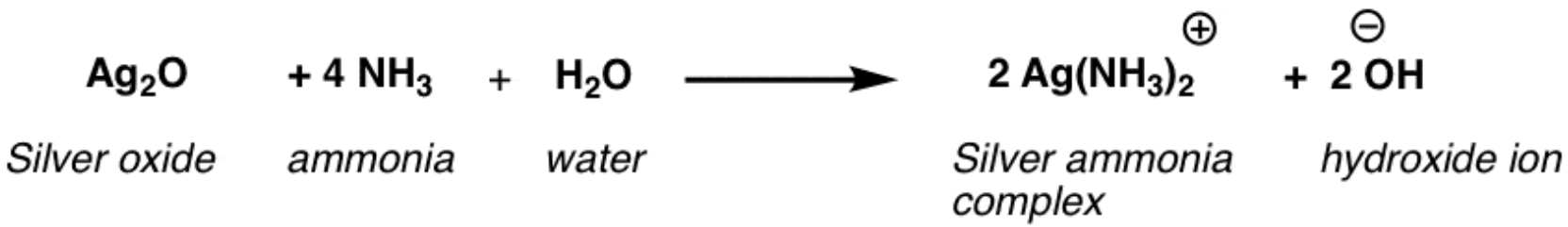
(red precipitate)

Tollens Test

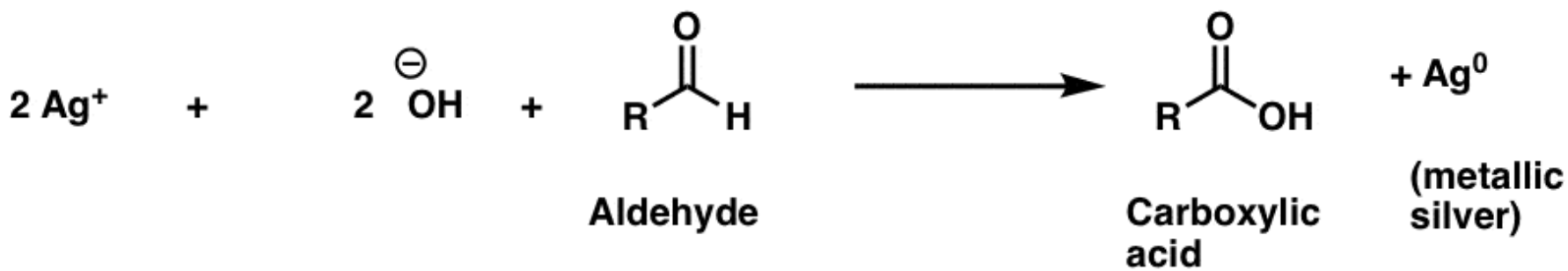
i) Preparation of the solution:







ii) Use in oxidation reaction



Physical properties of Monosaccharides

- Colorless

- Sweet Tasting

- Crystalline solids

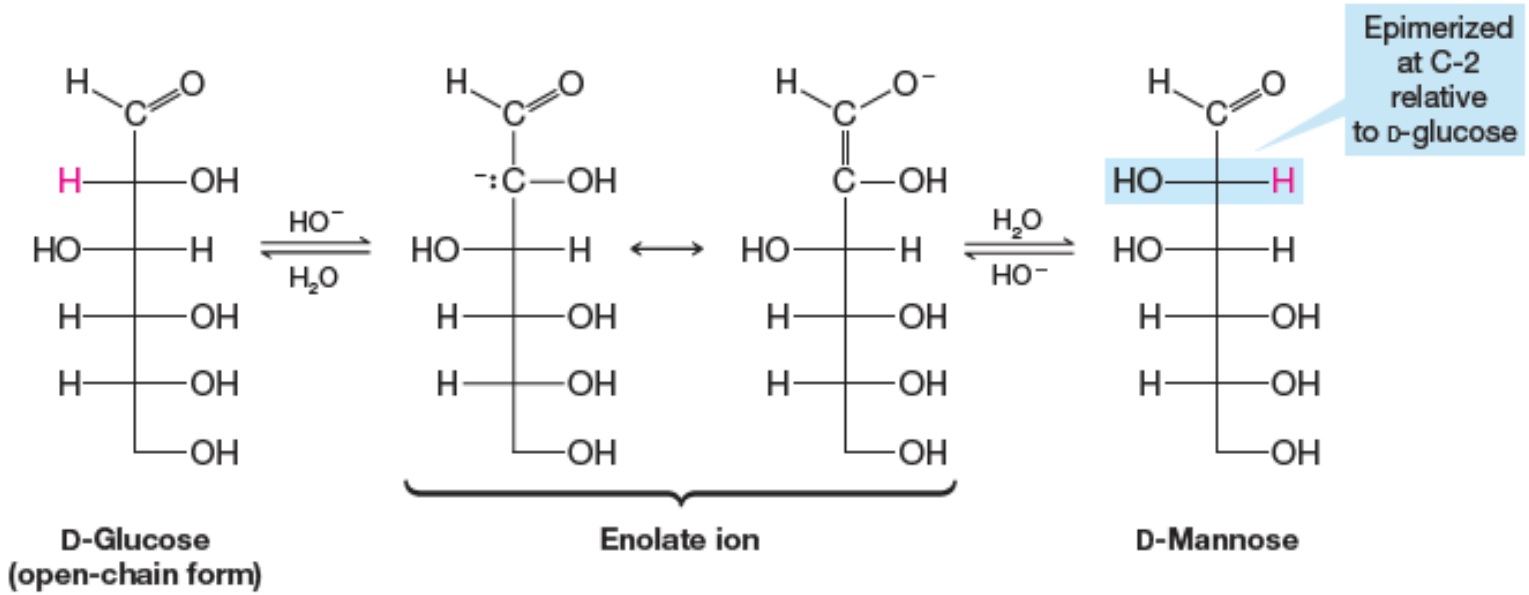
- Polar with high melting points (because of OH groups)

- Soluble in water and insoluble in nonpolar solvents
  (H-bond because of OH groups)

Chemical properties of Monosaccharides

1. Formation of Glycosides (Acetals)
2. Oxidation
3. Reduction

Lobry de Bruyn–Alberda van Ekenstein transformation



Aldose-ketose transformation

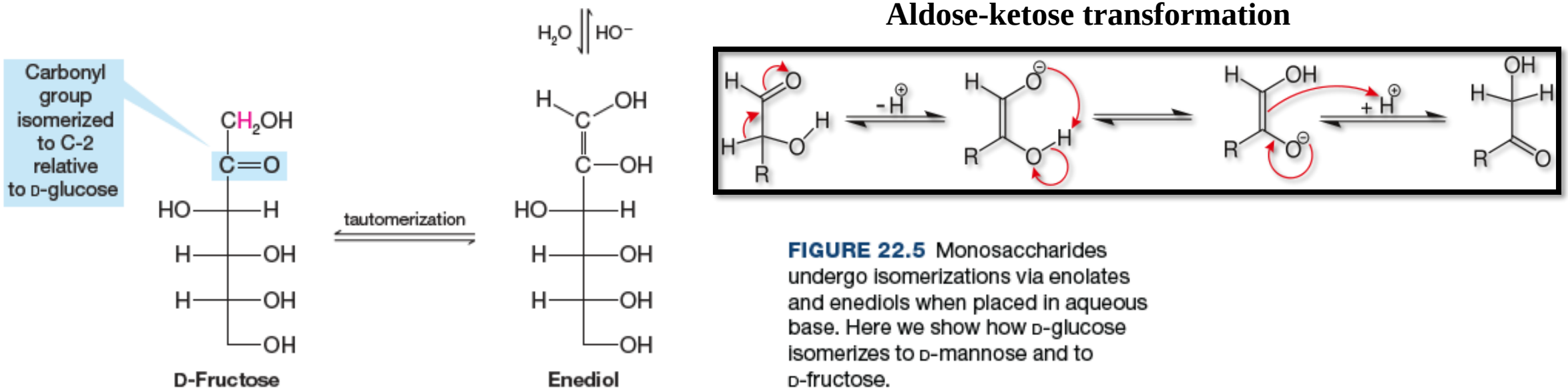
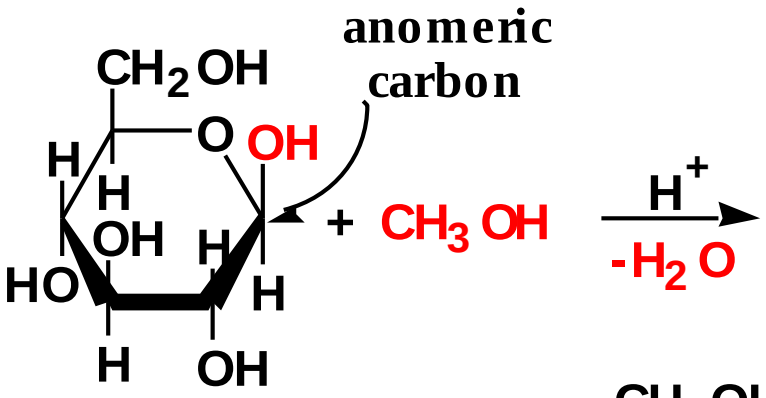


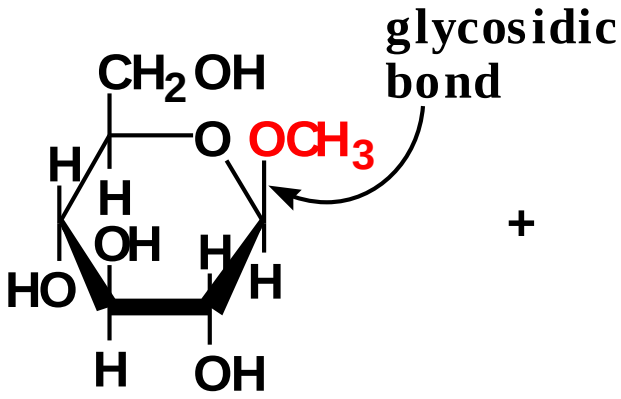
FIGURE 22.5 Monosaccharides undergo isomerizations via enolates and enediols when placed in aqueous base. Here we show how D-glucose isomerizes to D-mannose and to D-fructose.

Formation of Glycosides (Acetals)

- Exist almost exclusively in cyclic hemiacetal forms.
- They react with an alcohol to give acetals.
- Acetals are stable in water and bases but they are hydrolyzed in acids.

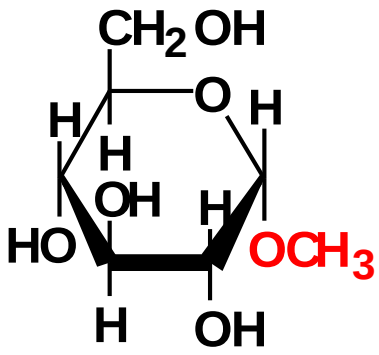


β-D-Glucose

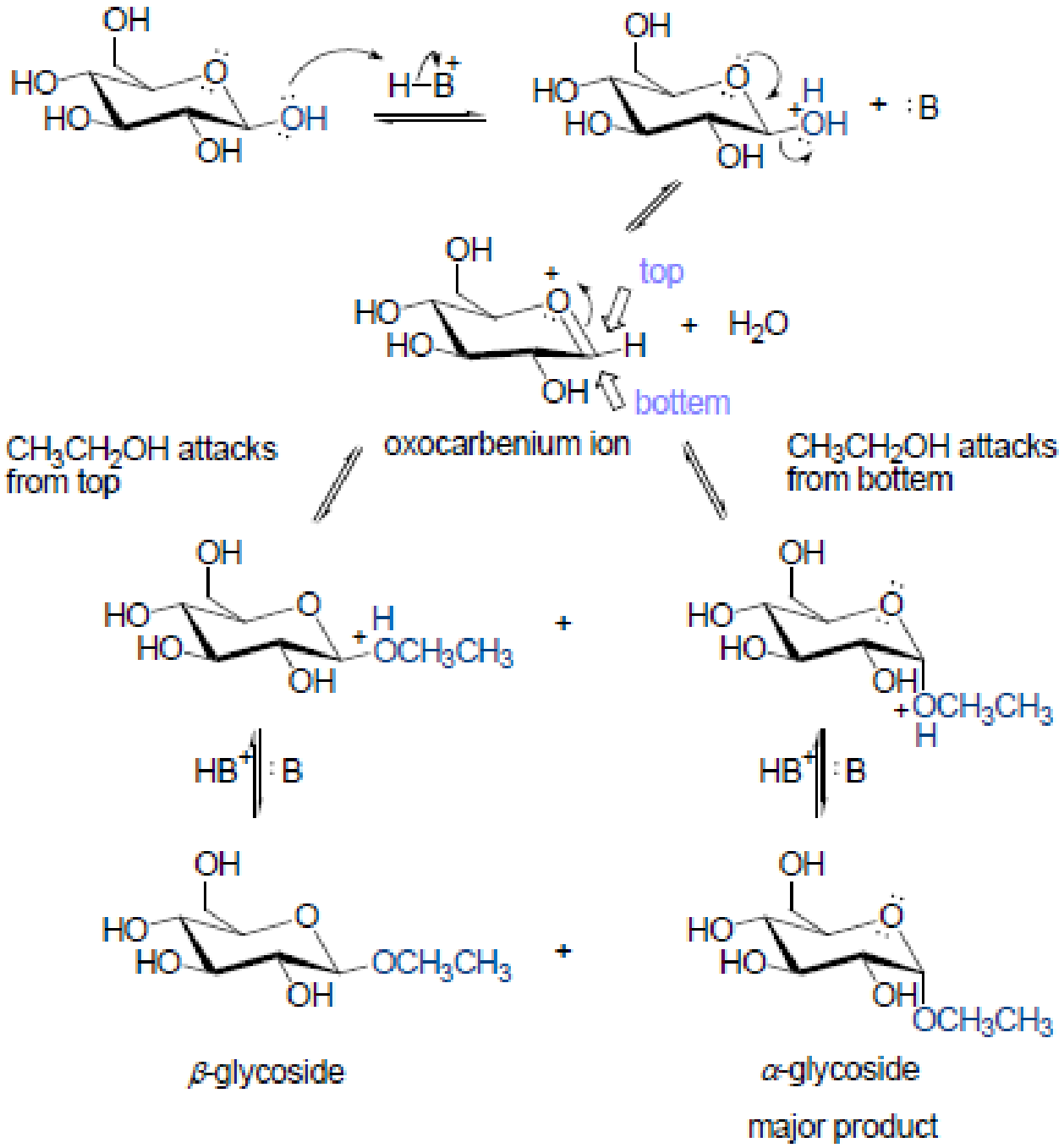


Methyl β-D-Glucoside

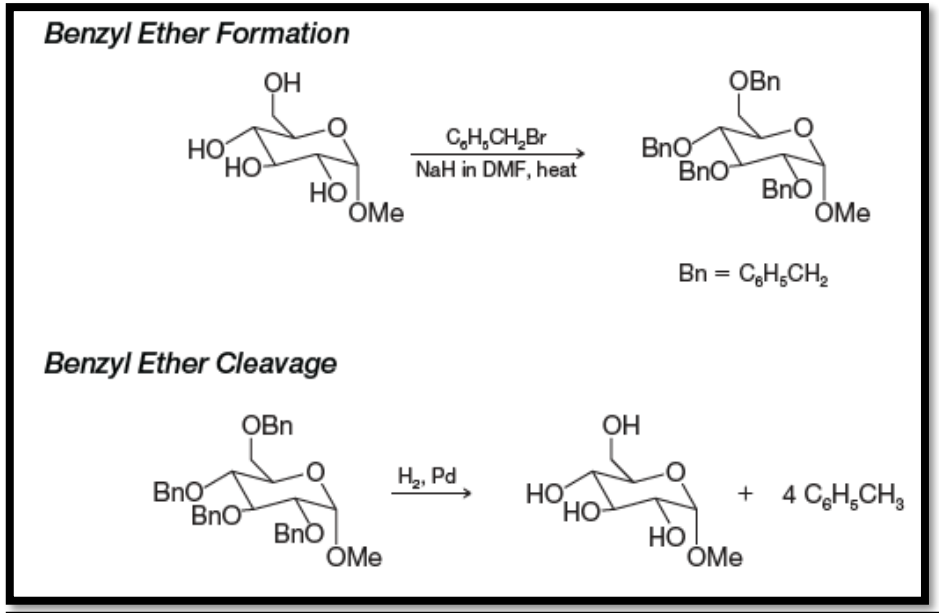
+

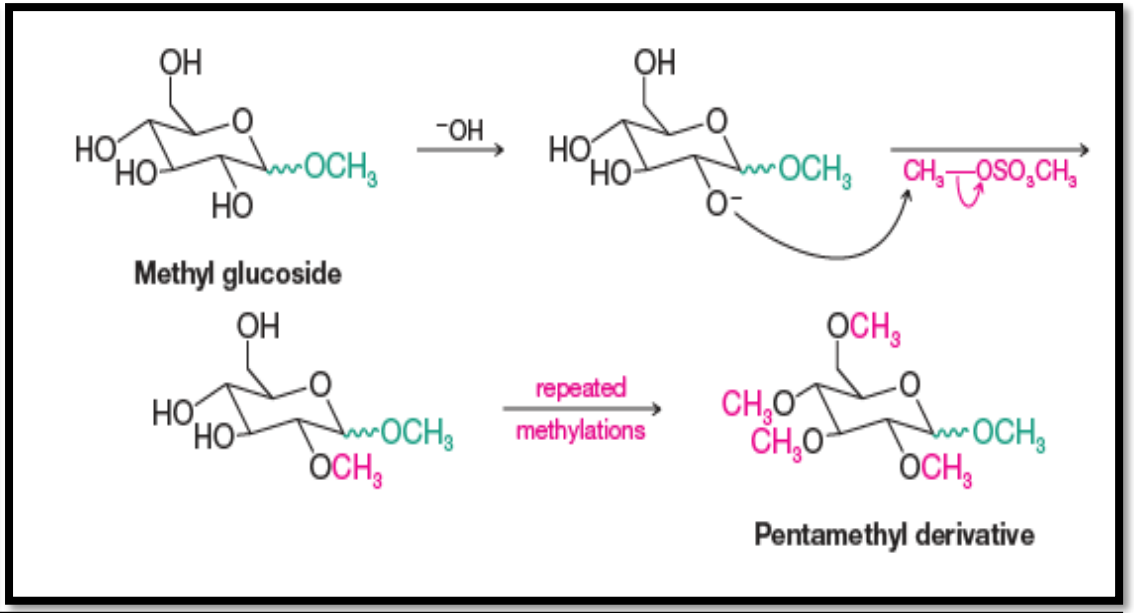


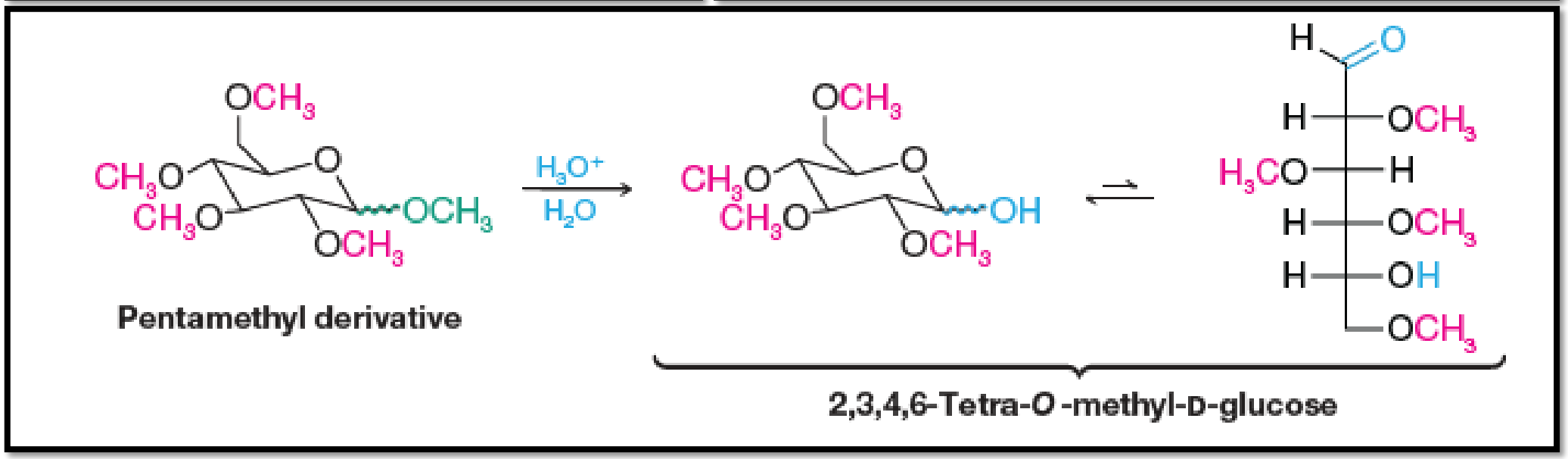
Methyl α-D-Glucoside

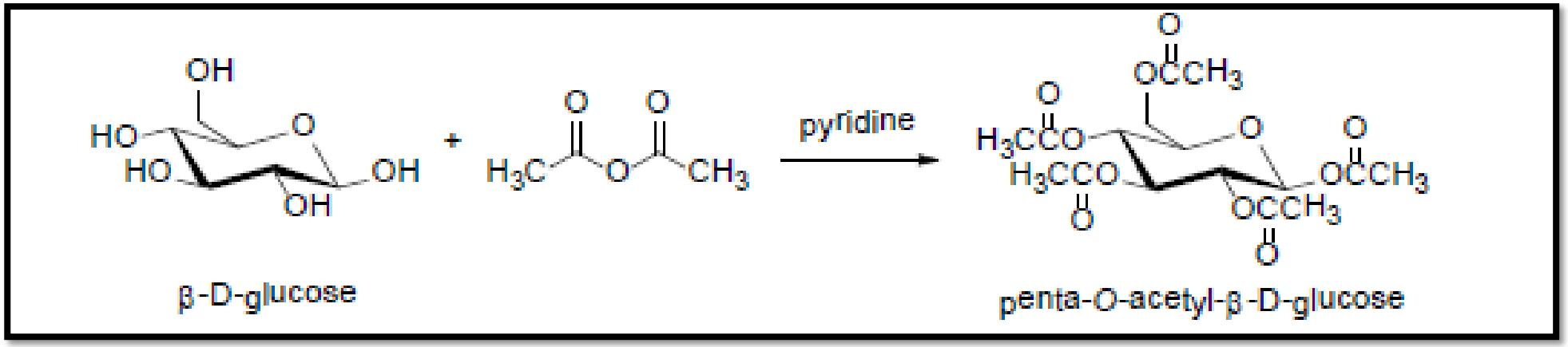

top
bottem
oxocarbenium ion
CH_3CH_2OH attacks from top
CH_3CH_2OH attacks from bottem
β-glycoside
α-glycoside
major product

Protecting Groups in Carbohydrate Synthesis

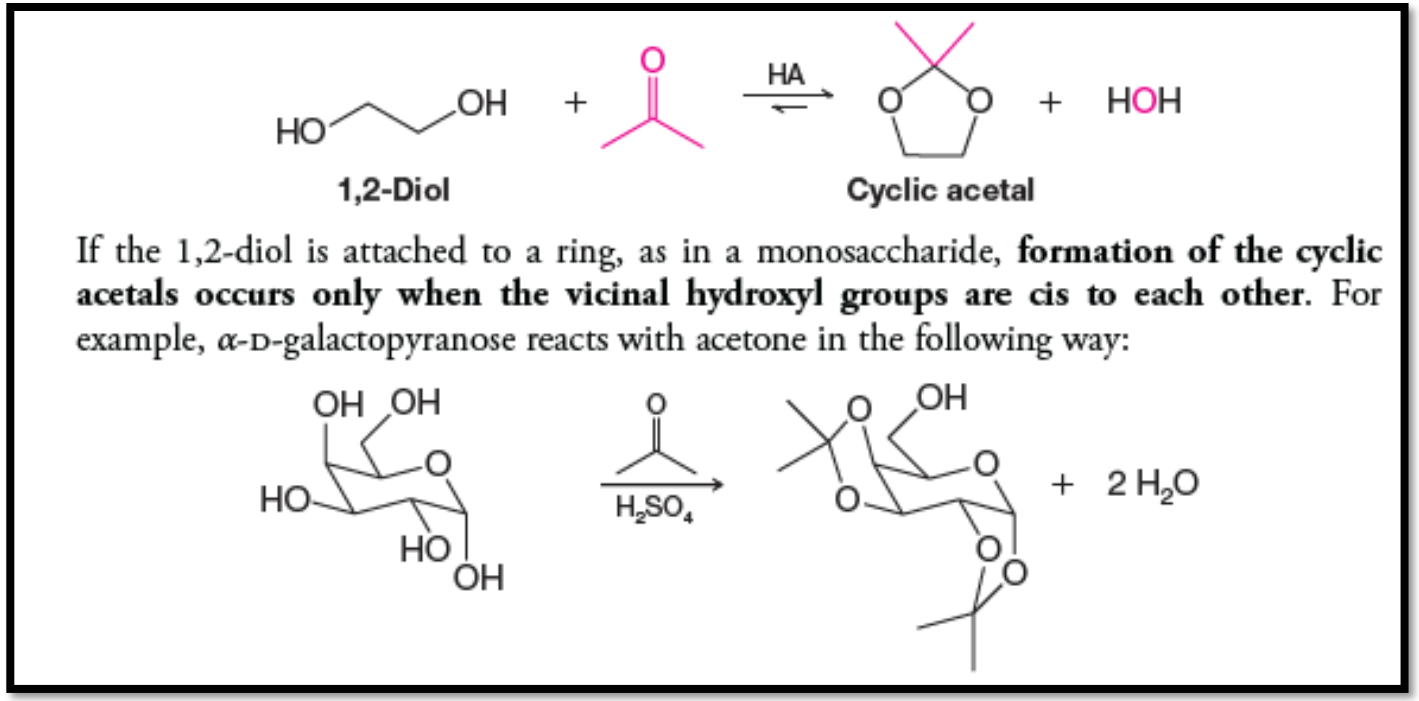






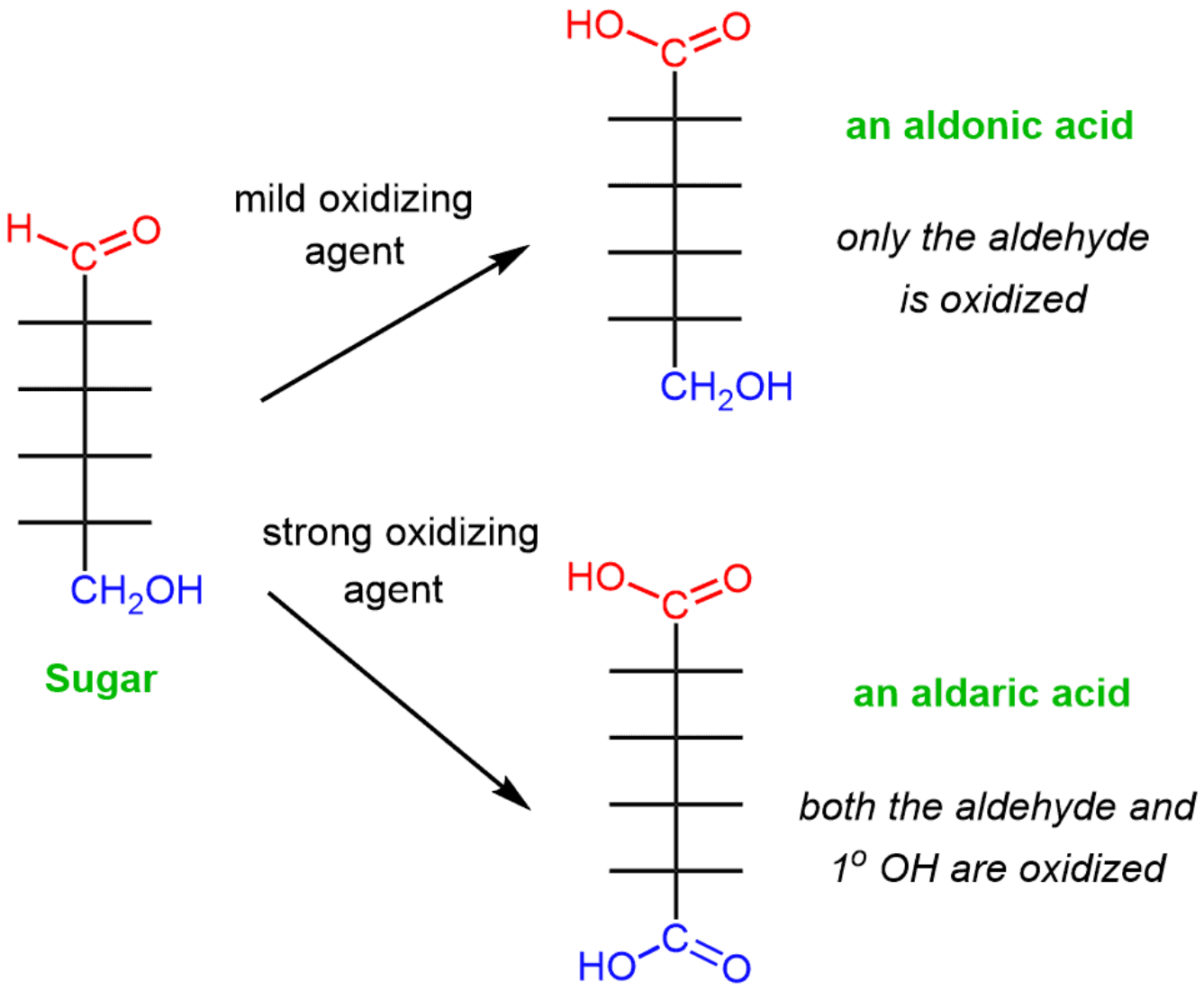


Acylation of Monosaccharides



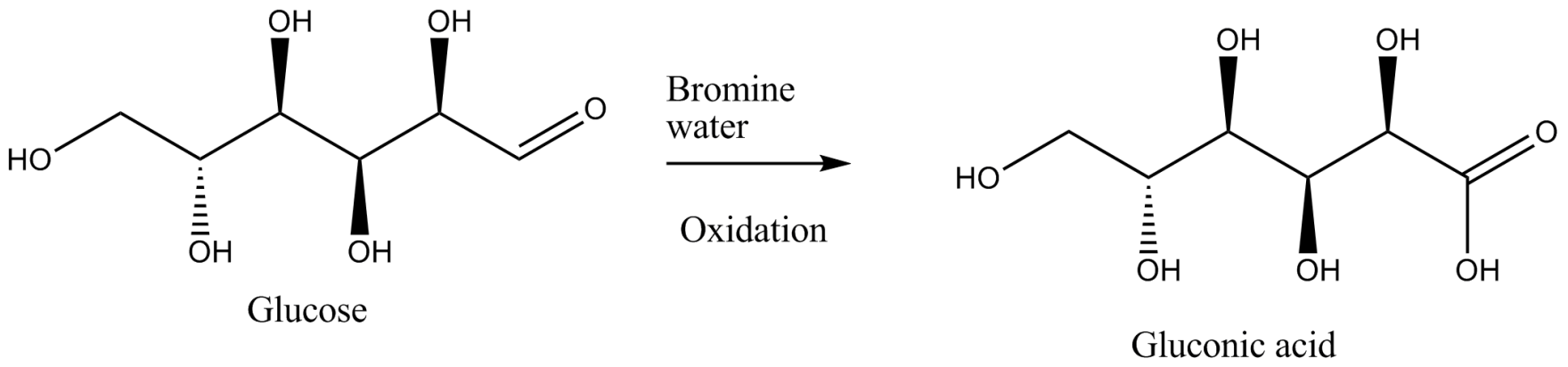
Conversion to Cyclic Acetals

Oxidation of Monosaccharides

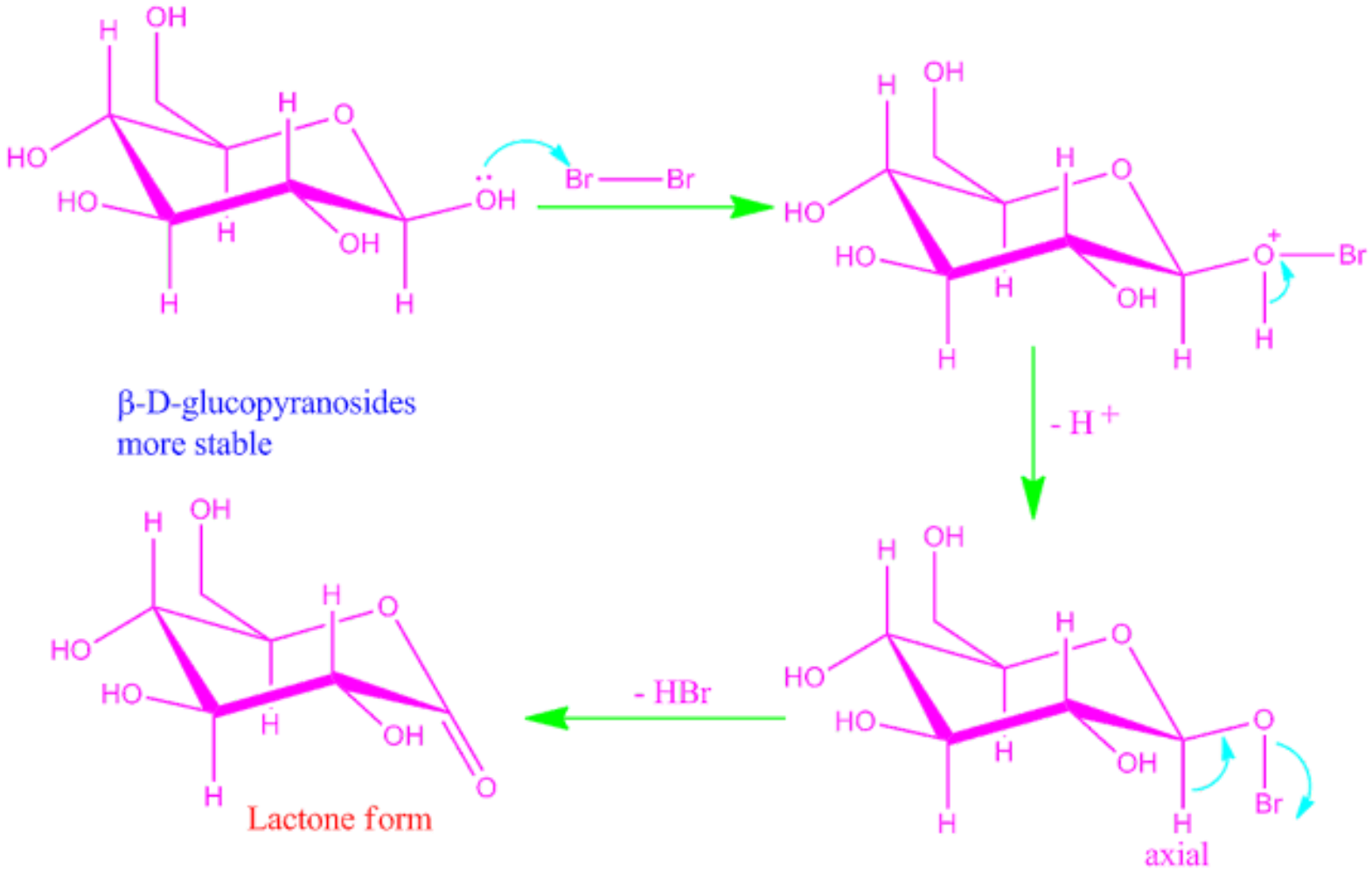


Oxidation of Monosaccharides

Bromine Water Oxidation: Mild Oxidising Agent

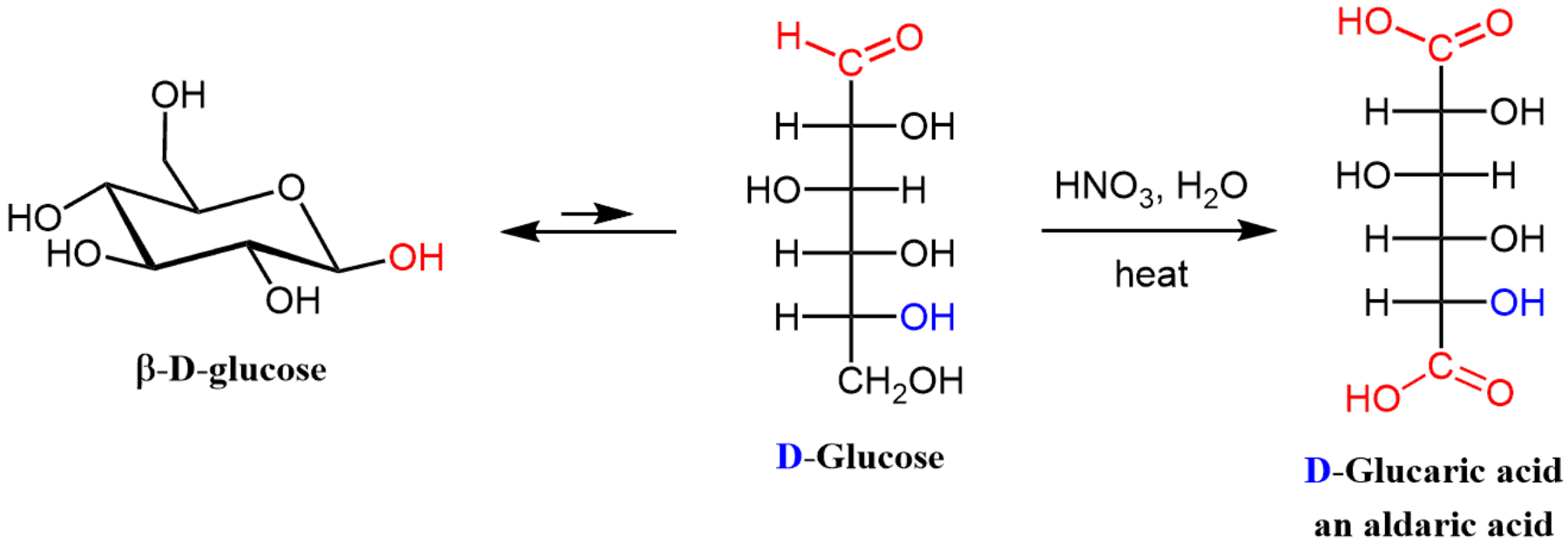


Bromine Water Oxidation: Mechanism

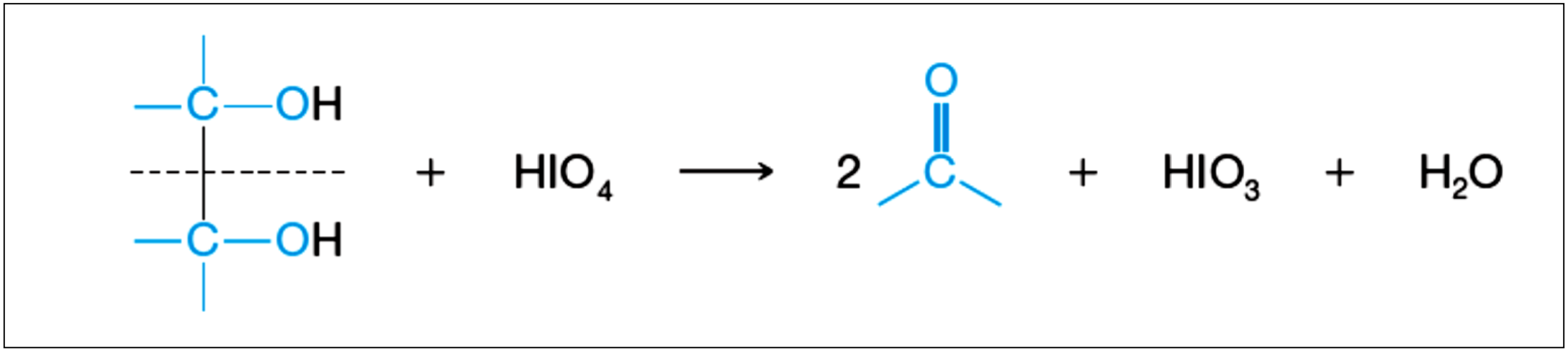


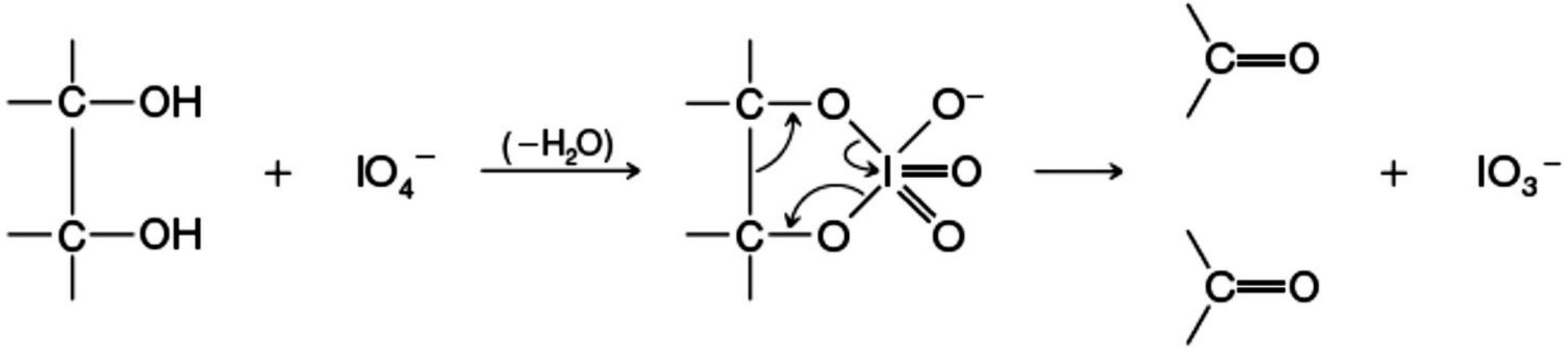
Nitric Acid Oxidation: Strong Oxidising Agent

Cyclic hemiacetals are always in equilibrium with the open chain form and can also be oxidized

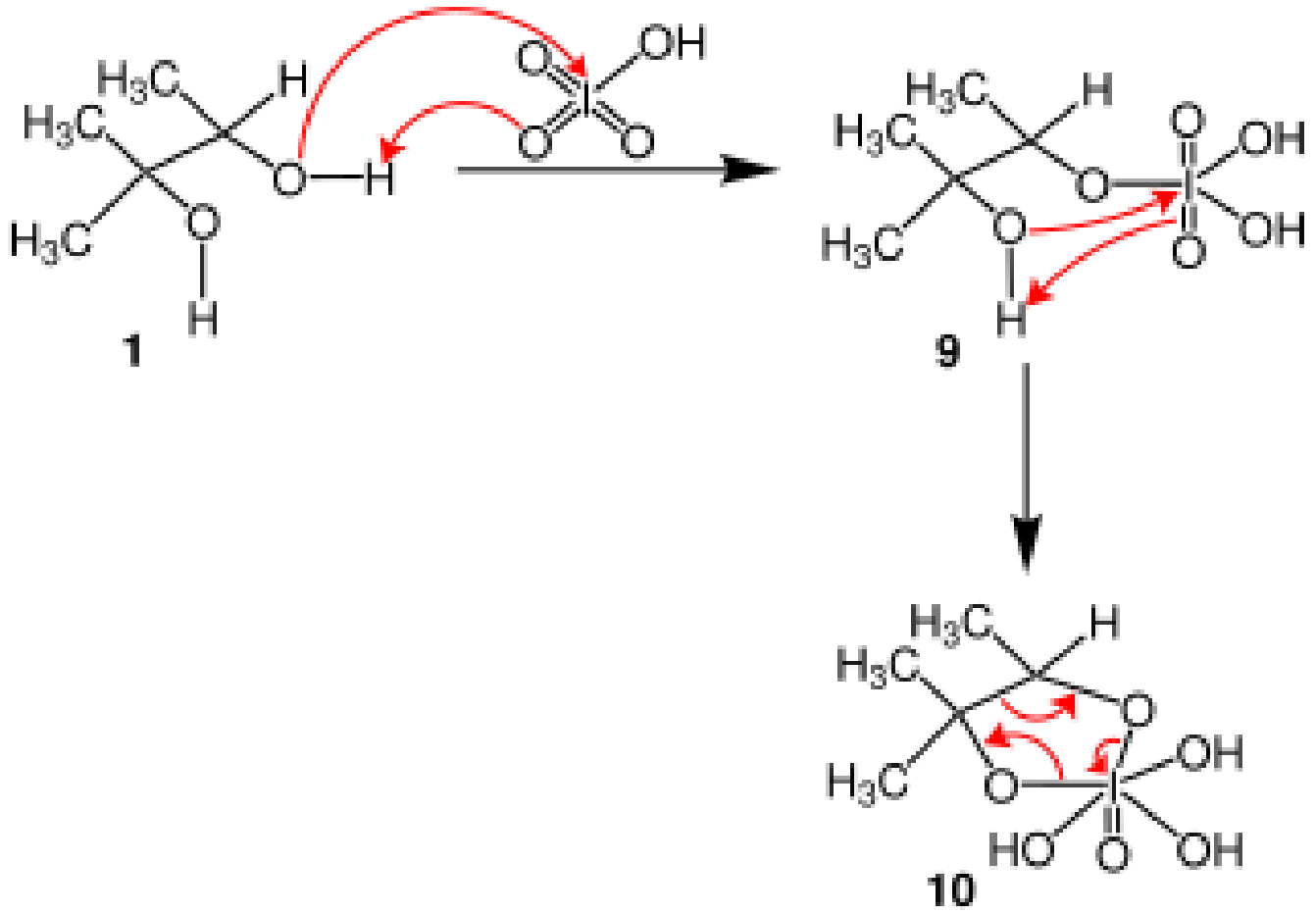


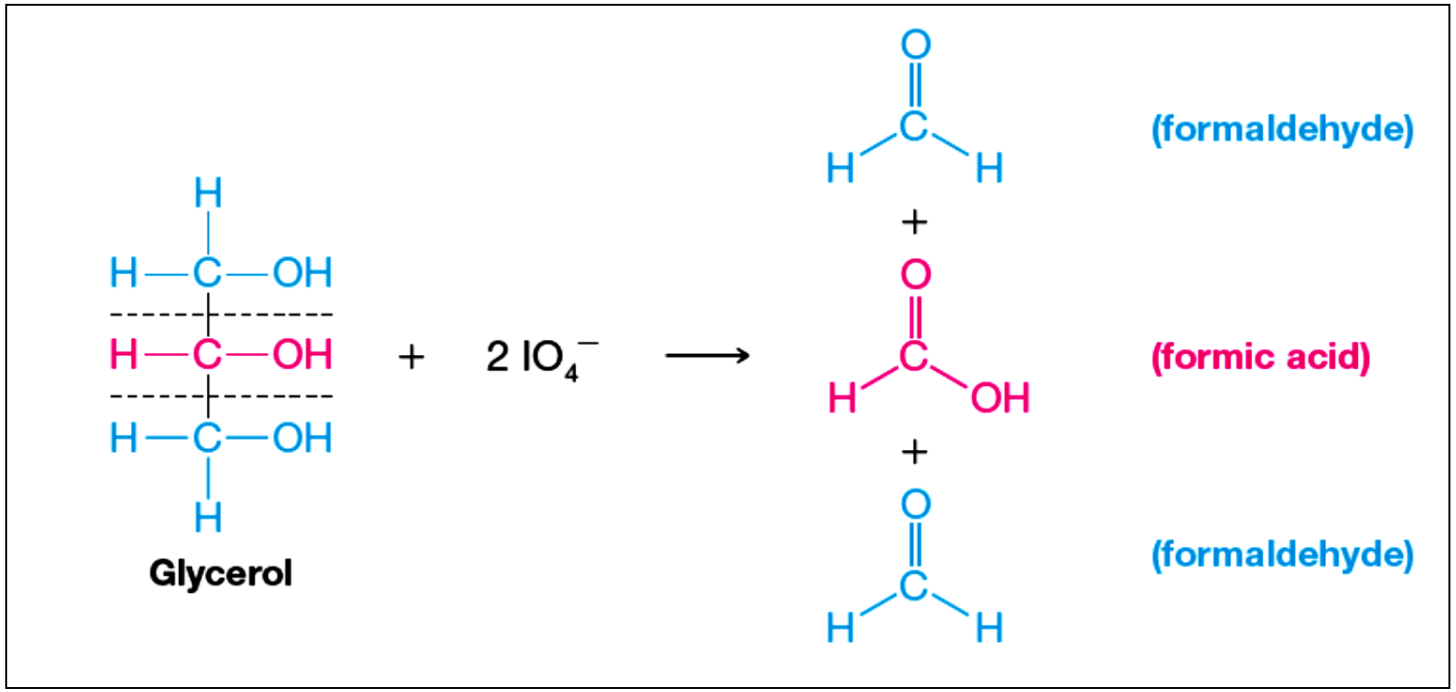
Periodic Acid oxidation: Oxidative cleavage of polyhydroxy compounds (Malaprade reaction)

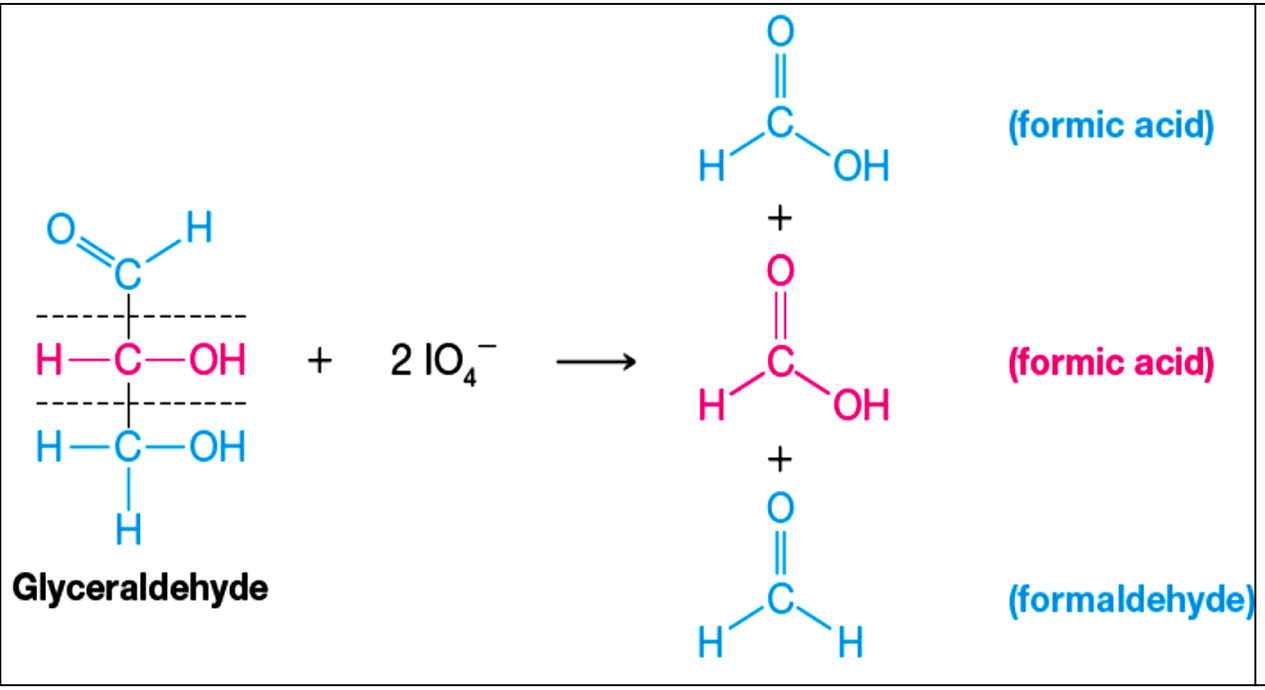


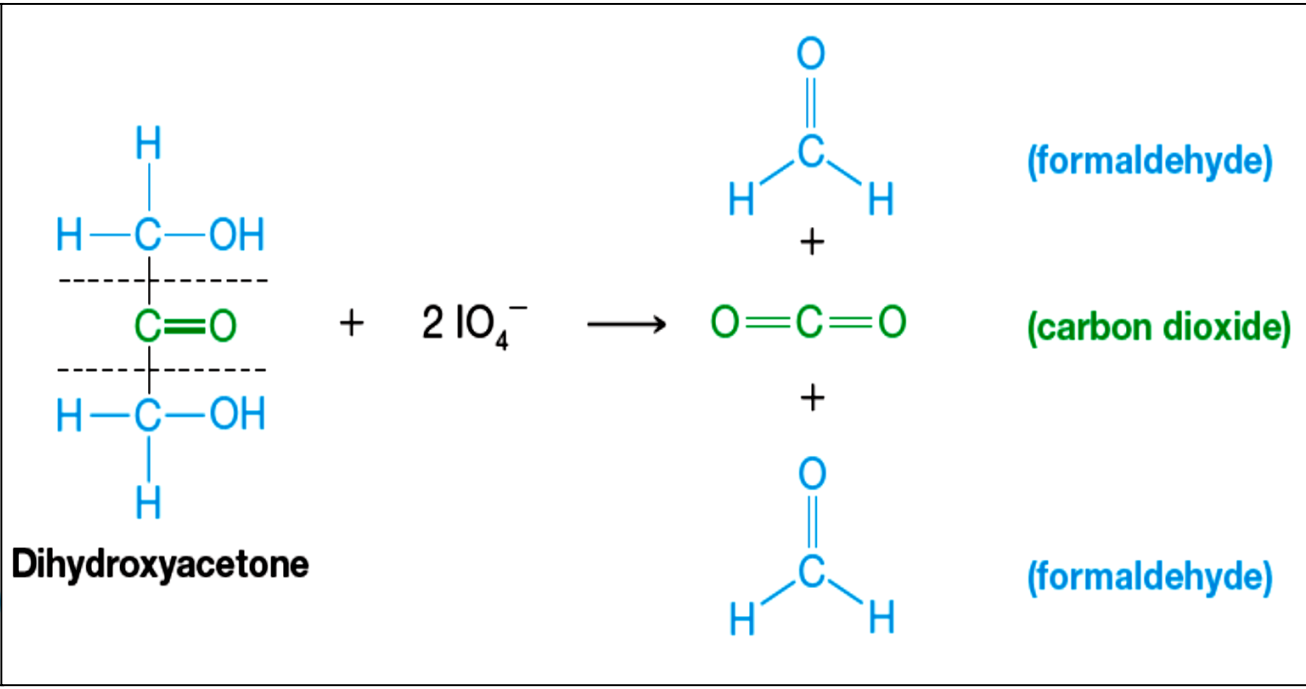


Mechanism:

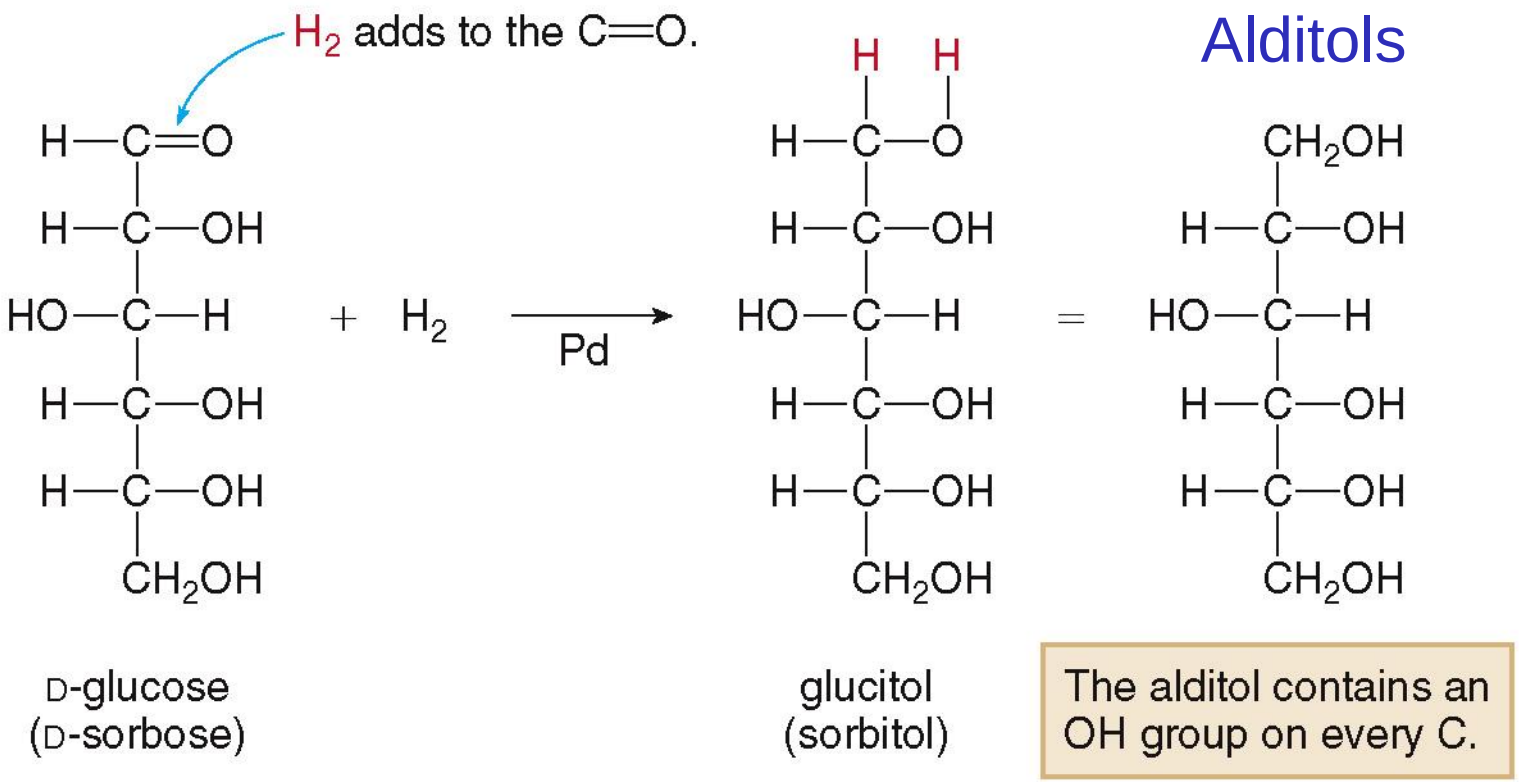



Glycerol
+ 2 IO4−
(formaldehyde)
+
(formic acid)
+
(formaldehyde)


Glyceraldehyde
+ 2 IO4−
(formic acid)
+
(formic acid)
+
(formaldehyde)


Dihydroxyacetone
+ 2 IO4−
(formaldehyde)
+
(carbon dioxide)
+
(formaldehyde)

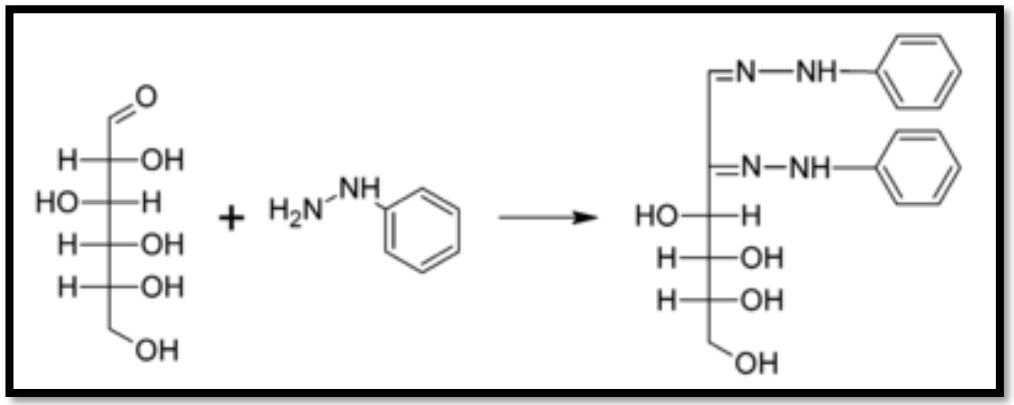
Reduction of Monosaccharides

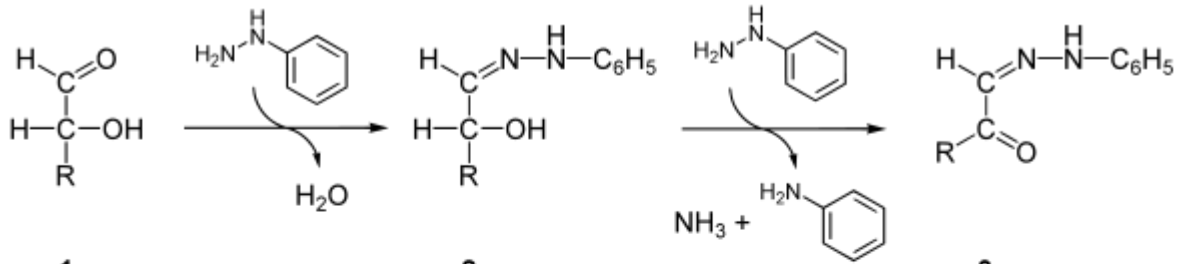


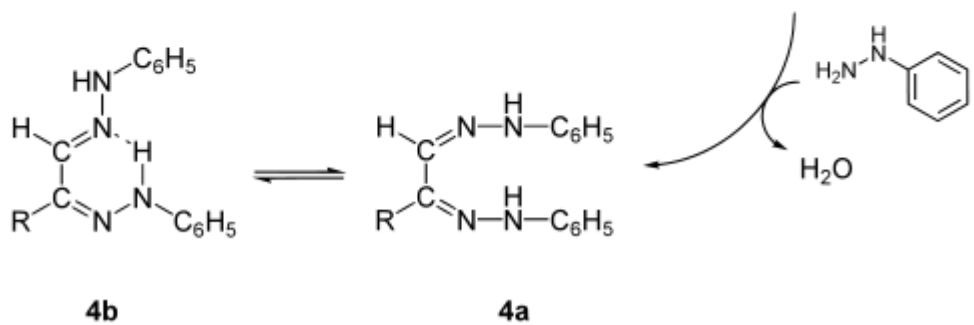
Sugars alcohols: sweetners in many sugar-free (diet drinks & sugarless gum).

Problem: diarrhea and cataract

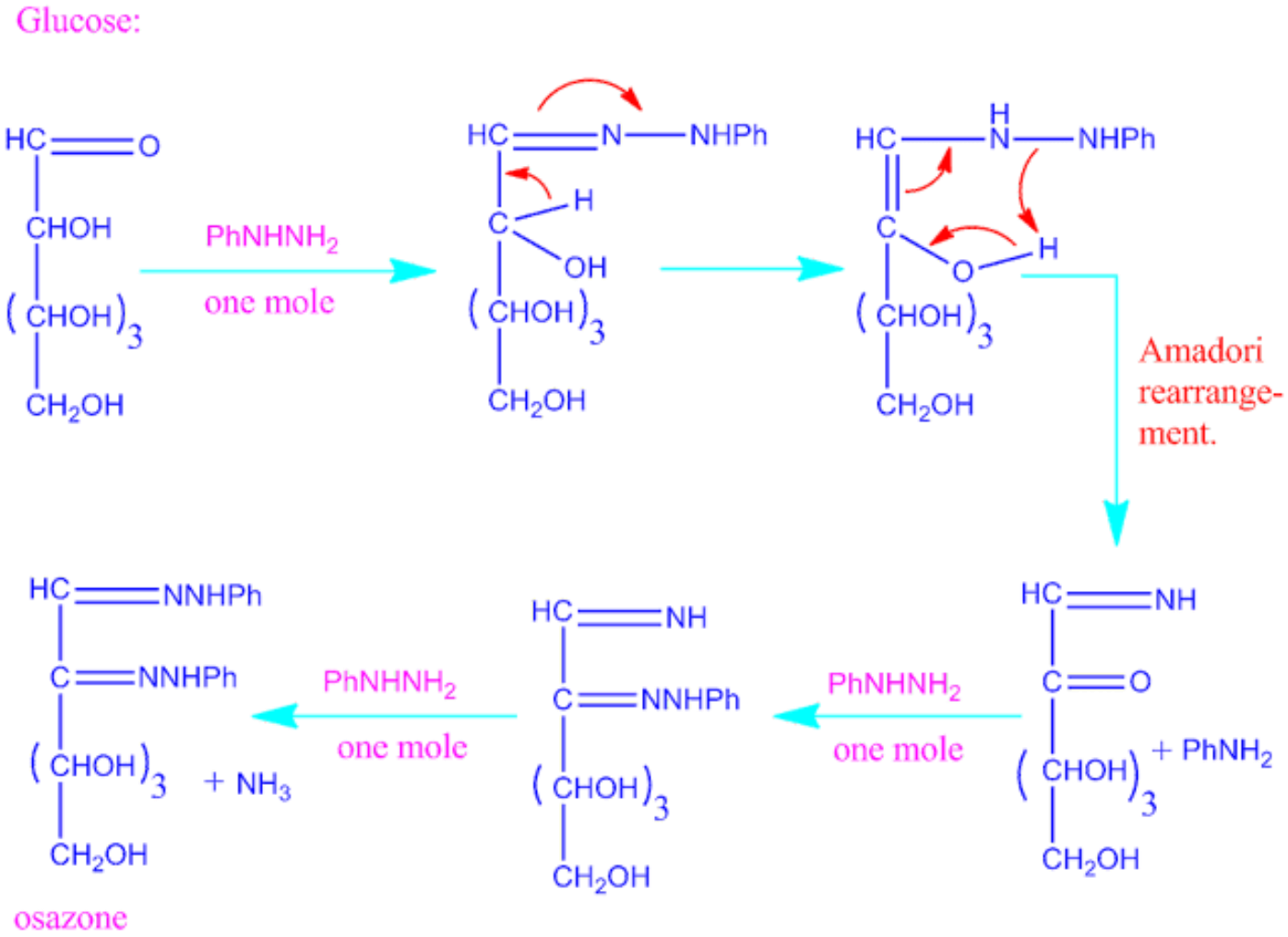
Reaction of Monosaccharides : Osazone Synthesis



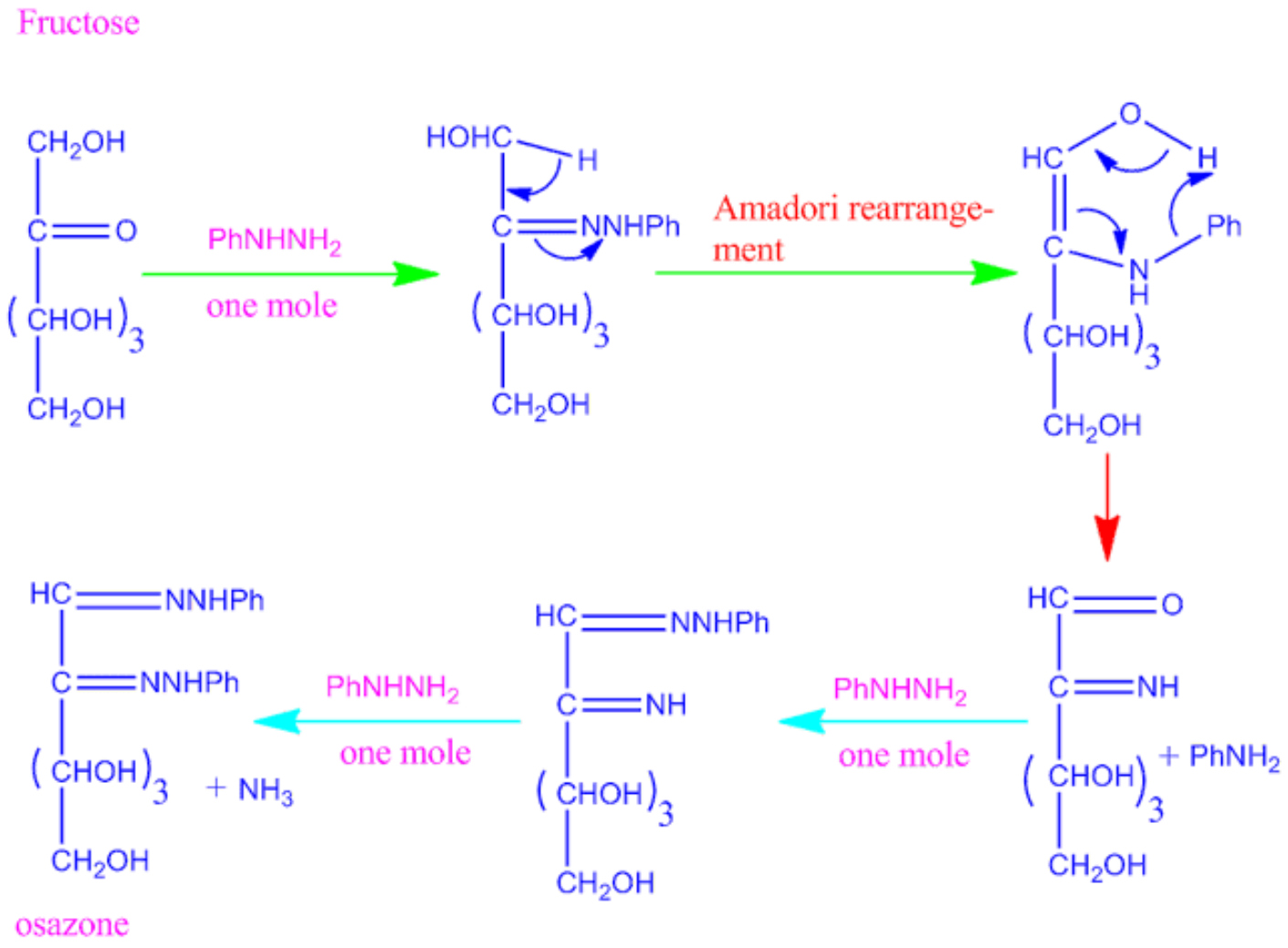




Amadori Rearrangement

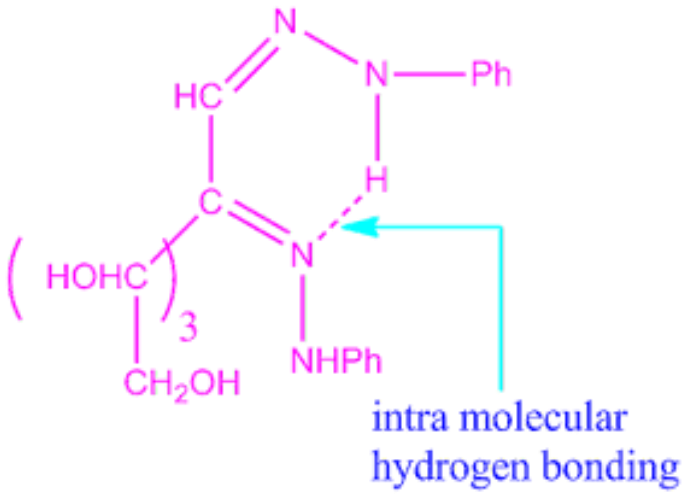


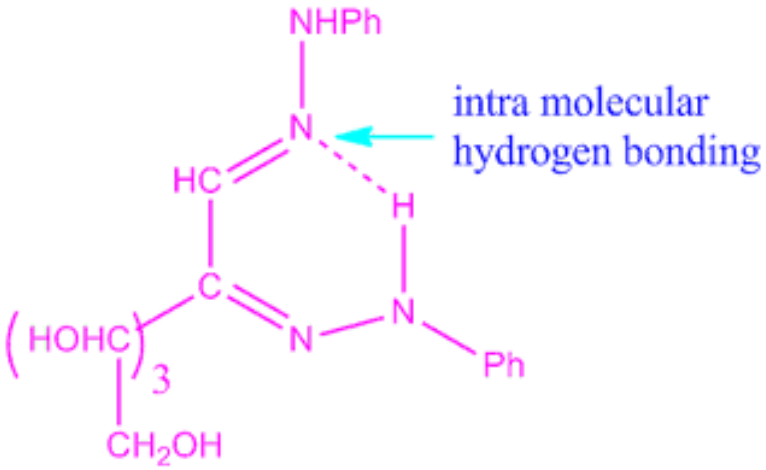
Osazone synthesis: Fructose



Osazone formation of monosaccharides involves only C1 and C2. **Amadori rearrangement** does not occur beyond C2 .

This is due to the fact that the osazone so formed is stabilized through intra molecular hydrogen bonding and forms stable 6-membered cyclic ring. Two hydrogen bonded structures are possible which are shown below.

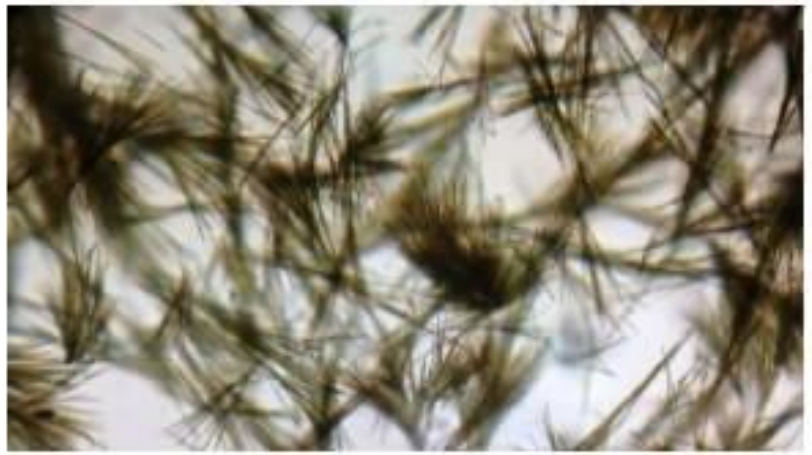




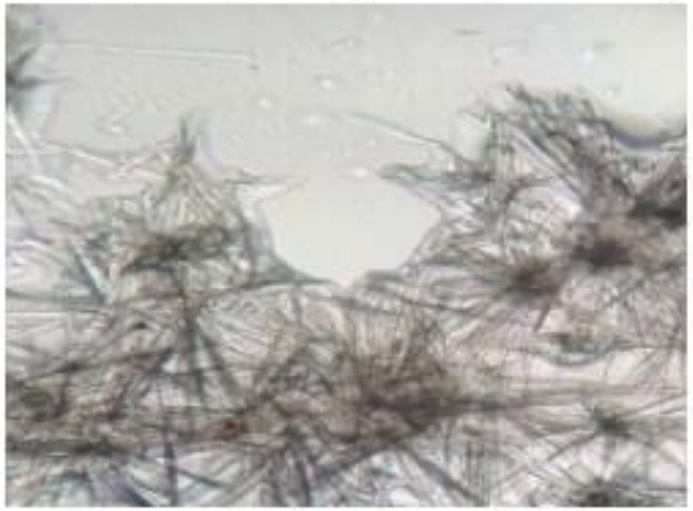
Crystals of different osazone

Needle shaped crystals (Glucose)

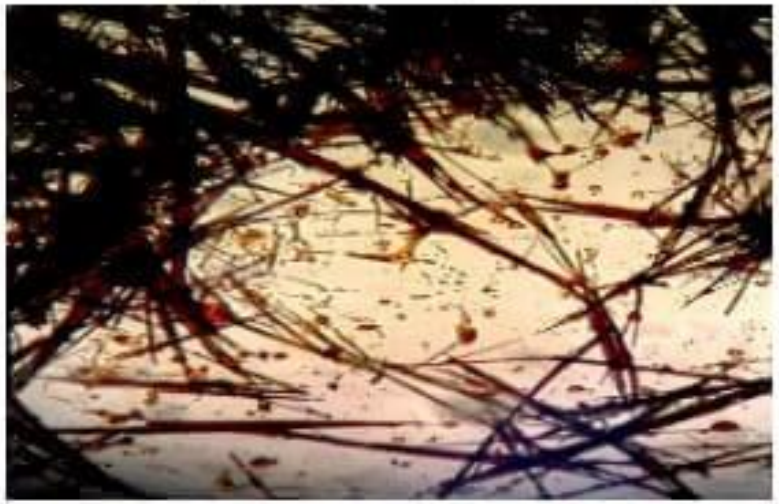
Needle shaped crystals (Fructose)



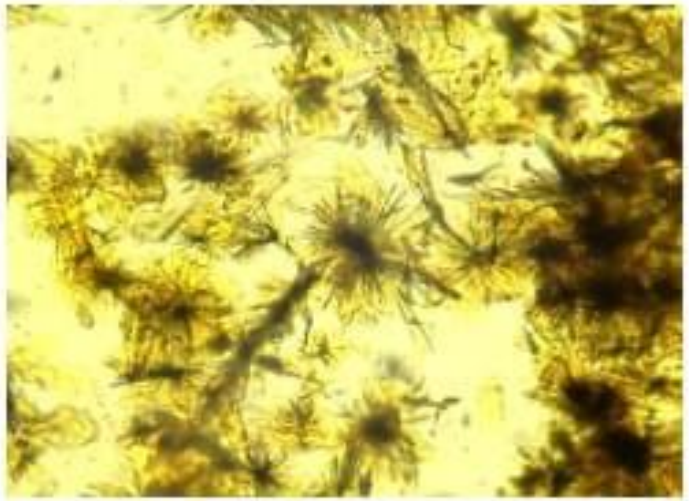
Needle shaped crystals (Mannose)



Balls with thorny edge shaped crystals (Galactose)

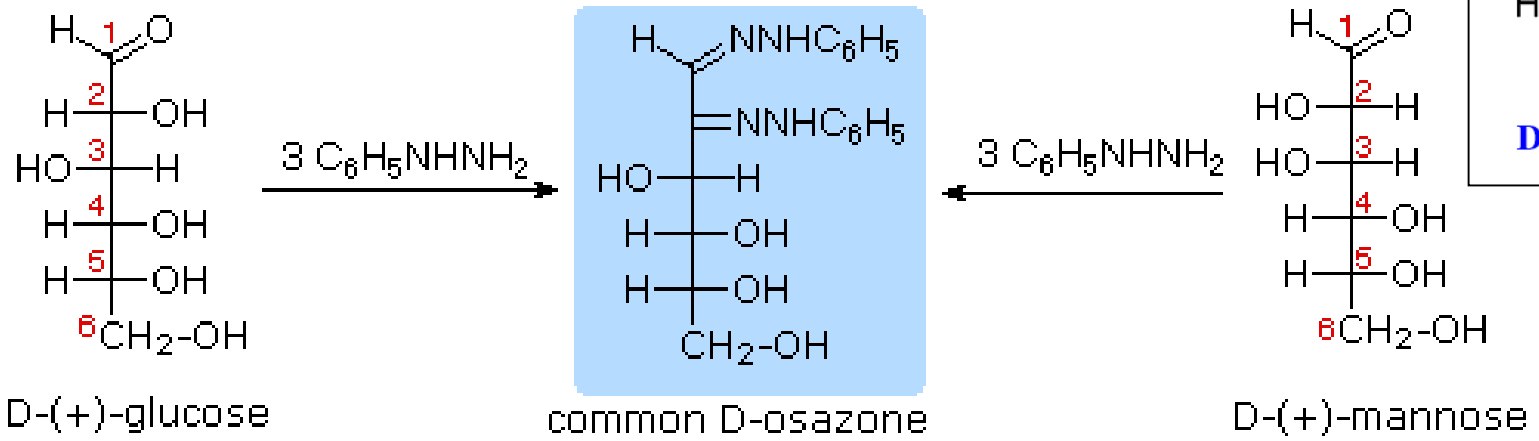


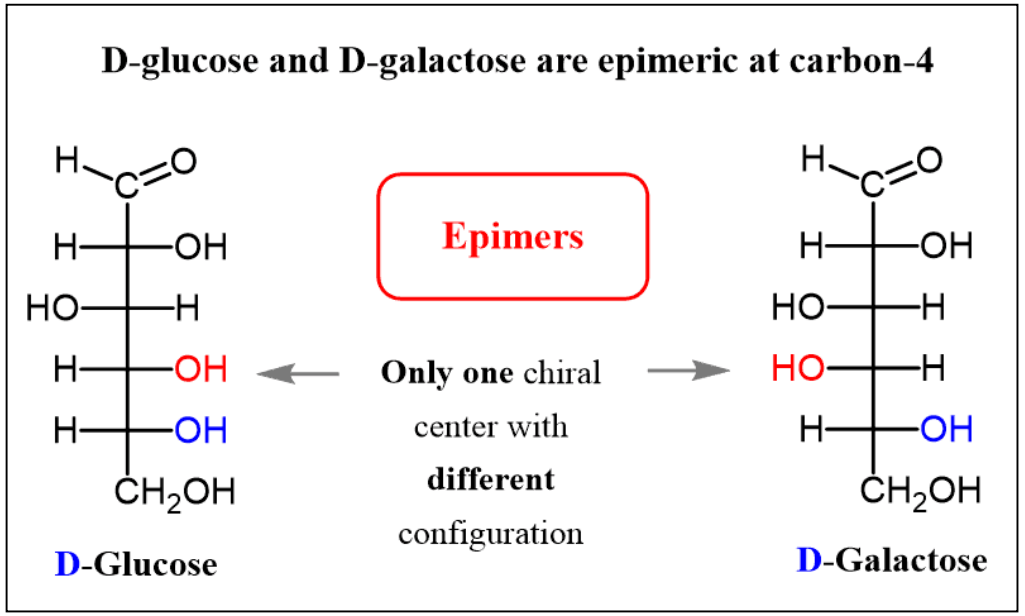
Fine-long needle shaped crystals (Xylose)



Sun flower shaped crystals (Maltose)

Epimers

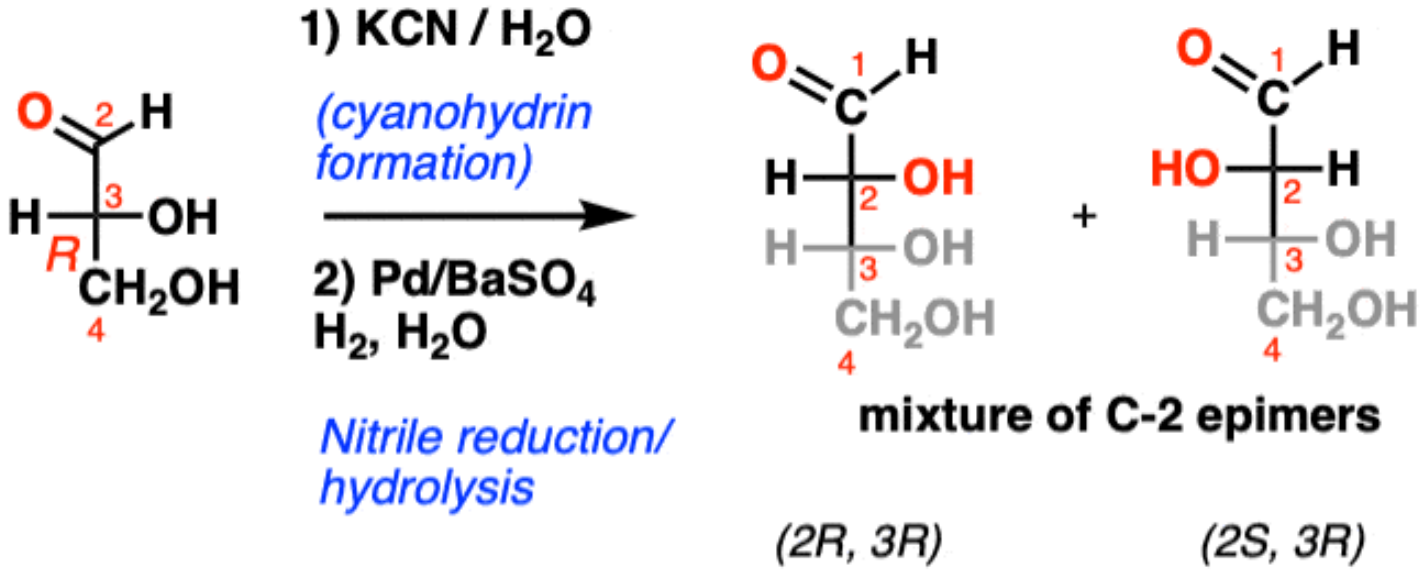




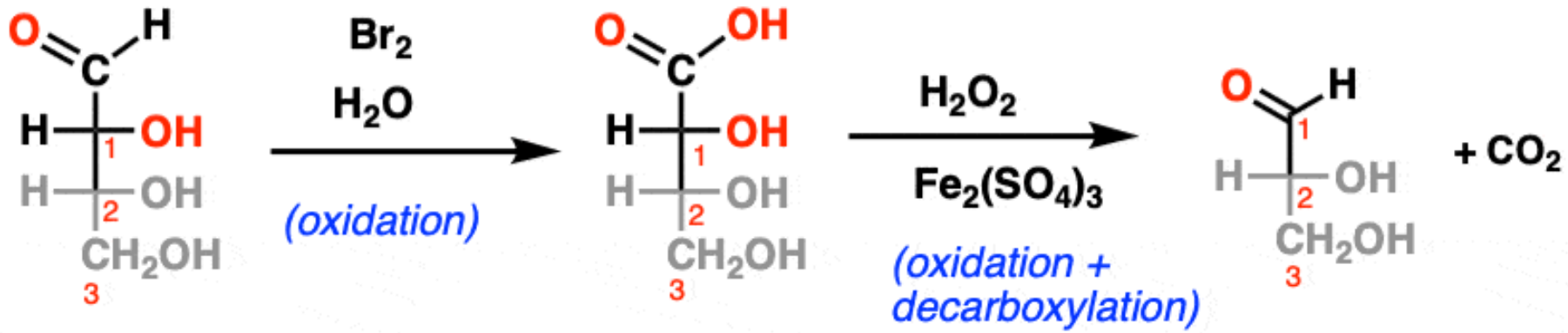
An **epimer** is one of a pair of diastereomers The two epimers have opposite configuration at only one stereogenic center out of at least two.All other stereogenic centers in the molecules are the same in each. **Epimerization** is the interconversion of one epimer to the other epimer

Step-Up & Step-Down Synthesis of Sugars

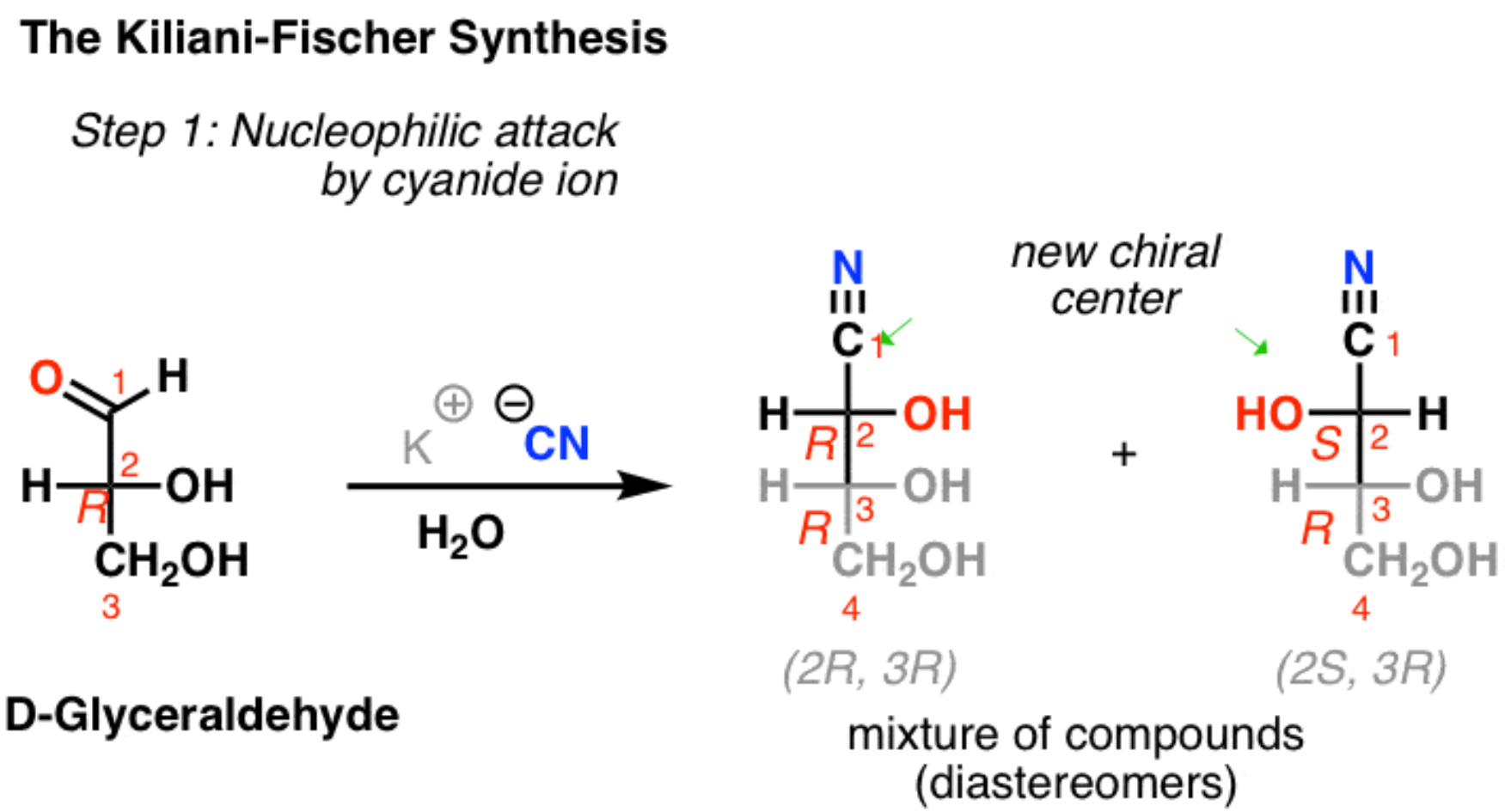
Kiliani-Fischer Synthesis - extending sugars by one carbon



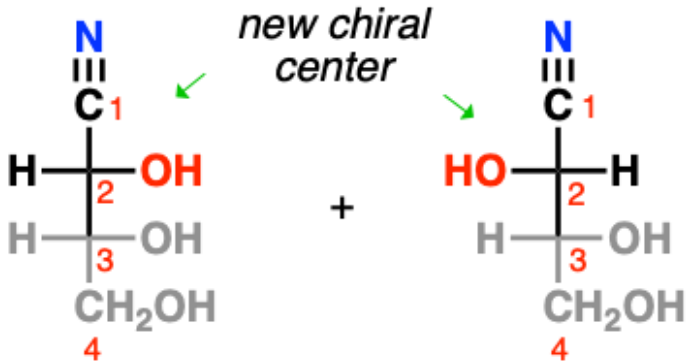
The Ruff Degradation - shortening sugars by one carbon



Killiani-Fischer Synthesis



Step 2: Hydrogenation

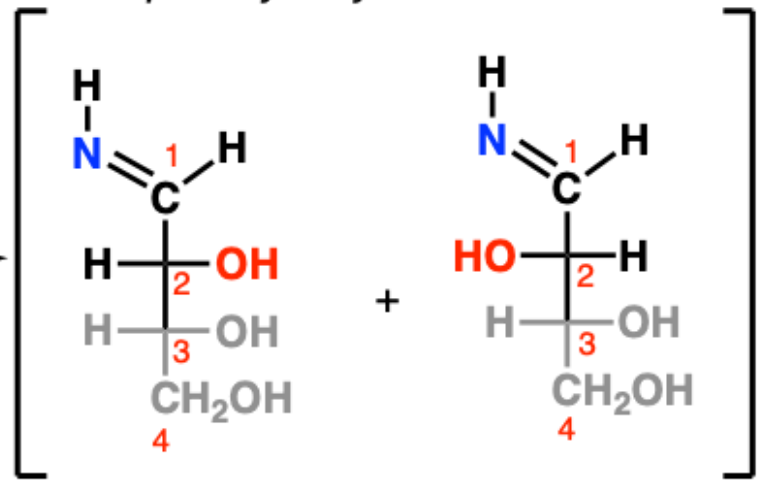


mixture of compounds
(diastereomers)

$Pd/BaSO_4$

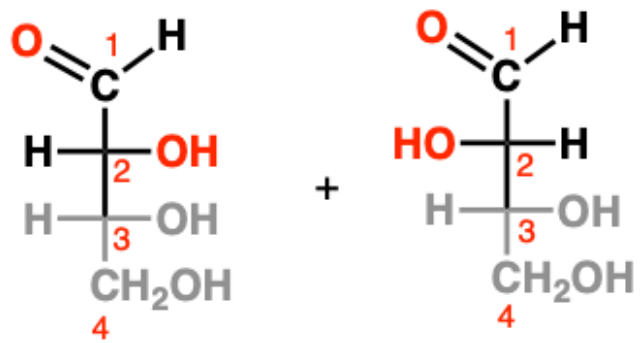
H_2

Step 3: Hydrolysis of Imines



two diastereomeric **imines**

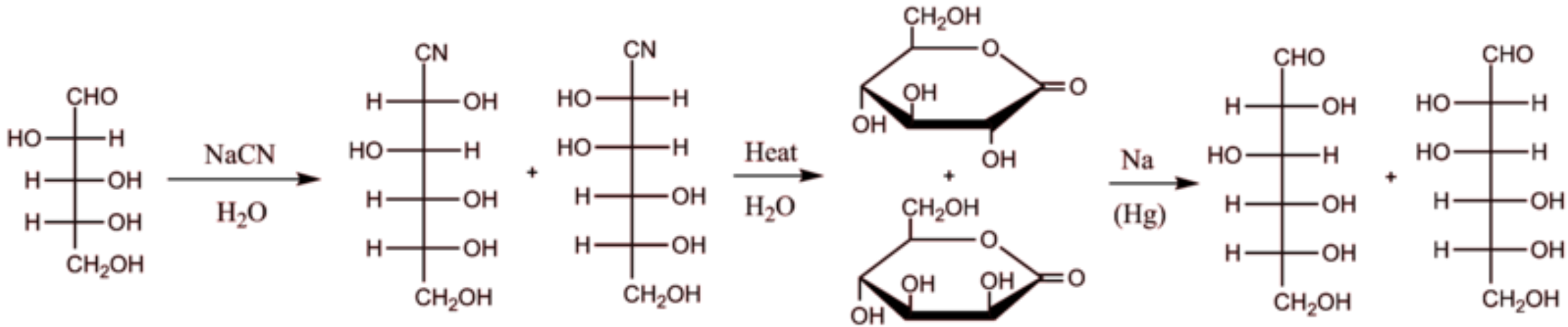
H_2O



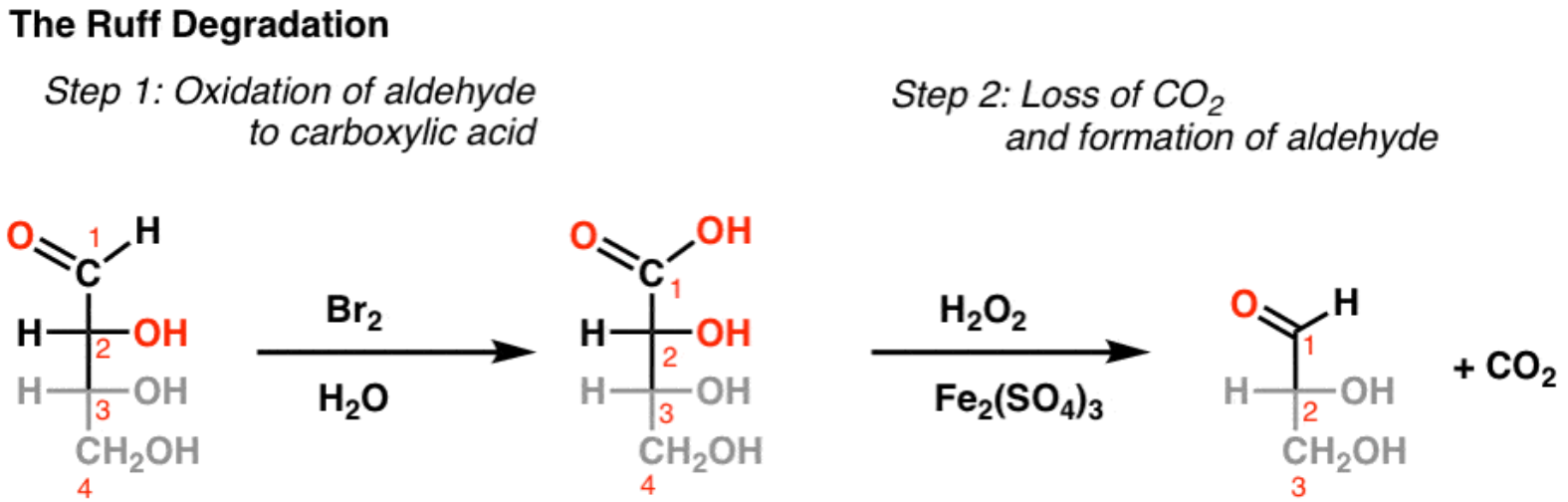
D-Erythrose
(2R, 3R)

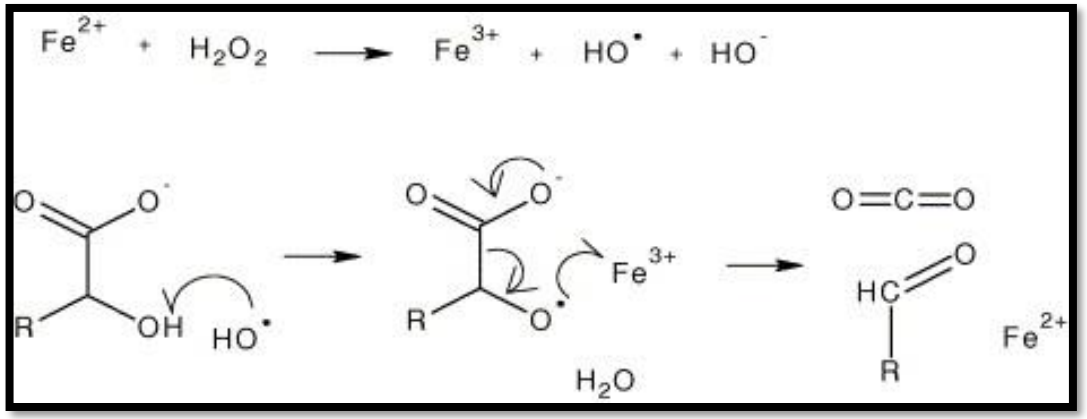
D-Threose
(2S, 3R)

The result of this synthesis is a mixture of two chain-extended aldoses (sugars)


CHO
HO
H
H
OH
H
OH
CH2OH
NaCN
H2O
CN
H
OH
HO
H
H
OH
H
OH
CH2OH
+
CN
HO
H
HO
H
H
OH
H
OH
CH2OH
Heat
H2O
CH2OH
O
OH
OH
O
+
CH2OH
O
OH
OH
O
OH
Na
(Hg)
CHO
H
OH
HO
H
H
OH
H
OH
CH2OH
+
CHO
HO
H
HO
H
H
OH
H
OH
CH2OH

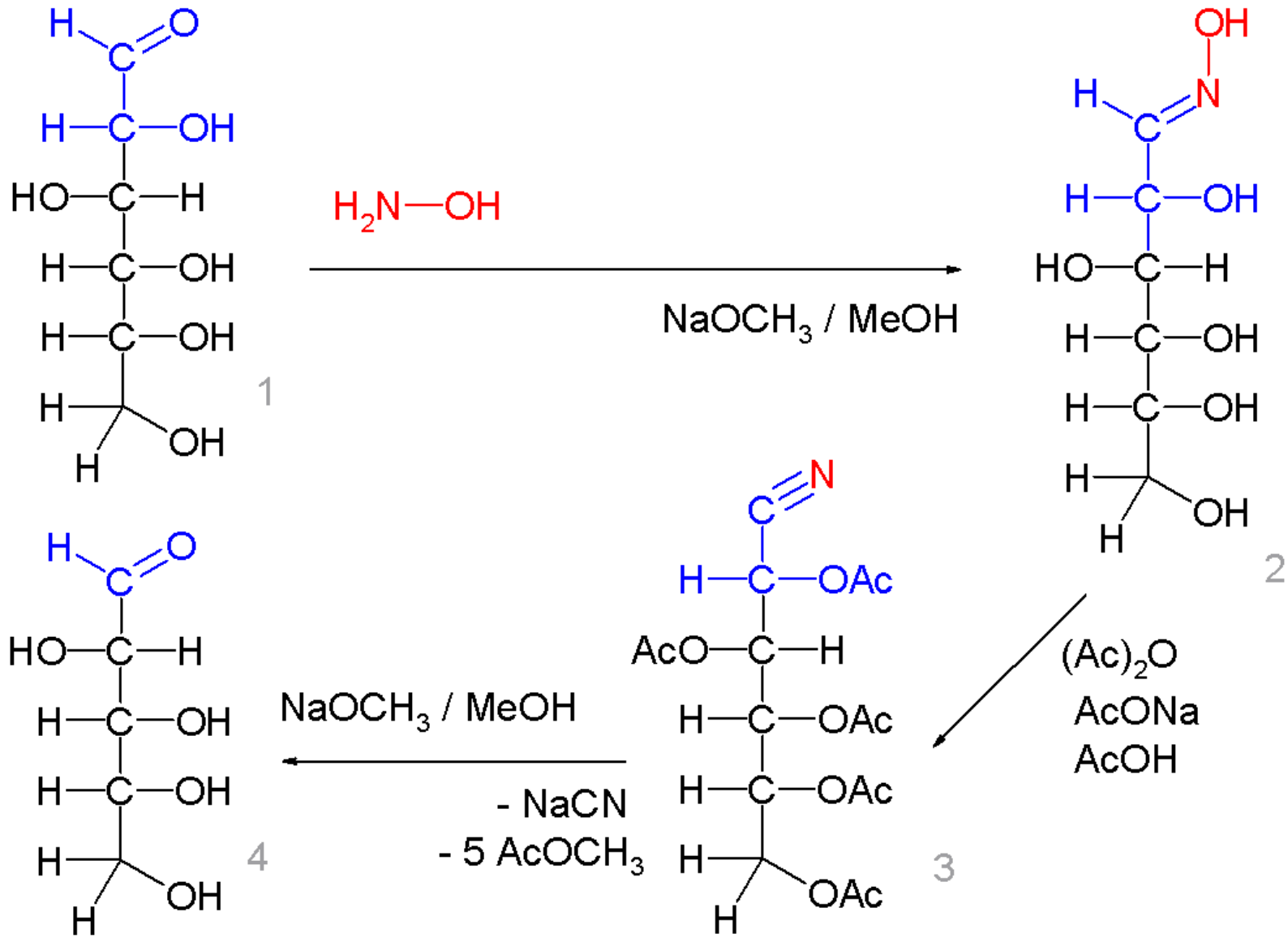
Ruff Degradation





Reaction Mechanism of Ruff Degradation

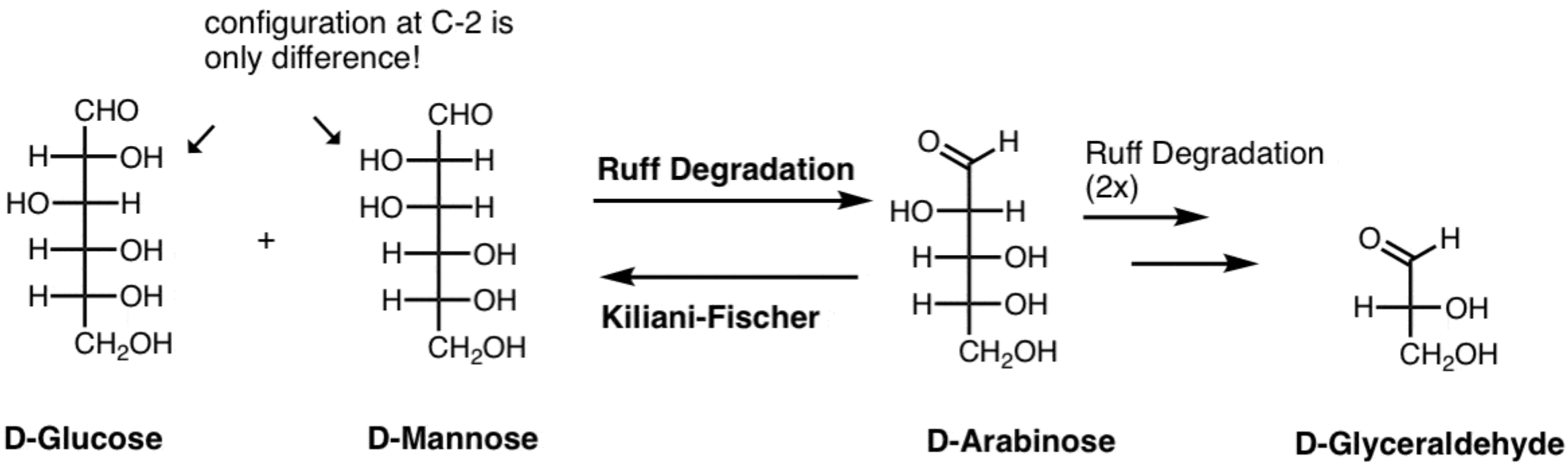
Wohl degradation



Application: Using The Ruff Degradation In Proving Configuration (1890's)

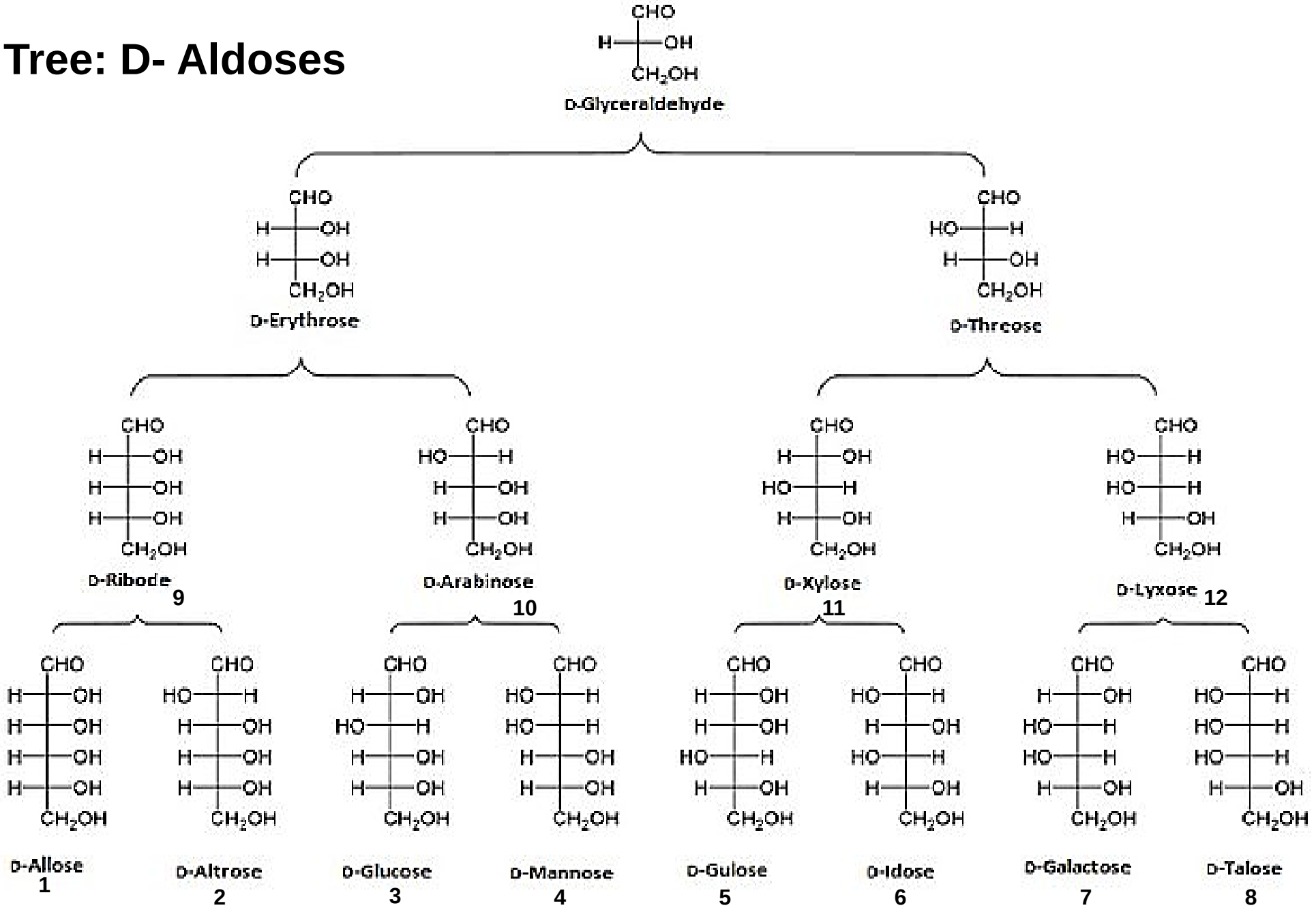
Upon Ruff degradation, D-Glucose and D-Mannose each form the same product (D-Arabinose) indicating that they are epimers

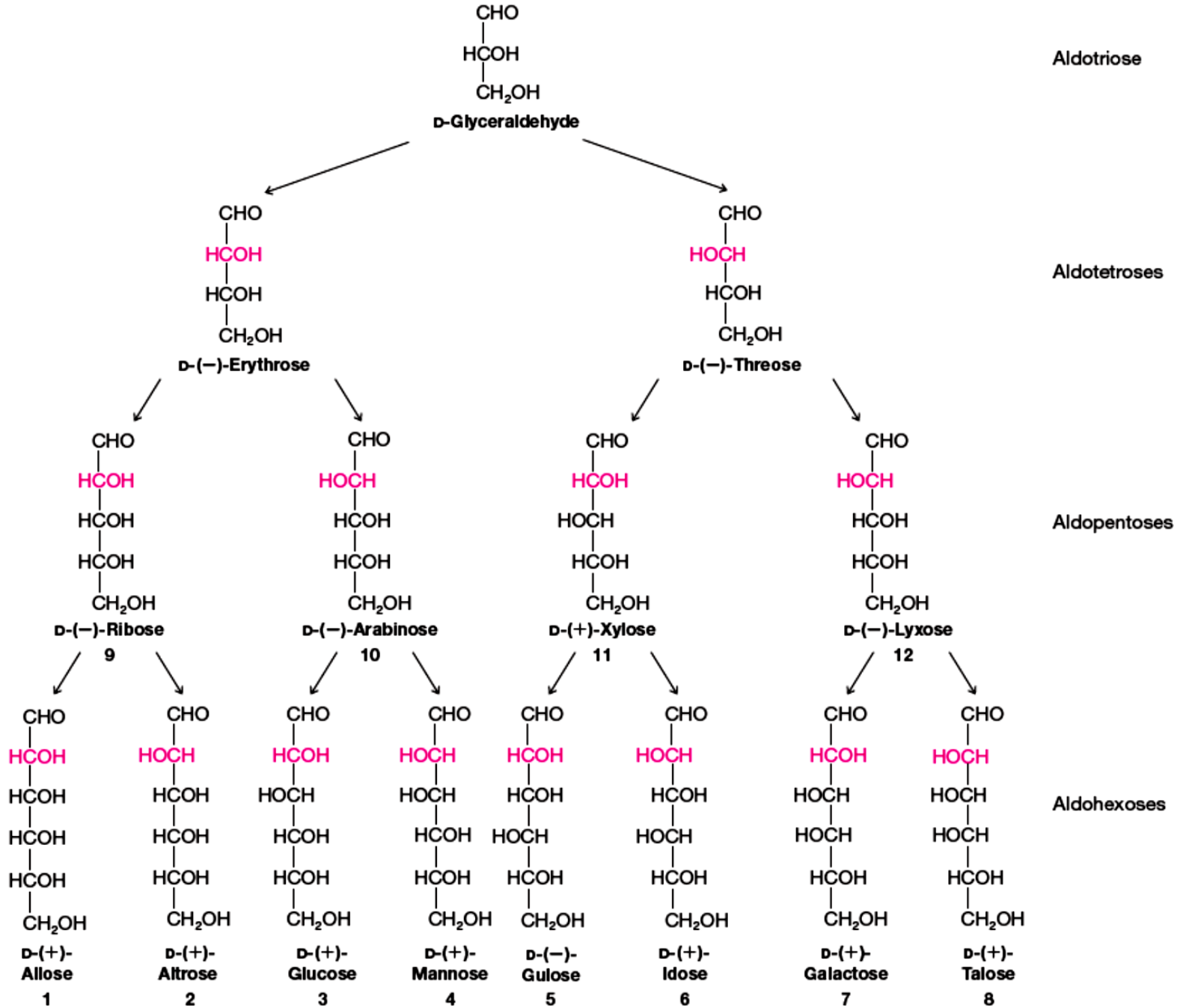
Further degradation gives D-glyceraldehyde



D-Glucose **D-Mannose** **D-Arabinose** **D-Glyceraldehyde**

Family Tree: D- Aldoses



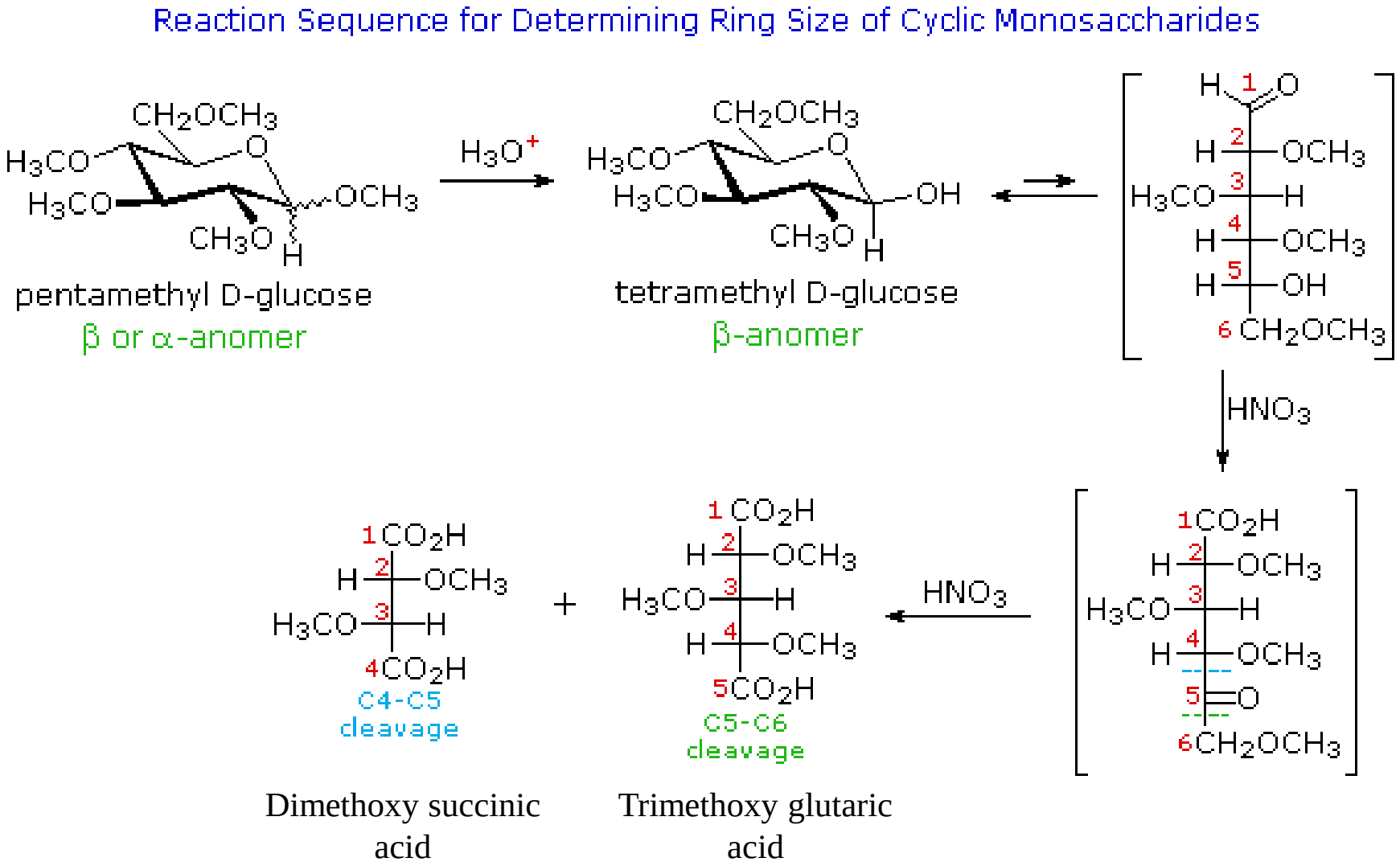

Aldotriose
D-Glyceraldehyde
Aldotetroses
D-(−)-Erythrose
D-(−)-Threose
Aldopentoses
D-(−)-Ribose
9
D-(−)-Arabinose
10
D-(+)-Xylose
11
D-(−)-Lyxose
12
Aldohexoses
D-(+)-Allose
1
D-(+)-Altrose
2
D-(+)-Glucose
3
D-(+)-Mannose
4
D-(−)-Gulose
5
D-(+)-Idose
6
D-(+)-Galactose
7
D-(+)-Talose
8

Evidences for the ring structures of sugars

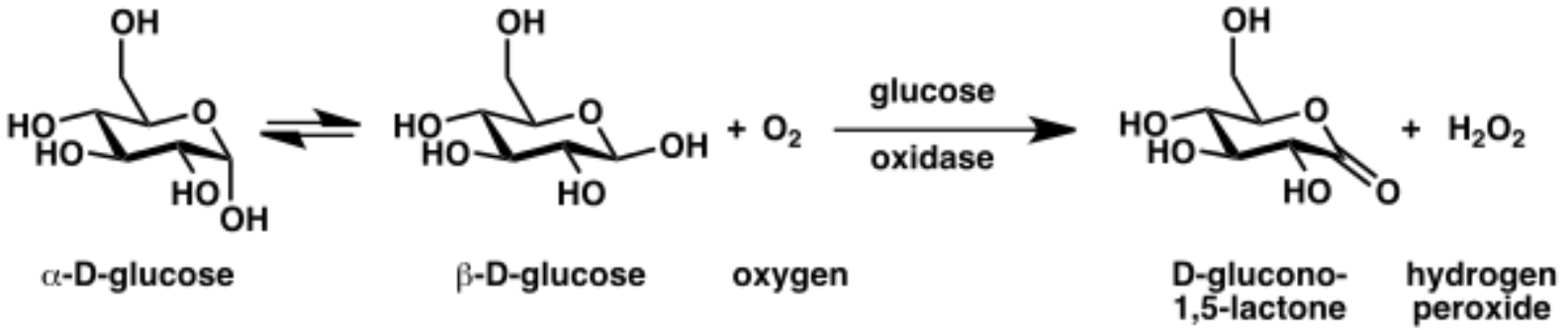
The cyclic structures of the sugars accounts for the following facts:

1. It fails to undergo certain reactions typical of aldehydes Schiff's Test , bisulfite test.
2. Exists in two anomeric forms α and β- glucose.
3. Exhibits mutarotation.

Determination of ring size



Monitoring Glucose Levels



Disaccharides

A disaccharide:

- Consists of two monosaccharides linked by a *glycosidic bond* (when one –OH group reacts with another –OH group).

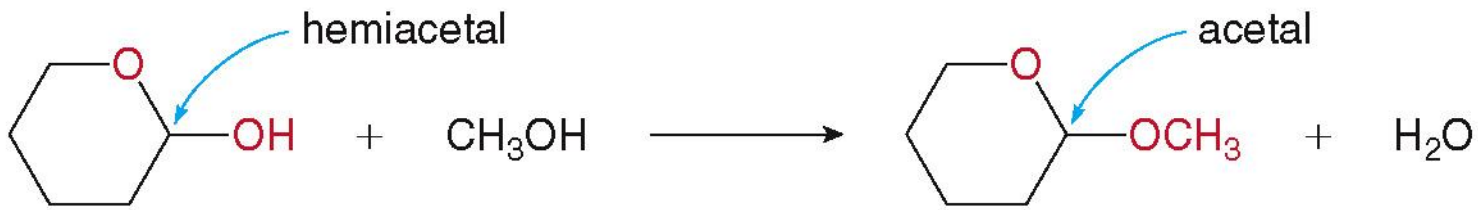
Glucose + Glucose ⟶ Maltose + H_2O

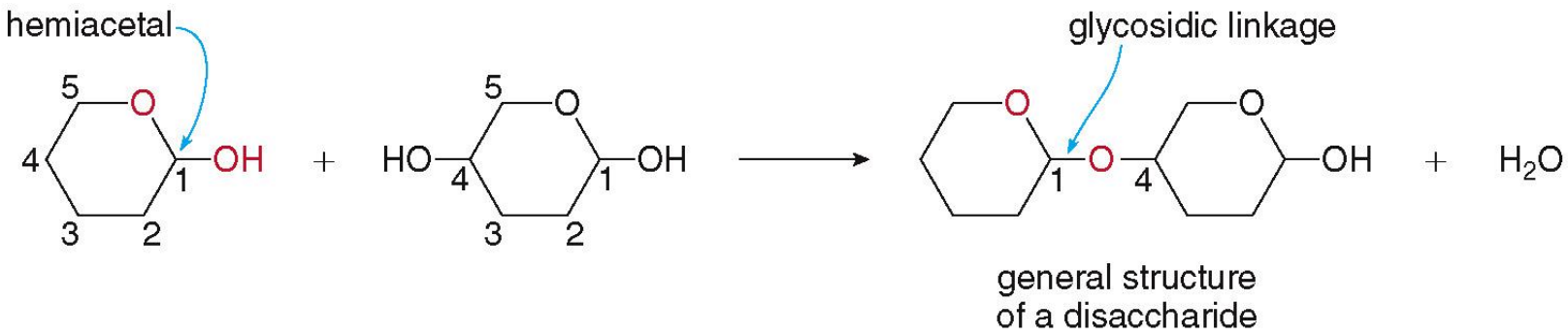
Glucose + Galactose ⟶ Lactose + H_2O

Glucose + Fructose ⟶ Sucrose + H_2O

Disaccharides

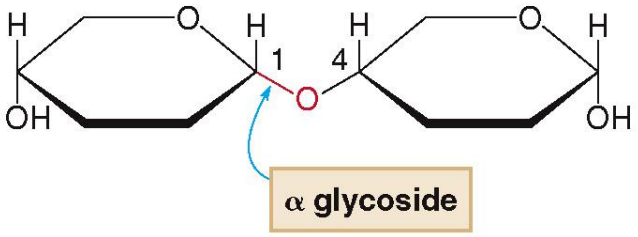
Disaccharides have at least one acetal carbon (a carbon atom singly bonded to two OR (alkoxy) groups.





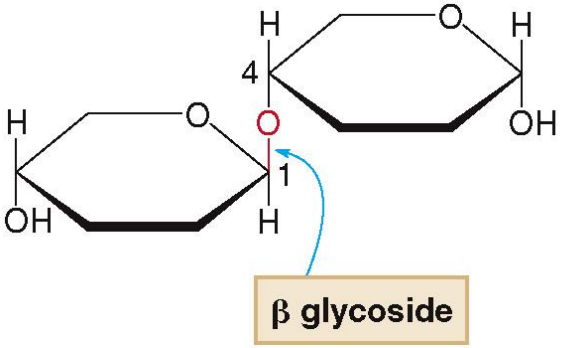
Disaccharides

The glycosidic bond joining the two rings can be alpha (α) or beta (β).



The glycoside bond is **down.**

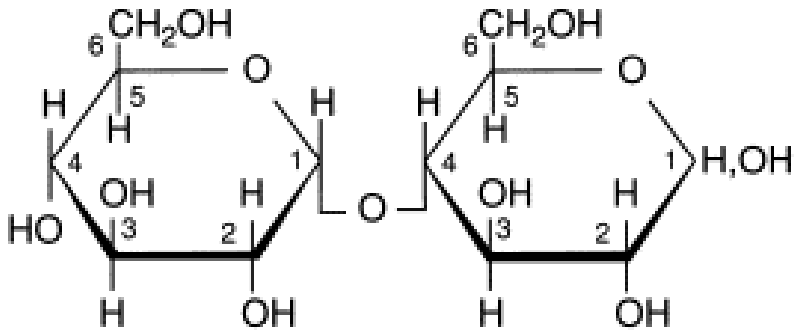
1→4-α-glycosidic linkage



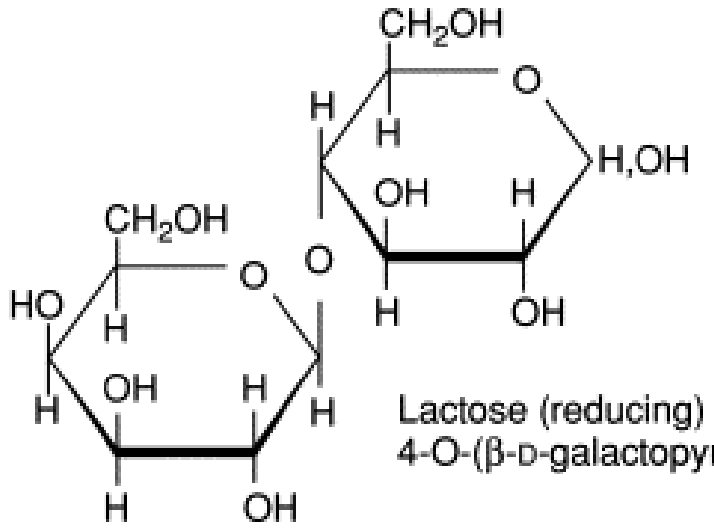
The glycoside bond is **up.**

1→4-β-glycosidic linkage

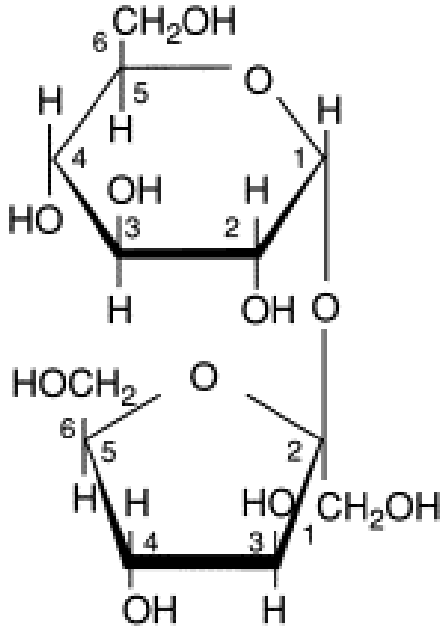
IUPAC Nomenclature of disaccharides



Maltose (reducing)
4-O-(α-D-glucopyransyl)-D-glucopyranose
or O-α-D-glucopyranosyl-(1→ 4)-α-D-glucopyranoside



Lactose (reducing)
4-O-(β-D-galactopyranosyl)-D-glucopyranose

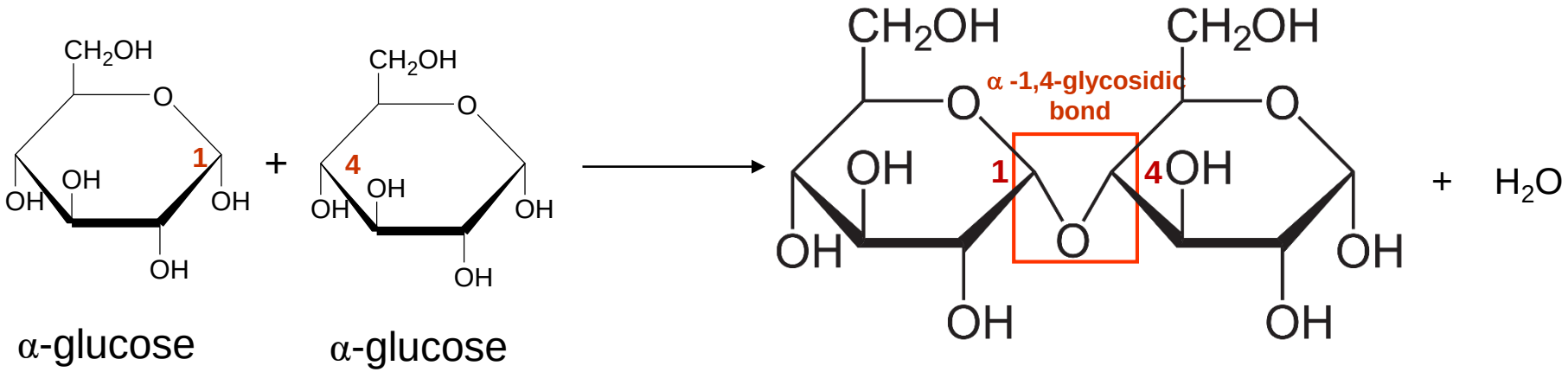


Sucrose (non-reducing)
α-D-glucopyranosyl-β-D-fructofuranoside
or (β-D-fructopyranosyl)-α-D-glucopyranoside
or O-α-D-glucopyranosyl-(1→ 2)-β-D-fructopyranoside

Disaccharides

Maltose:

- Is a disaccharide of two glucose molecules, obtained from partial hydrolysis by acid or enzymatic hydrolysis by *diastase* of starch .
- Has a ***α* -1,4-glycosidic bond** (between two α-glucoses).
- Is obtained from the breakdown of starches.
- Is used in cereals and candies.
- Is a reducing sugar (carbon 1 can open to give a free aldehyde to oxidize).



α-glucose α-glucose

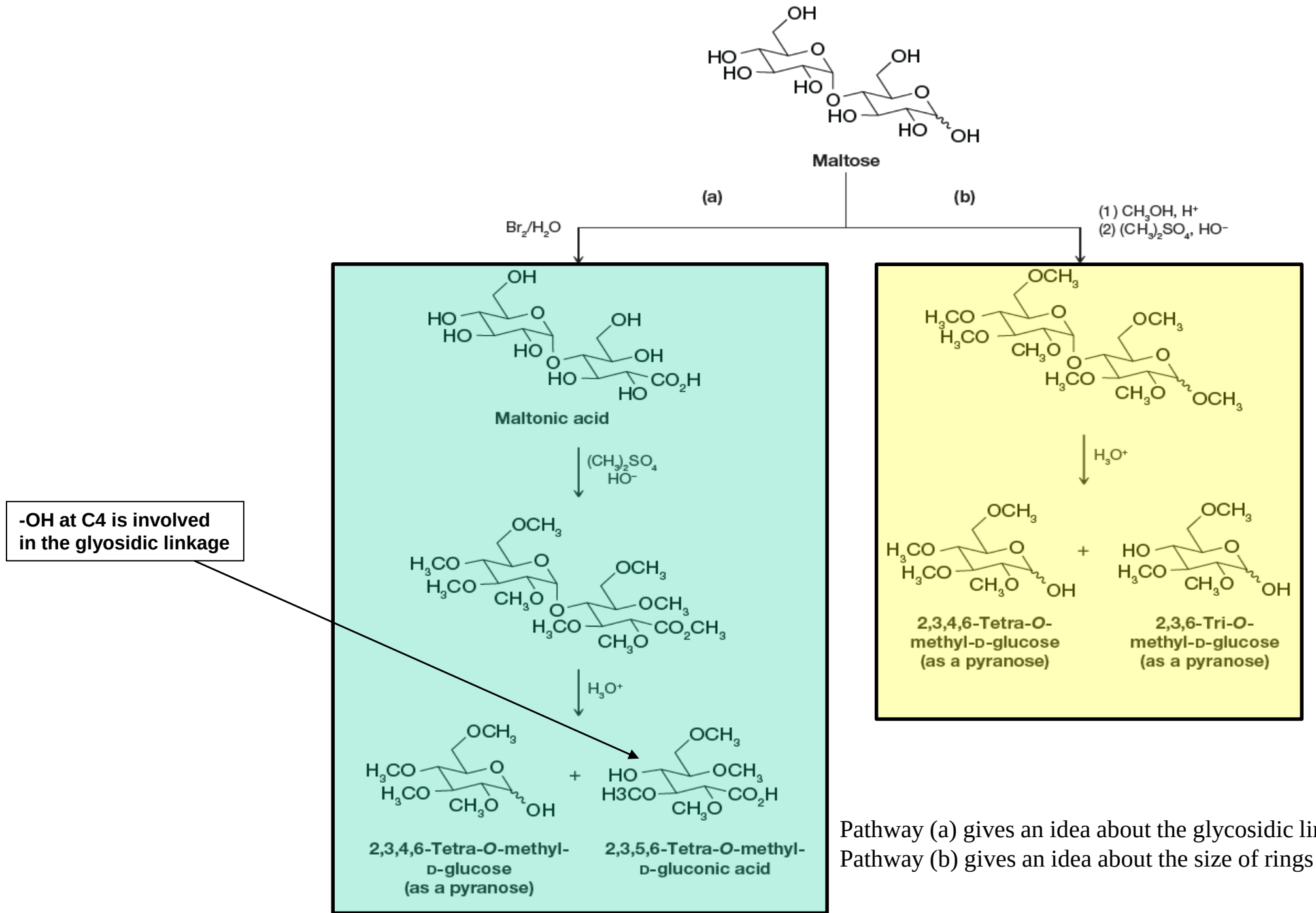
Maltose (4-O-α-D-glycopyranosyl-D-glycopyranose

Structure of Maltose: Elucidation

The structure elucidation of maltose can be made on following facts:

1. When 1 mole of maltose is subjected to acid-catalyzed hydrolysis, it yields **2 mole** of D-(+)-glucose.
2. Maltose gives **positive tests** with Fehling's, Benedict's, and Tollens' solutions. Maltose also reacts with phenylhydrazine to form a **monophenylosazone**.
3. Maltose exists in two anomeric forms: α-(+)-maltose, $[\alpha]_d^{25} = +168$, and β-(+)-maltose, $[\alpha]_d^{25} = +112$. The maltose anomers undergo **mutarotation** to yield an equilibrium mixture, $[\alpha]_d^{25} = +136$.

Fact 2 and 3 points out that one of the glucose ring is present as pyranose and other as glycoside. The linkage about the two units is inferred as **α**, as maltose was hydrolysed by **α- glycosidase** enzyme not by **β-glycosidase** enzymes,



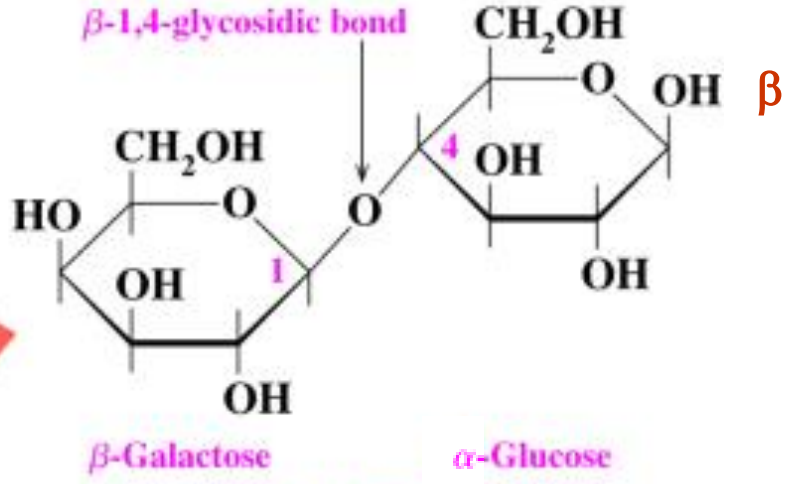
-OH at C4 is involved in the glyosidic linkage

Pathway (a) gives an idea about the glycosidic linkage between two glucose units
Pathway (b) gives an idea about the size of rings present maltose

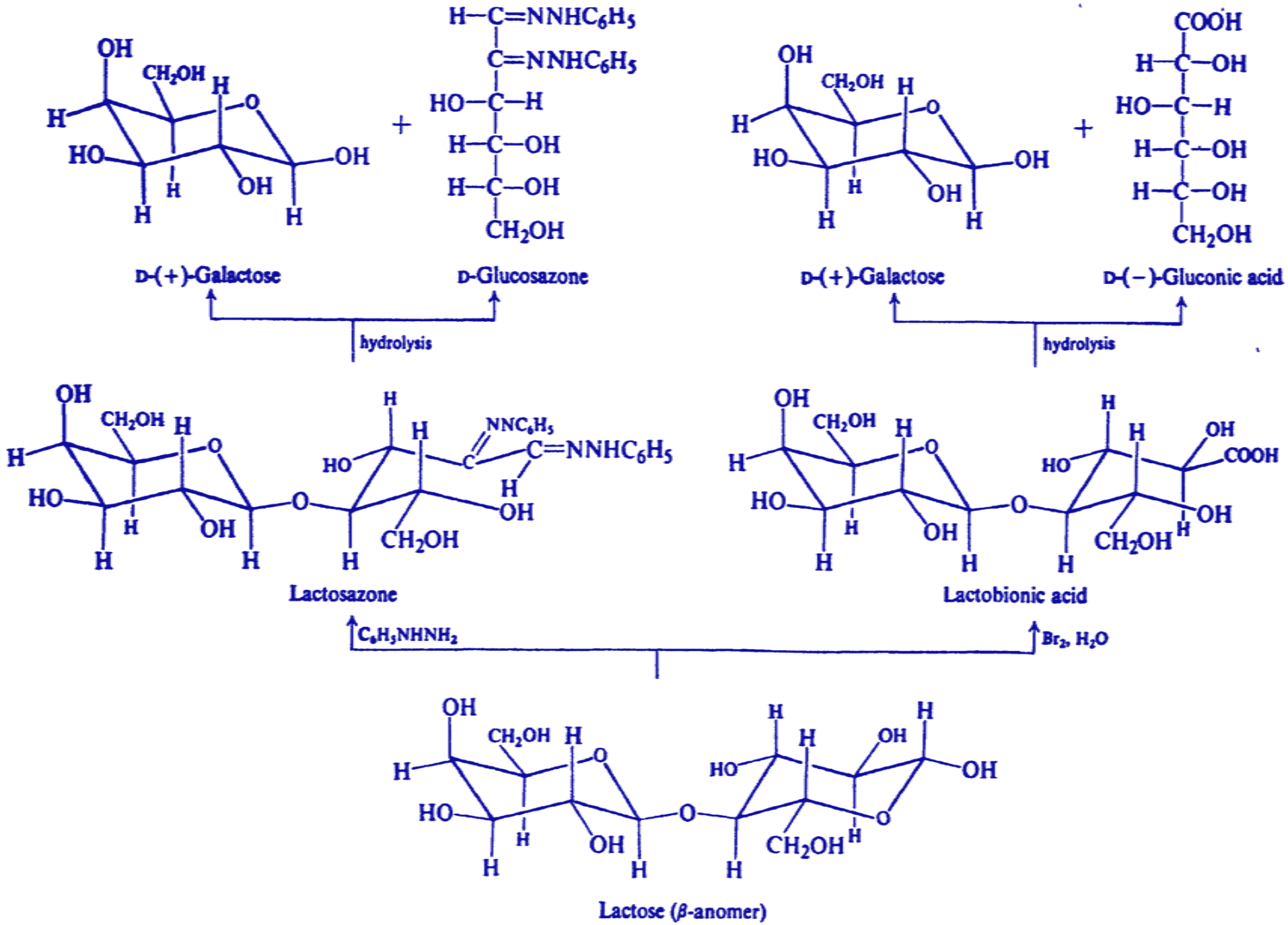
Disaccharides

Lactose:

- Is a disaccharide of galactose and glucose.
- Has a ***β* -1,4-glycosidic bond** (between *β*-galactose and α-gulcose).
- Is found in milk and milk products (almost no sweet).
- Is a reducing sugar (carbon 1 can open to give a free aldehyde to oxidize).



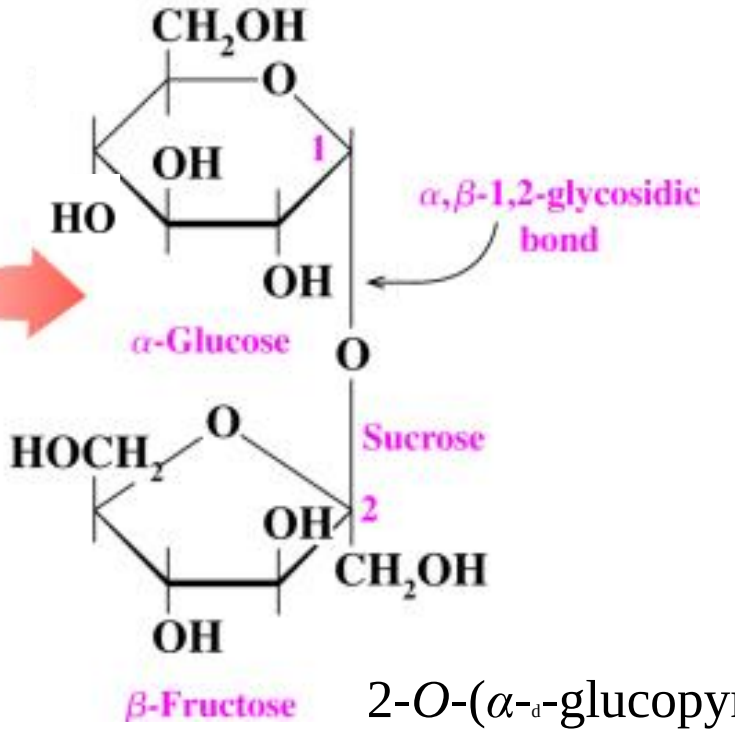
β-lactose (4-O-β-D-Galactopyranosyl-D-glucose)


D-(+)-Galactose
D-Glucosazone
hydrolysis
D-(+)-Galactose
D-(−)-Gluconic acid
hydrolysis
Lactosazone
Lactobionic acid
$C_6H_5NHNH_2$
Br_2, H_2O
Lactose (β-anomer)

Disaccharides

Sucrose:

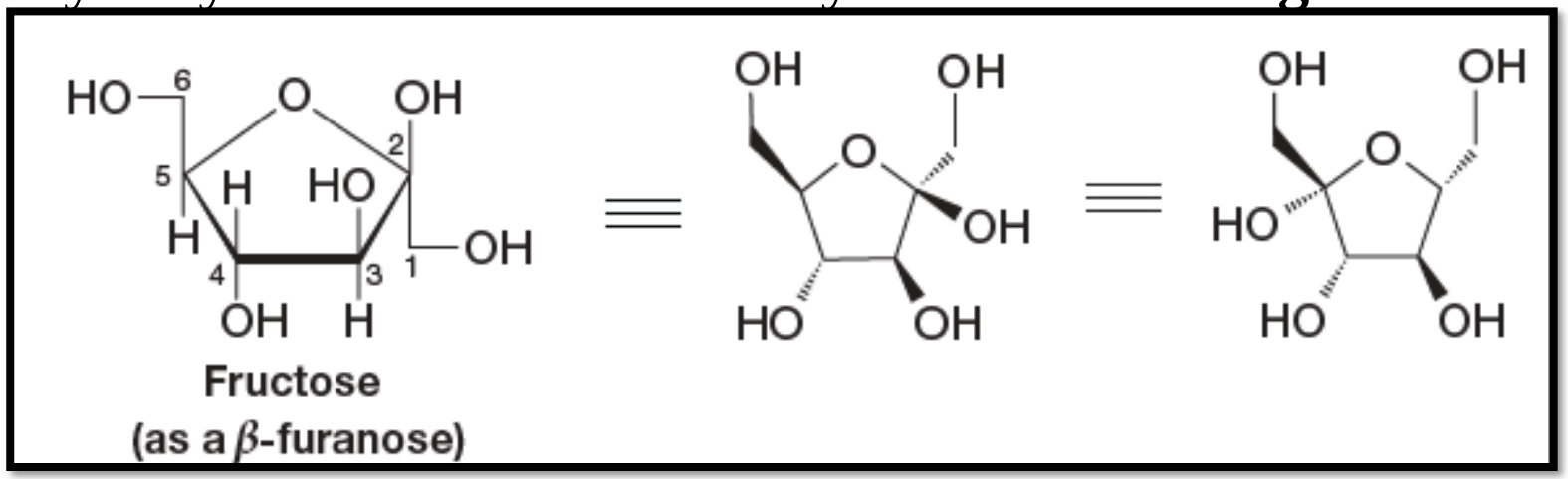
- Is found in table sugar (obtained from sugar cane and sugar beets).
- Consists of glucose and fructose.
- Has an ***α,β*-1,2-glycosidic** bond (between α-glucose and β-fructose).
- Is not a reducing sugar (carbon 1 cannot open to give a free aldehyde to oxidize).



2-*O*-(α-$_d$-glucopyranosyl)-β-$_d$fructofuranoside

1. Sucrose has the molecular formula $\mathbf{C_{12}H_{22}O_{11}}$

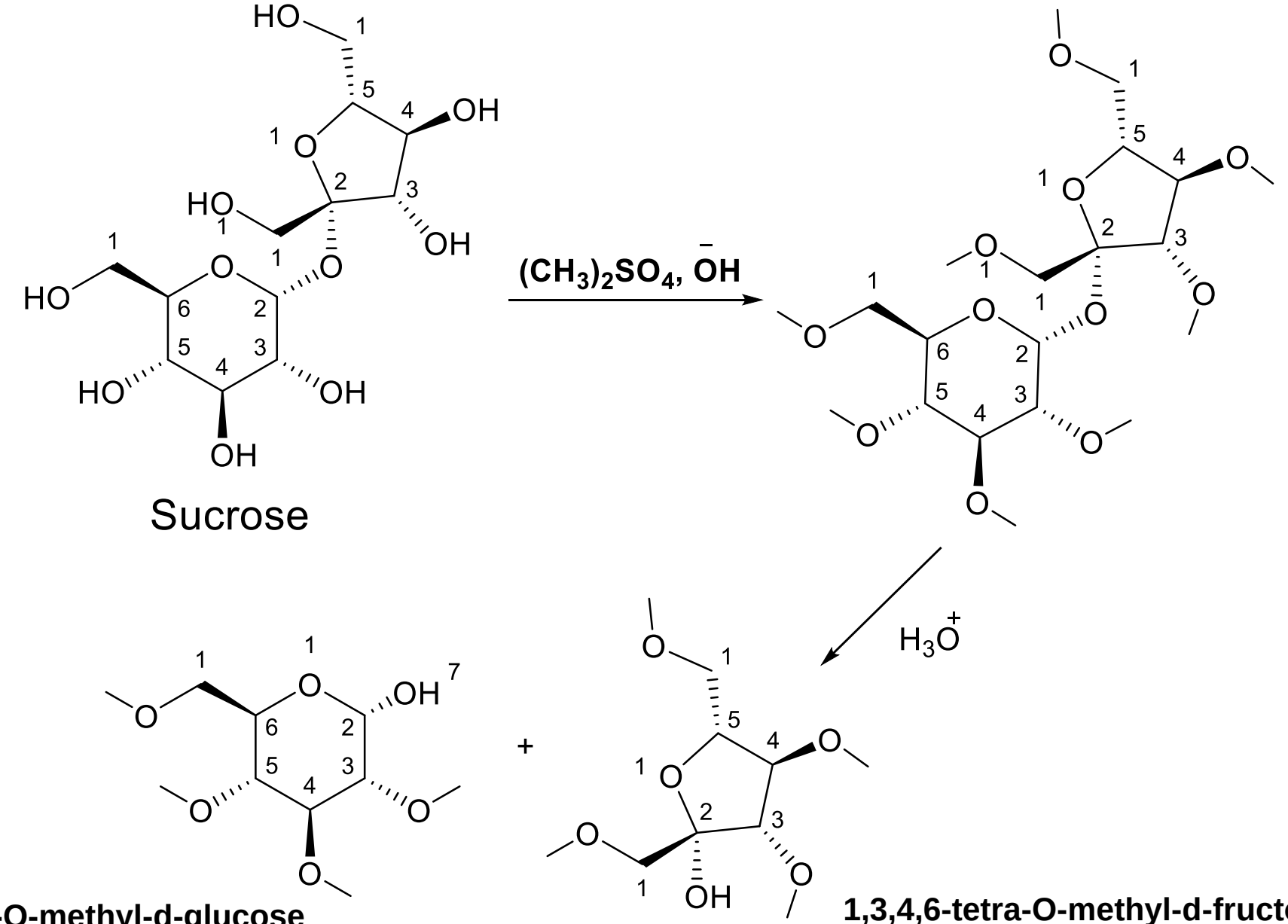
2. Acid-catalyzed hydrolysis of 1 mol of sucrose yields 1 mol of **d-glucose** and 1 mol of **d-fructose**.



3. Sucrose is **a nonreducing** sugar; it gives negative tests with Benedict's and Tollens' solutions. Sucrose **does not** form an **osazone** and **does not** undergo **mutarotation**. These facts mean that neither the glucose nor the fructose portion of sucrose has a hemiacetal group. Thus, the two hexoses must have a glycosidic linkage that involves C1 of glucose and C2 of fructose, for only in this way will both carbonyl groups be present as full **acetals** (i.e., as glycosides).

4. The stereochemistry of the glycosidic linkages can be inferred from experiments done with enzymes. Sucrose is hydrolyzed by an ***α-glucosidase*** obtained from yeast but not by *β*-glucosidase enzymes. This hydrolysis indicates *an α configuration at the glucoside portion*. Sucrose is also hydrolyzed by ***sucrase***, an enzyme known to hydrolyze *β*-fructofuranosides but not *α*-fructofuranosides. This hydrolysis indicates a *β* configuration at the fructoside portion.

5. Methylation of sucrose gives an octamethyl derivative that, on hydrolysis, gives 2,3,4,6-tetra-O-methyl-d-glucose and 1,3,4,6-tetra-O-methyl-d-fructose. The identities of these two products demonstrate that the glucose portion is a pyranoside and that the fructose portion is a furanoside.


Sucrose
$(CH_3)_2SO_4$, $\bar{O}H$
H_3O^+
+
2,3,4,6-tetra-O-methyl-d-glucose
1,3,4,6-tetra-O-methyl-d-fructose

Disaccharides

Sucrose:

Sucrose is very sweet, but contains many calories.

To reduce caloric intake, many artificial sweeteners have been developed.

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TABLE 20.1 Relative Sweetness of Some Carbohydrates and Artificial Sweeteners

Compound	Relative Sweetness
Sorbitol	0.60
Glucose	0.75
Sucrose	1.00
Fructose	1.75
Aspartame	150
Saccharin	350
Sucralose	600

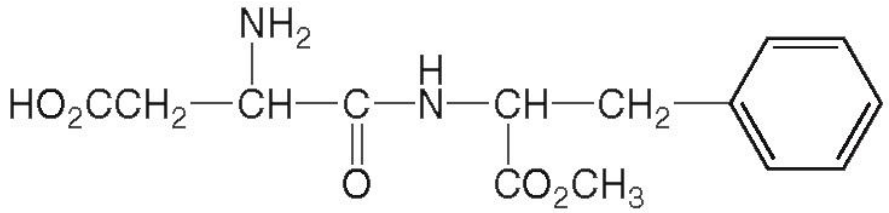
Aspartame, Saccharin, Sucralose

These artificial sweeteners were discovered accidentally.

Artificial sweeteners

Aspartame:

It (sold as Equal) is hydrolyzed into phenylalanine, which cannot be processed by those individuals with the condition phenylketonuria.



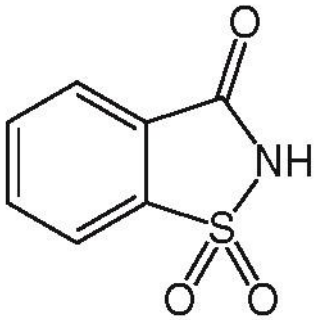
aspartame
(Trade name: Equal)

Artificial sweeteners

Saccharine:

It (sold at Sweet'n Low) was used extensively during World War I.

There were concerns in the 1970s that saccharin causes cancer.

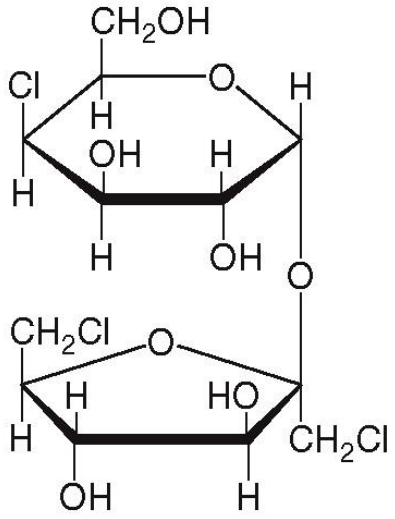


saccharin
(Trade name: Sweet'n Low)

Artificial sweeteners

Sucralose:

It (sold as Splenda) has a very similar structure to sucrose.



sucralose
(Trade name: Splenda)

Polysaccharides

- Polymers of many monosaccharides units.
- Starch
  - Amylose (20%)
  - Amylopectin (80%)

(starch that stores glucose in plants such as rice, potatoes, beans, and wheat - energy storage).

- Glycogen (an energy storage in animals & humans)

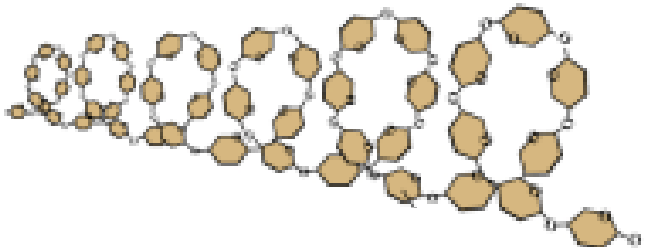
- Cellulose (plant and wood structures).

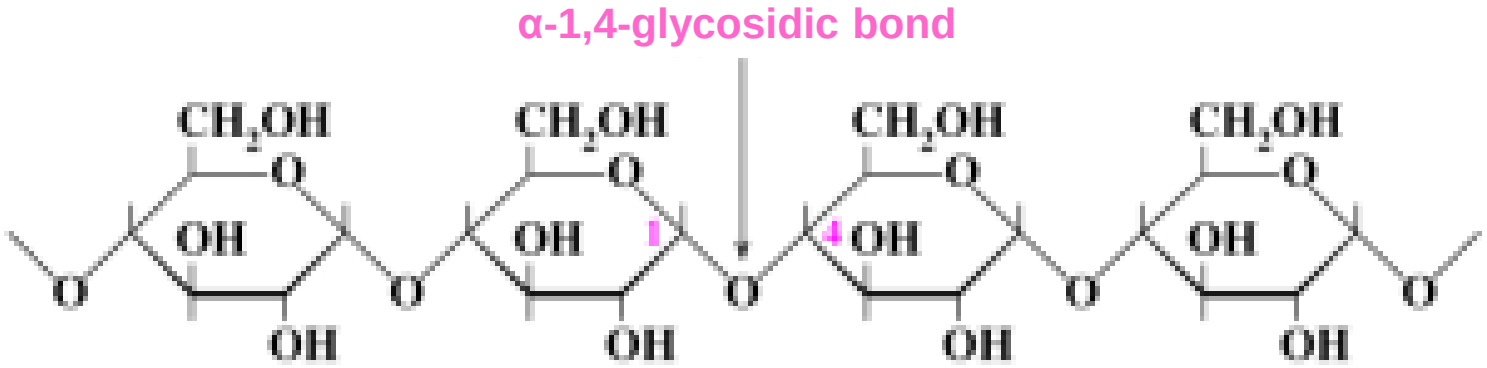
Polysaccharides

Amylose:

- Is a polysaccharide of *α*-glucose in a continuous (unbranched) chain (helical or coil form).

- Has α-1,4-glycosidic bonds between the *α*-glucose units (250 to 4000 units).



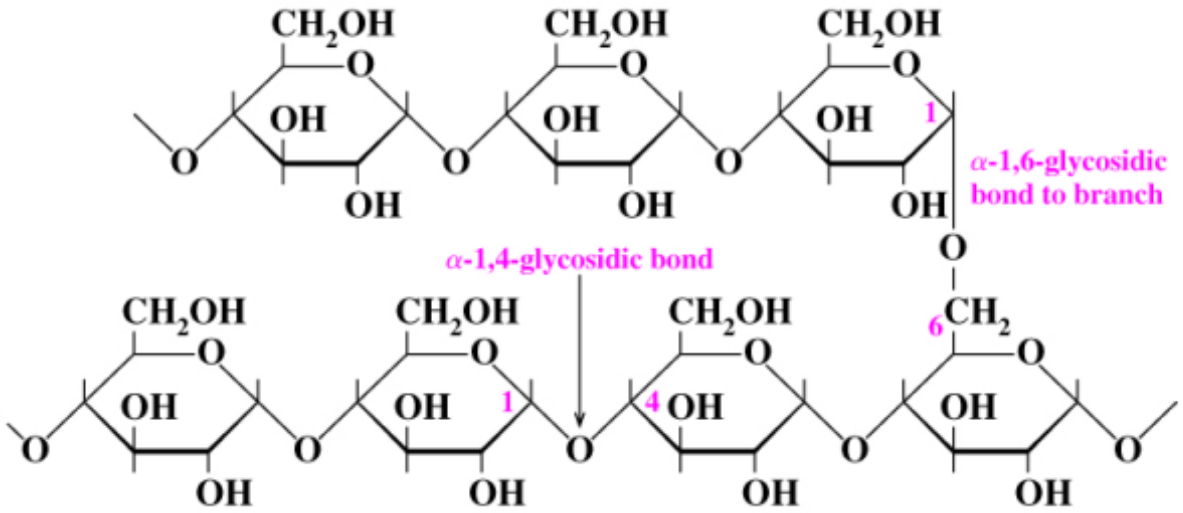


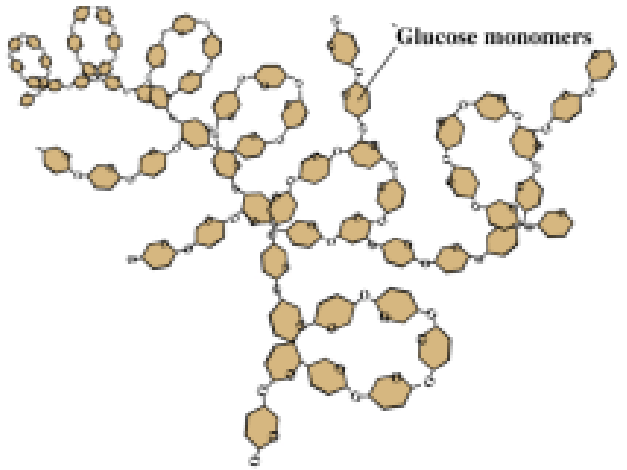
Polysaccharides

Amylopectin:

- Is a polysaccharide of glucose units in branched chains.
- Has α-1,4-glycosidic bonds between the *α*-glucose units.
- Has *α*-1,6 bonds to branches of glucose units.

  (at about every 25 glucose units, there is a branch).
- Both forms of starch are water soluble.





Polysaccharides

Glycogen:

- It is similar to amylopectin (more highly branched-every 10-15 units).

- It is an energy storage molecule found in animals/humans.

- It is stored mainly in the liver and in muscle cells.

- When glucose is needed for energy, glucose units are hydrolyzed from the ends of the glycogen polymer.

- Because glycogen is highly branched, there are many ends available for hydrolysis.

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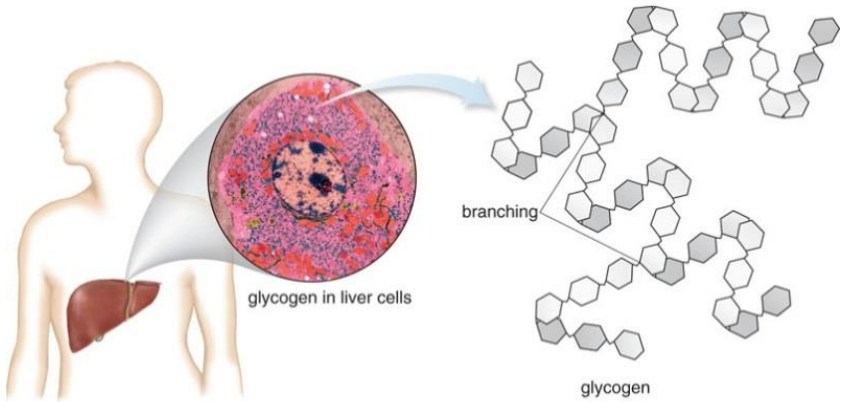


© Dennis Kunkel/Visuals Unlimited

Polysaccharides

Amylose, Amylopectin (starch)

↓ H^+ or α-amylase (enzyme in saliva)

Dextrins (6-8 glucose units)

Digestion process

↓ H^+ or α-amylase (enzyme in pancreas)

Maltose (2 glucose units)

↓ H^+ or α-maltase (enzyme)

Many *α*-D-glucose units

Respiration

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O + \text{energy}$$

glucose

Fermentation

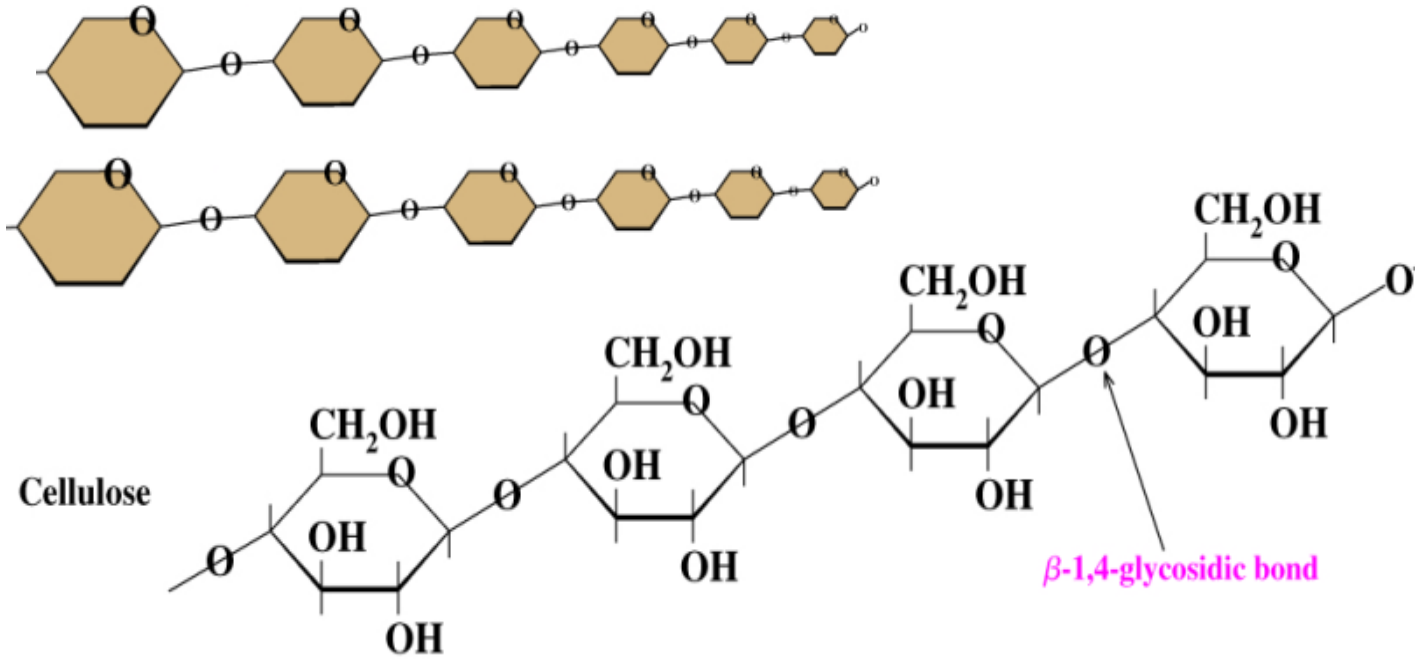
$$C_6H_{12}O_6 \xrightarrow{\text{Yeast}} 2C_2H_5OH + CO_2 + \text{energy}$$

Ethanol

Polysaccharides

Cellulose:

- Is a polysaccharide of glucose units in unbranched chains with β-1,4-glycosidic bonds (2200 glucose units).
- Has rigid structure (H-bond) and insoluble in water.
- Is the major structural material of wood & plants (cotton: 100%).
- Cannot be digested by humans because of the **β-1,4-glycosidic bonds** (needs an enzyme: β-glycosidase).



Polysaccharides

Cellulose:

- Cellulose makes up the insoluble fiber in our diets.

- It passes through the digestive system without being metabolized.

- Fiber is important in adding bulk to waste to help eliminate it more easily (even though it gives us no nutrition).

Useful Carbohydrates

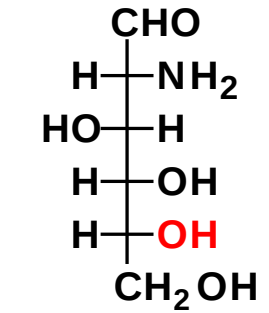
Amino Sugars

They contain an -NH_2 group in place of an -OH group.

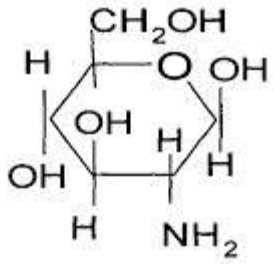
- The most abundant amino sugar in nature is **D-glucosamine**.

- Glucosamine helps keep the cartilage in joints healthy. But natural glucosamine levels drop as people age.

- As a supplement, glucosamine is most often used to try to ease the joint pain caused by arthritis.



D-Glucosamine



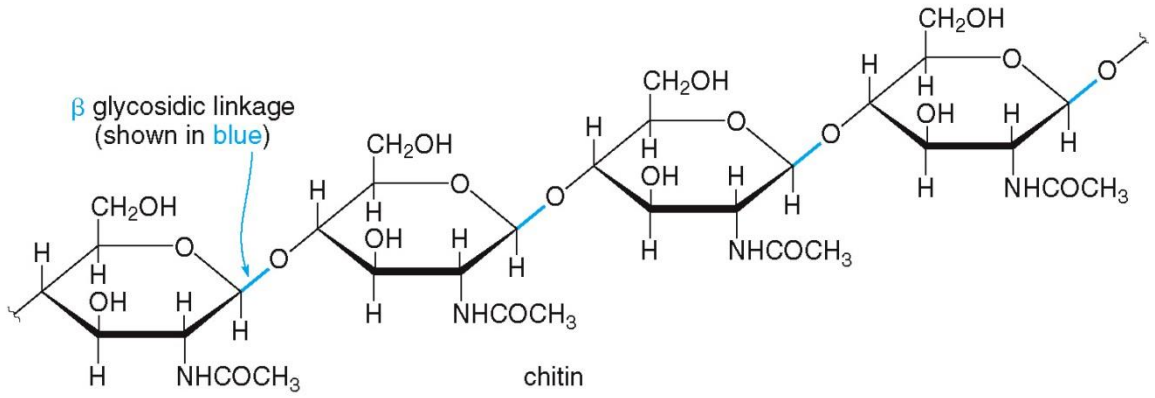
Useful Carbohydrates

Amino Sugars

- The second most abundant amino sugar in nature is **Chitin**.

- It is a polysaccharide formed from *N*-acetyl-D-glucosamine units joined together by 1,4-β-glycosidic bonds.

- Its structure is similar to cellulose (insoluble in water).

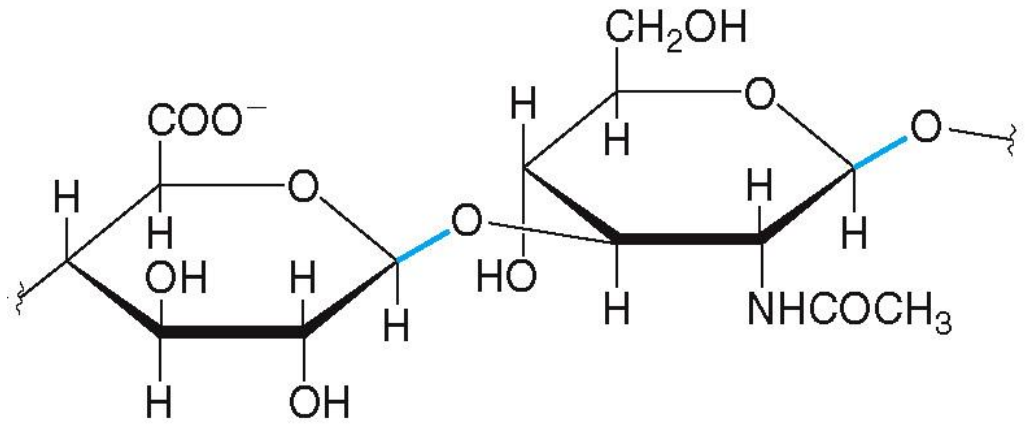


Useful Carbohydrates

Glycosaminoglycans (GAGs)

They are a group of unbranched carbohydrates derived from alternating amino sugar and glucuronate units.

Hyaluronate: extracellular fluids that lubricate joints and in the vitreous humor of the eye.



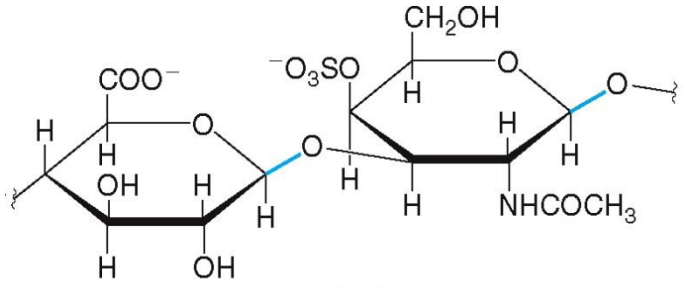
hyaluronate

β-glycosidic bond

Useful Carbohydrates

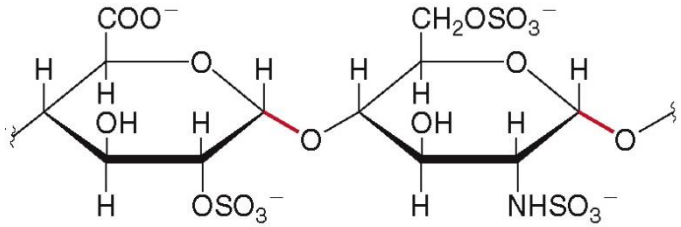
Glycosaminoglycans (GAGs)

Chondroitin: a component of cartilage and tendons.



chondroitin β-glycosidic bond

Heparin: stored in the mast cells (allergy cells) of the liver, helps prevent blood clotting.



heparin

α-glycosidic bond

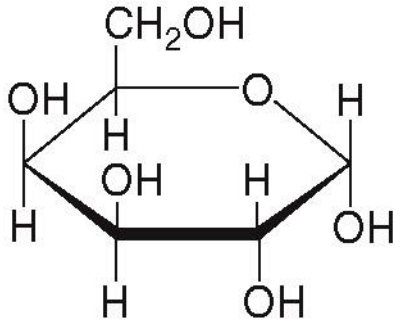
Useful Carbohydrates

Blood Type

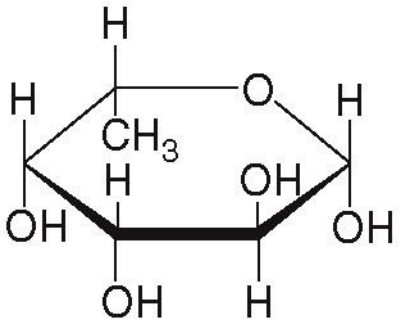
- There are four blood types—A, B, AB, and O.

- Blood type is based on 3 or 4 monosaccharides attached to a membrane protein of red blood cells.

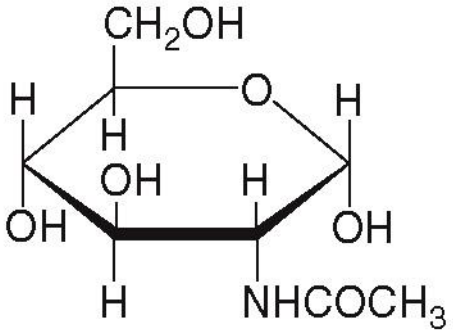
- Each blood type has the monosaccharides below:



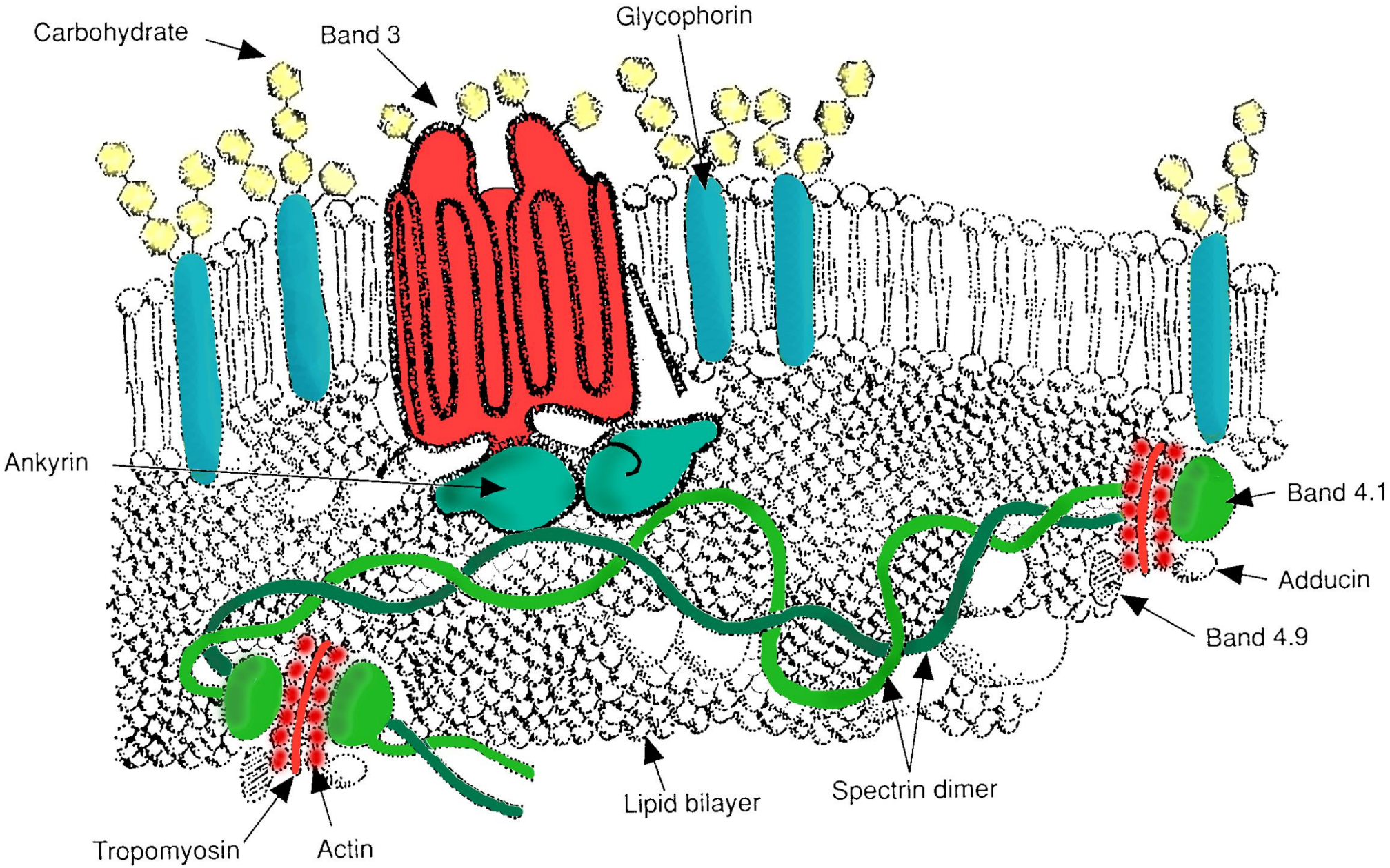
D-galactose



L-fucose



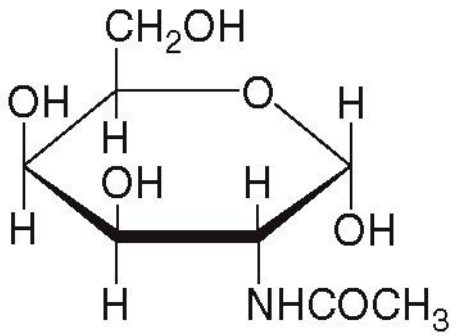
N-acetyl-D-glucosamine


Carbohydrate
Band 3
Glycophorin
Ankyrin
Band 4.1
Adducin
Band 4.9
Lipid bilayer
Spectrin dimer
Tropomyosin
Actin

Useful Carbohydrates

Blood Type

Type A blood contains a fourth monosaccharide:



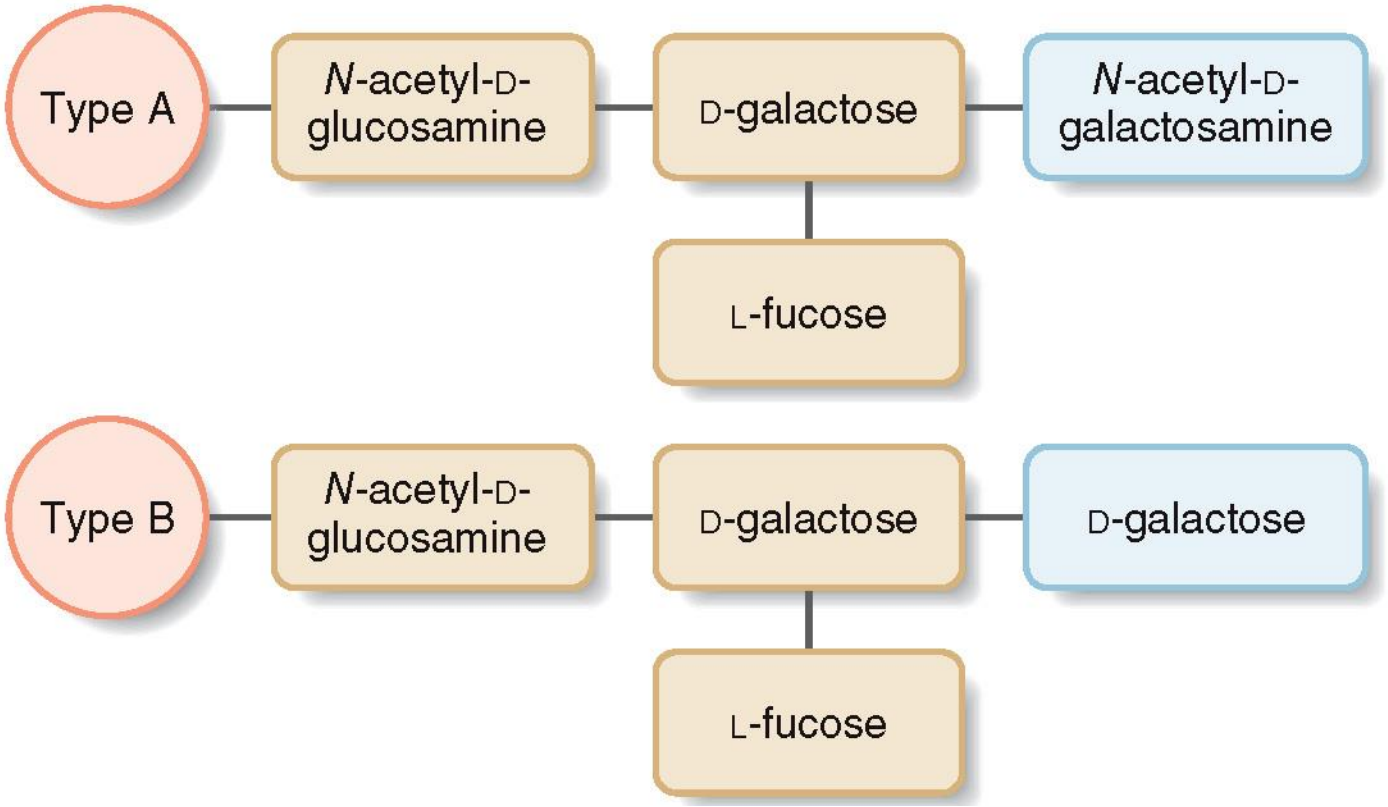
N-acetyl-D-galactosamine

Type B contains an additional D-galactose unit.

Type AB has both type A and type B carbohydrates.

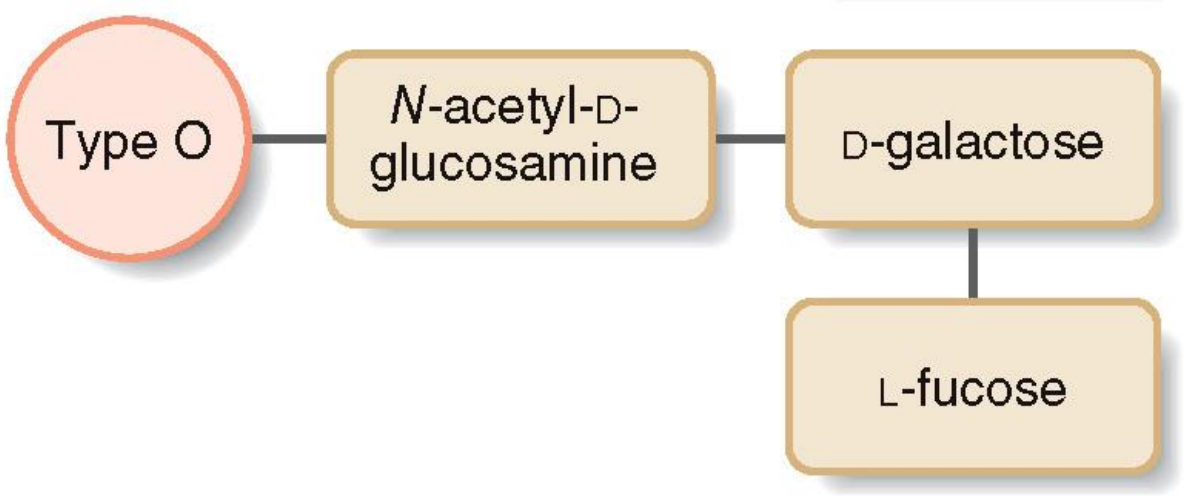
Useful Carbohydrates

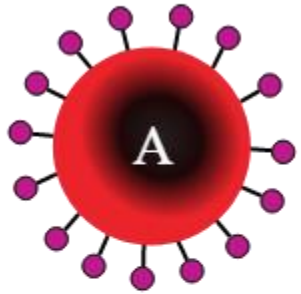
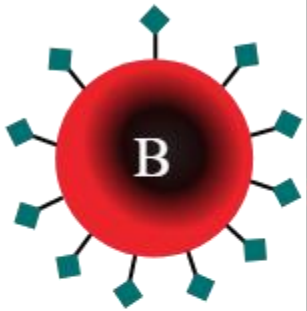
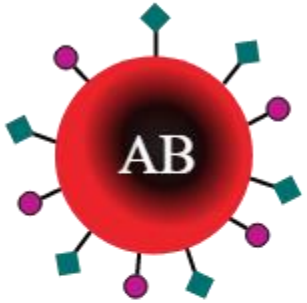
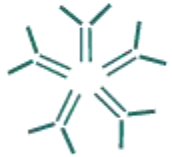
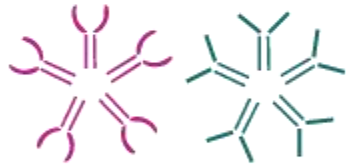
Blood Type



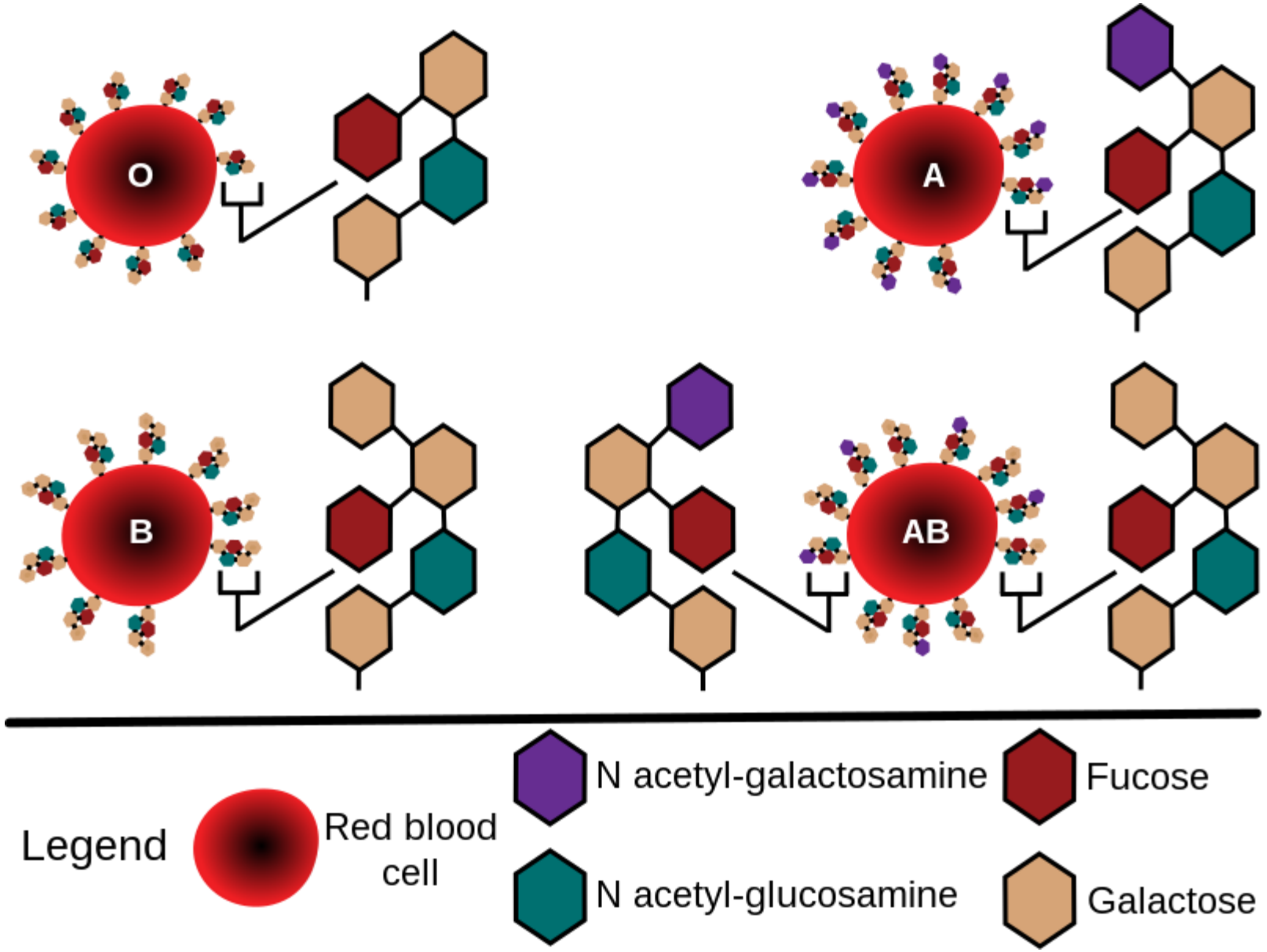
Useful Carbohydrates

Blood Type



	Group A	Group B	Group AB	Group O
Red blood cell type				
Antibodies in plasma	 Anti-B	Anti-A	None	 Anti-A and Anti-B
Antigens in red blood cell	A antigen	B antigen	A and B antigens	None

ABO blood group system: diagram showing the carbohydrate chains that determine the ABO blood group



Useful Carbohydrates

Blood Type

- The short polysaccharide chains distinguish one type of the red blood cell from another, and signal the cells about the foreign viruses, bacteria, and other agents.

- The blood of one individual may contain antibodies to another type.

- Those with type O blood are called universal donors, because people with any other blood type have no antibodies to type O.

- Those with type AB blood are universal recipients because their blood contains no antibodies to A, B, or O.

Useful Carbohydrates

Blood Type

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TABLE 20.2 Compatibility Chart of Blood Types

Blood Type	Can Receive Blood Type:	Can Donate to Someone of Blood Type:
A	A, O	A, AB
B	B, O	B, AB
AB	A, B, AB, O	AB
O	O	A, B, AB, O