CARBOHYDRATES

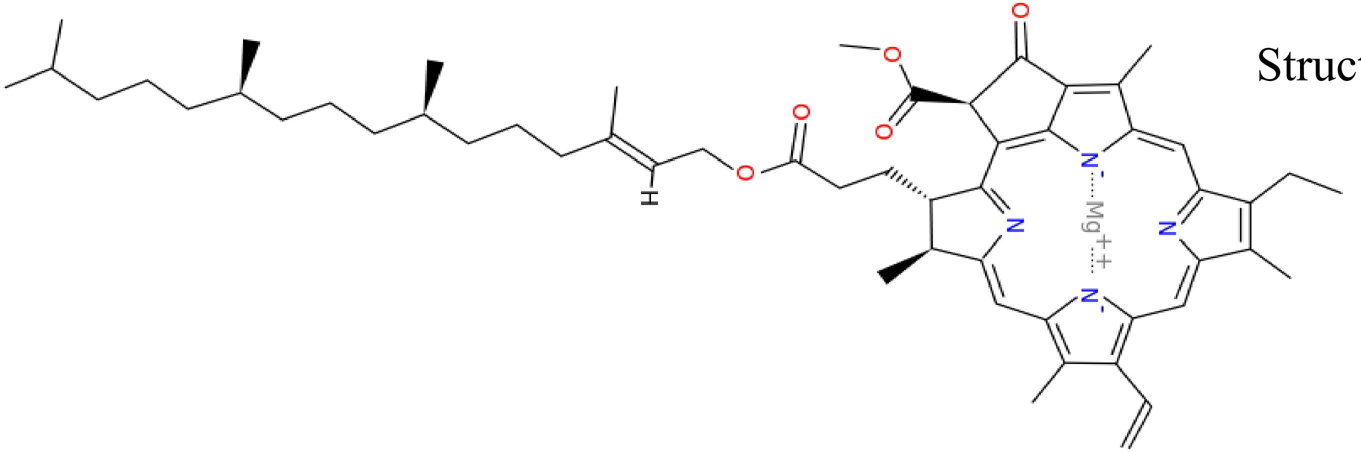
Deepak Kumar
Assistant Professor
Department Of Chemistry
C.L. Jain College, Firozabad

What are Carbohydrates?

- The Polyhydroxy Carbonyl Compounds (Aldehydes or Ketones) or the compounds that can be hydrolysed to either of the two

- Carbohydrates are produced by a process called Photosynthesis in green Plants

- Photosynthesis involves conversion of carbon dioxide and water into Glucose and Oxygen (In presence of Chlorophyll & sunlight)



Structure of Chlorophyll

Classification of Carbohydrates

- Carbohydrates can be classified as Sugars and Non-Sugars

- Sugars are further classified as

  - **Mono-Saccharide** : Simplest Carbohydrates which cannot be further hydrolysed into smaller units

    - Ex- Erythrose(A-3), Threose(A-3), Erythrulose(K-4), Ribose (A-5), Arabinose(A-5), Xylose (A-5), Lyxose (A-5) etc.
      (A-Aldose, K-Ketose): For simplifications (3- Triose, 4-Tetrose etc.)

  - **Oligo-Saccharide**: Which can be hydrolysed into definite number of monosaccharides (Generally books refer 2-10 units)
    - Ex- Sucrose (Di), Raffinose(Tri)

- Non-Sugars are also known as Polysaccharides (Glycan)

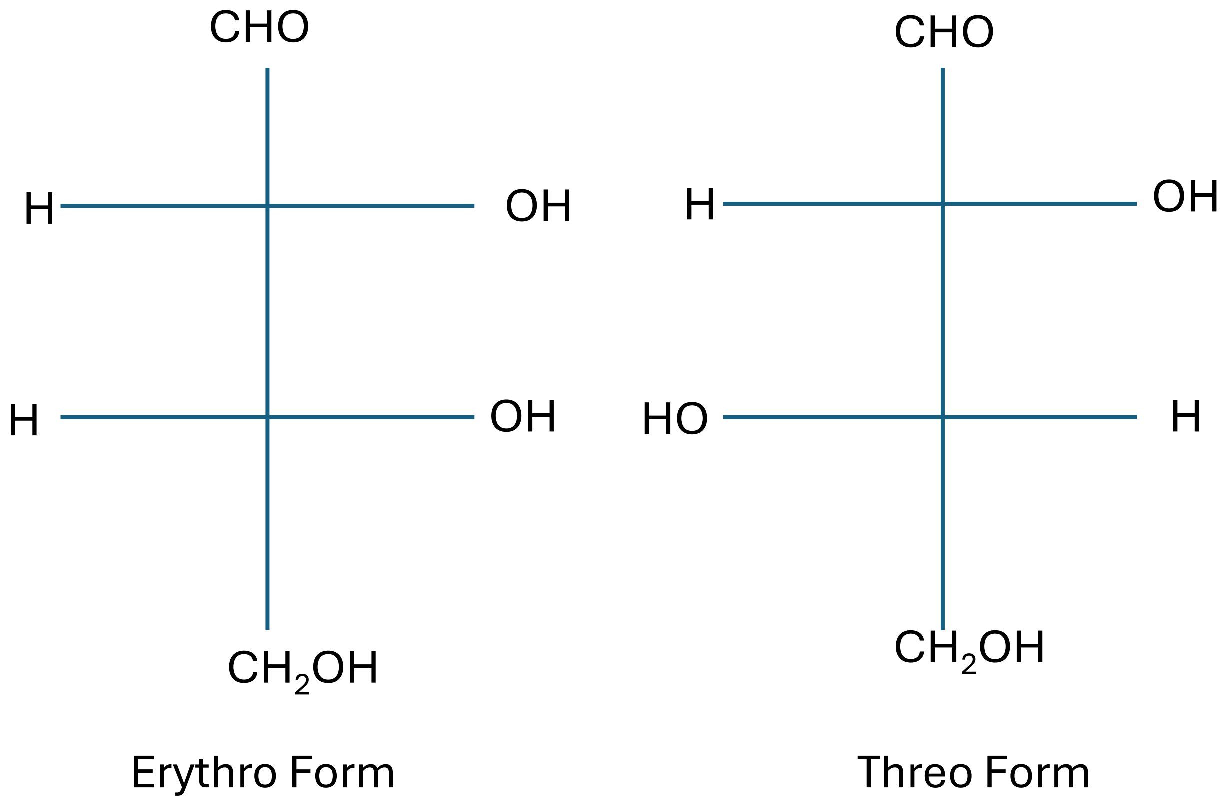
  - These are generally of high molecular weight, hydrolysed to very large number of monosaccharides (Hundreds or Thousands)

  - Homo polysaccharides: Are made up of all the same residue repeating
    - Ex- Starch (Glucose), glycogen (Glucose), and cellulose (Glucose),Inulin (Fructo-furanose) etc.

  - Hetero polysaccharides: Are made of various different types of residues
    - Ex- Heparin (Useful for Blood clotting) and peptidoglycan (Related to bacterial cytoplasmic membrane), Hyaluronic Acid (D-Gluconic acid + N-acetyl-glucosamine)

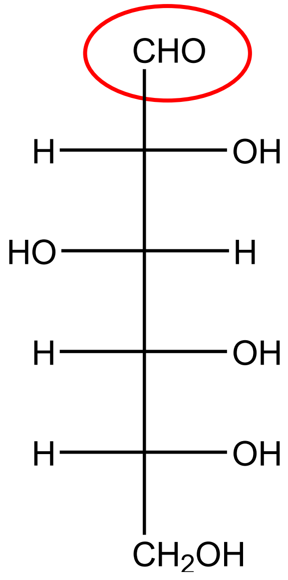
Erythro & Threo Diastereomers

- Compounds in which adjacent stereo-centres are located next to bottom carbon and two groups are same side of the fisher Projection, are known as Erythro and the other one is Threo (Useful for two stereo-genic Centres)

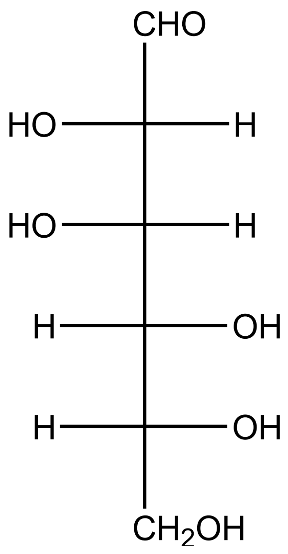


Epimers

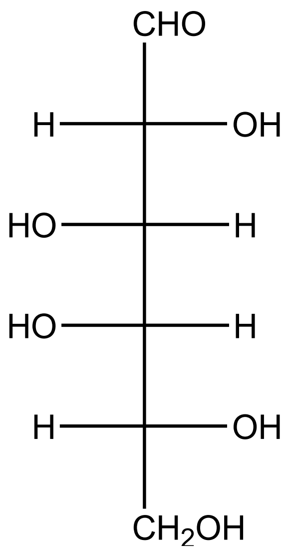
- Sugars having common configuration except at one carbon are called Epimers
    - Example 1- Glucose and Mannose are C-2 Epimers
    - Example 2- Glucose and Galactose are C-4 Epimers



D-Glucose



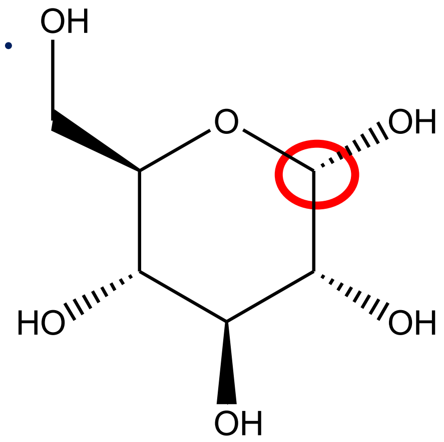
D-Mannose



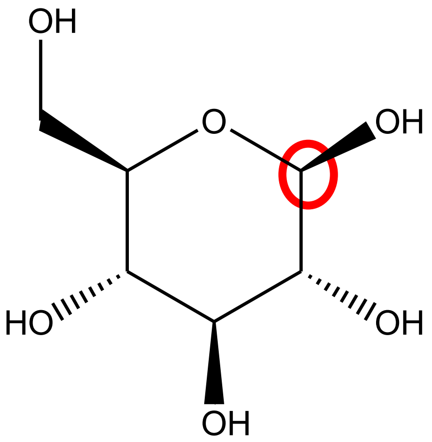
D-Galactose

Anomers

- Sugars having common configuration except at C-1 are called Anomers
  - Sugar must be in its Cyclic Form to exhibit Anomers
  - In open chain form the carbon will be Achiral as it’s in planar form
- Anomer is an Epimer at Hemiacetal/ Hemiketal carbon in cyclic saccharide
- Different Anomers have different Physical Properties, melting point, specific rotation etc.



alpha-D-Glucose

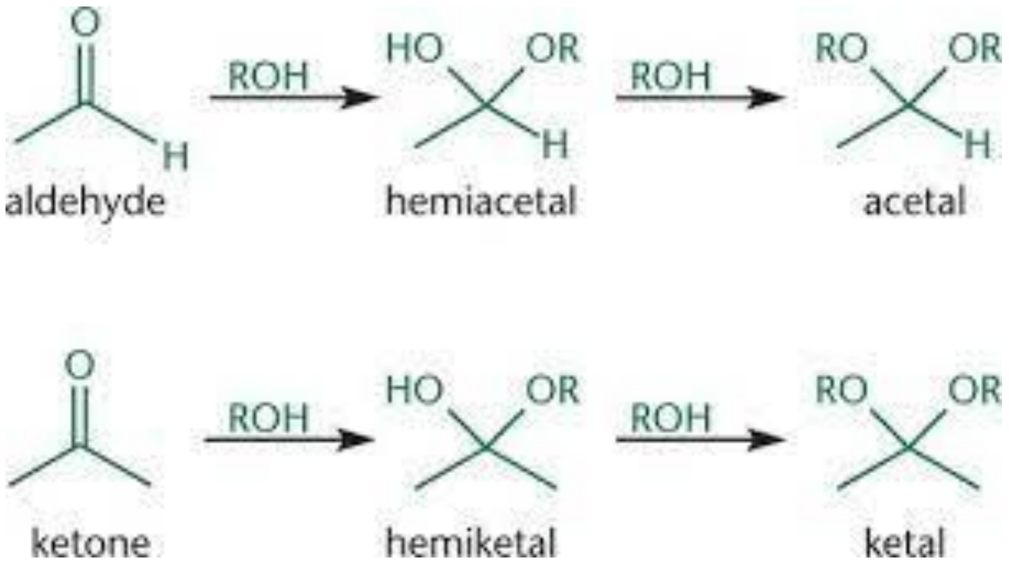


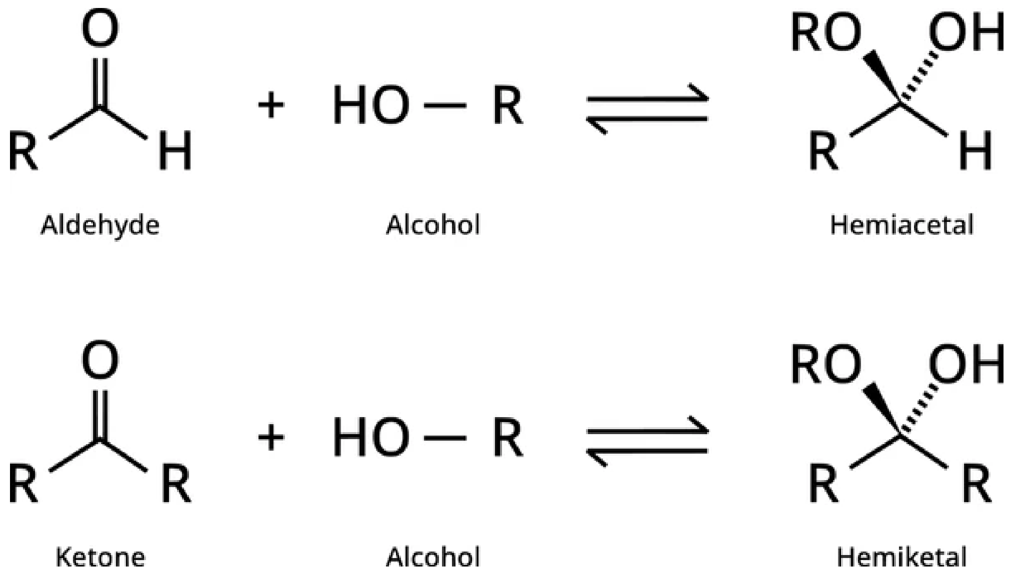
beta-D-Glucose

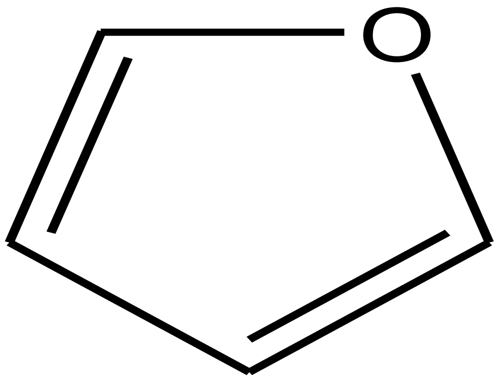
Glucose

- One of the most important Sugars
- Occurrence: Honey, Ripe Grapes, Mangoes, Human blood etc.
- Colourless, Crystalline compound (Melting point 419 K)
- Solubility: Water > Alcohol > ethers
- Contains lesser sweetness as compared to Sucrose (Sugarcane, Dates, sugar beets etc.)

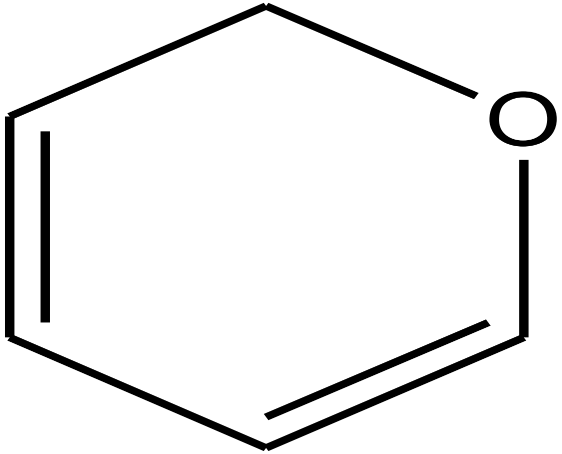
Acetals & Ketals Vs Hemiketals and Hemiketals





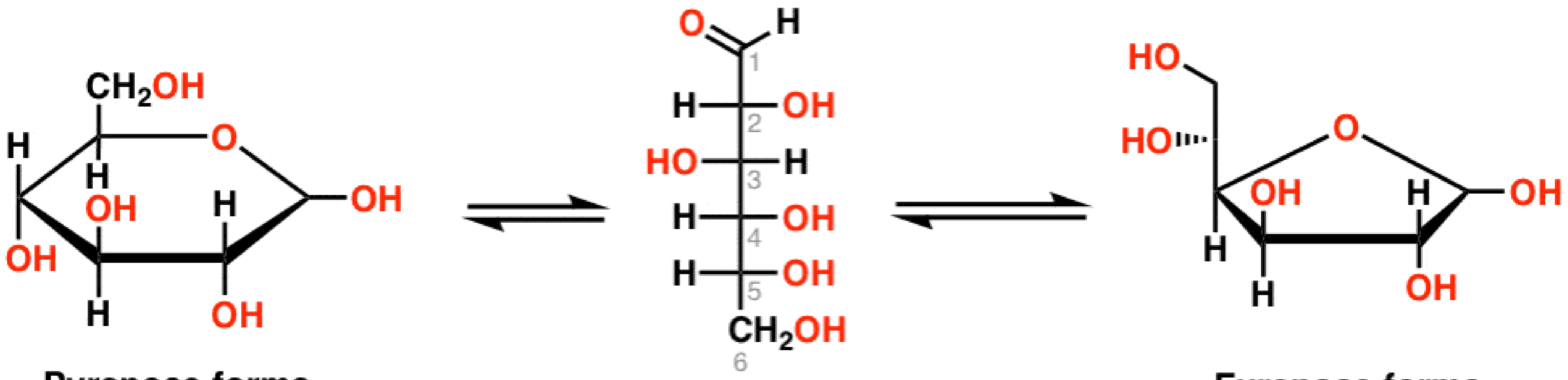


Furan



Pyran

The pyranose form of glucose dominates (>99%) at equilibrium in aqueous solution



Pyranose forms
(α + β)

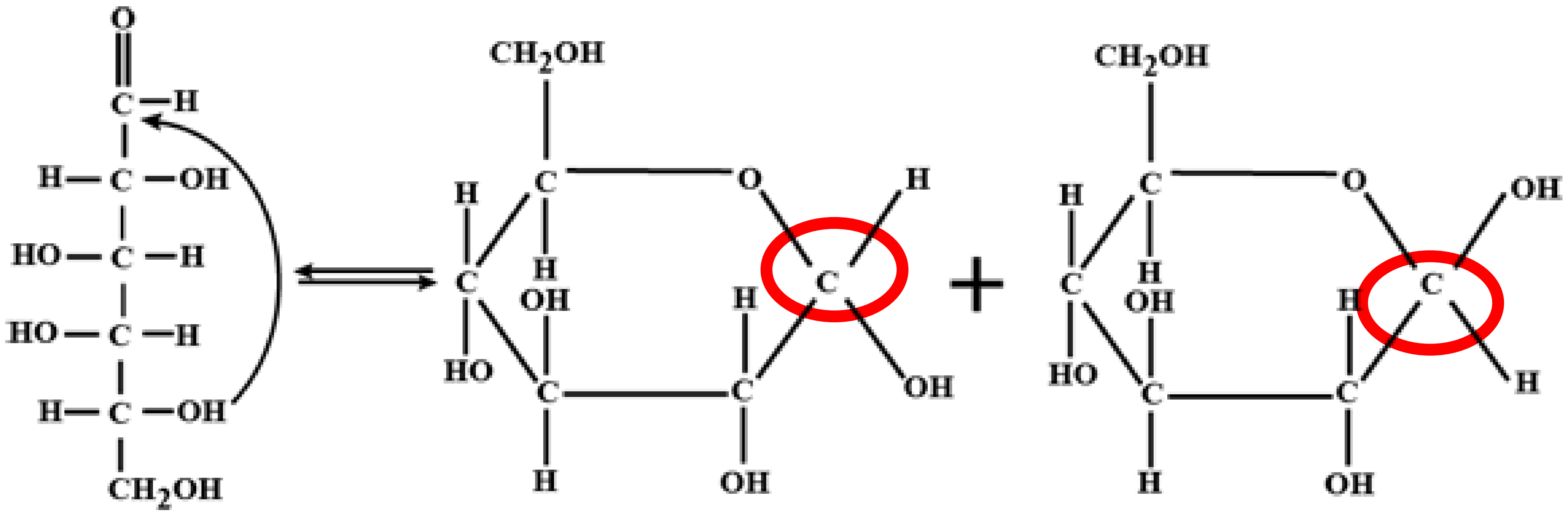
Open-chain form

Furanose forms
(α + β)

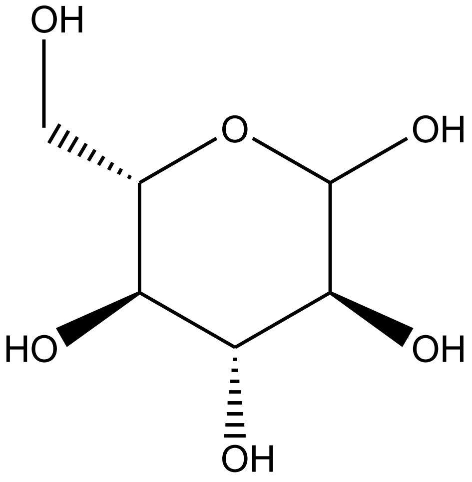
99%

0.25%

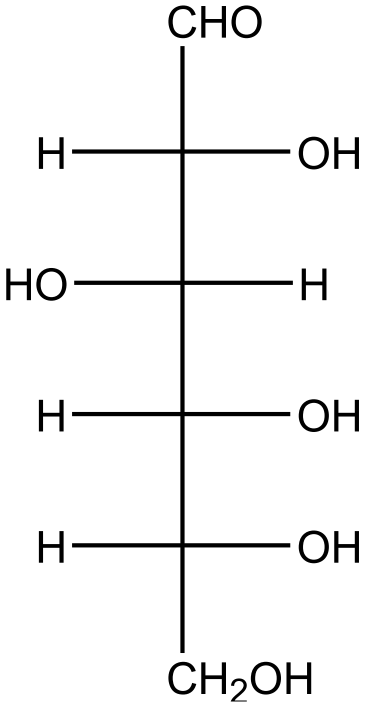
< 1%

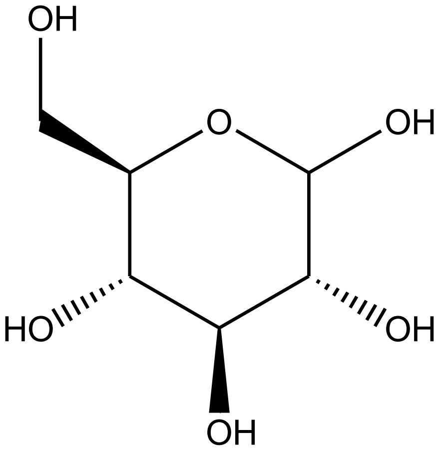


D-glucose α-D-glucopyranose β-D-glucopyranose

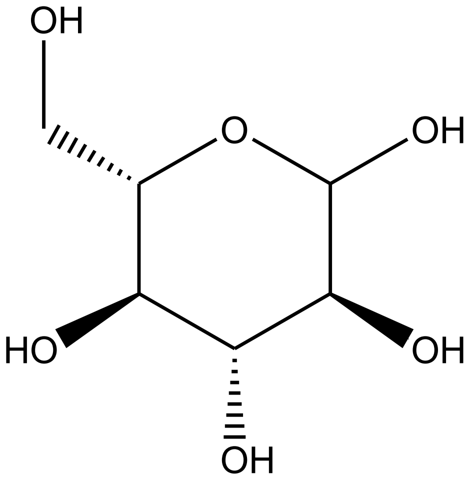


L-glucopyranose

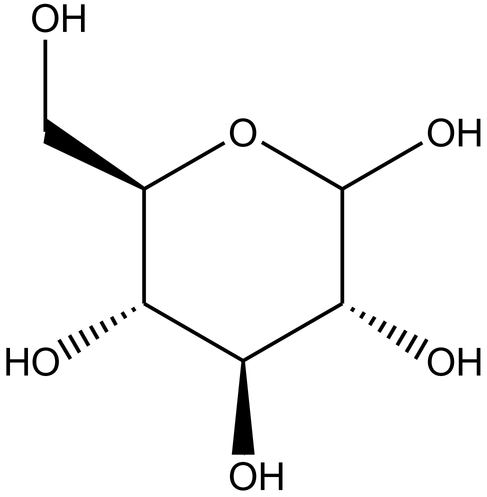




D-glucopyranose



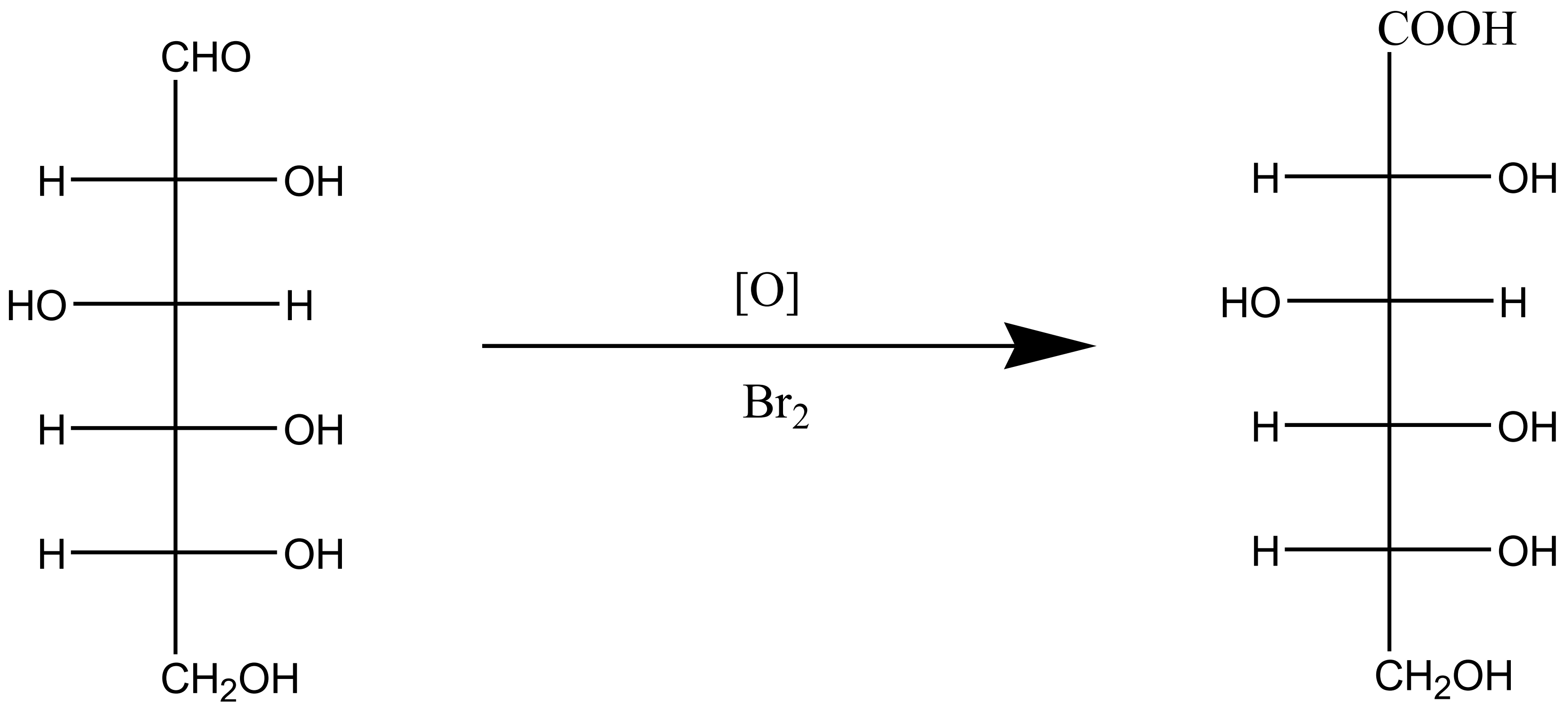
l-glucopyranose



d-glucopyranose

Chemical Properties of Glucose

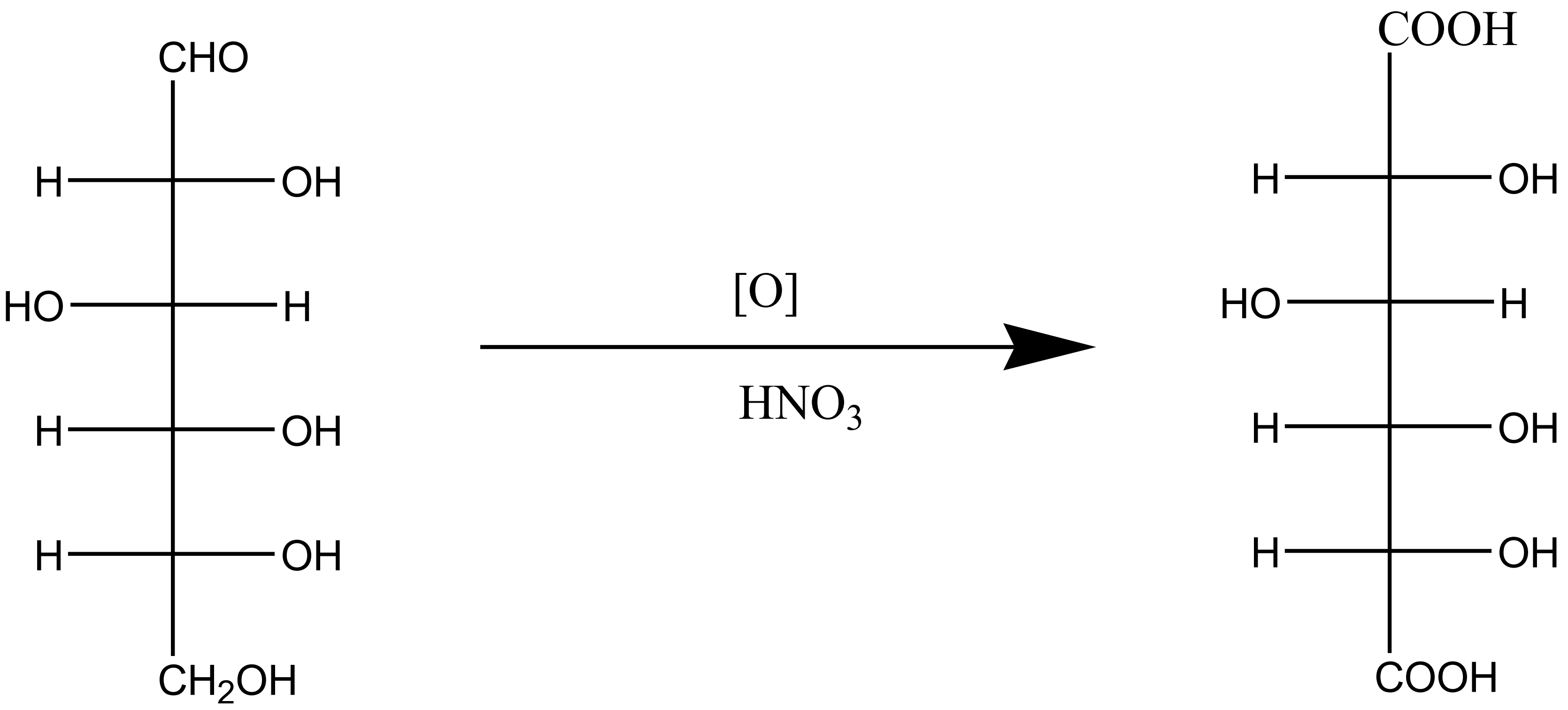
Mild Oxidation : Reagents- Tollen's Reagent, Fehling Solution, Bromine-water etc.



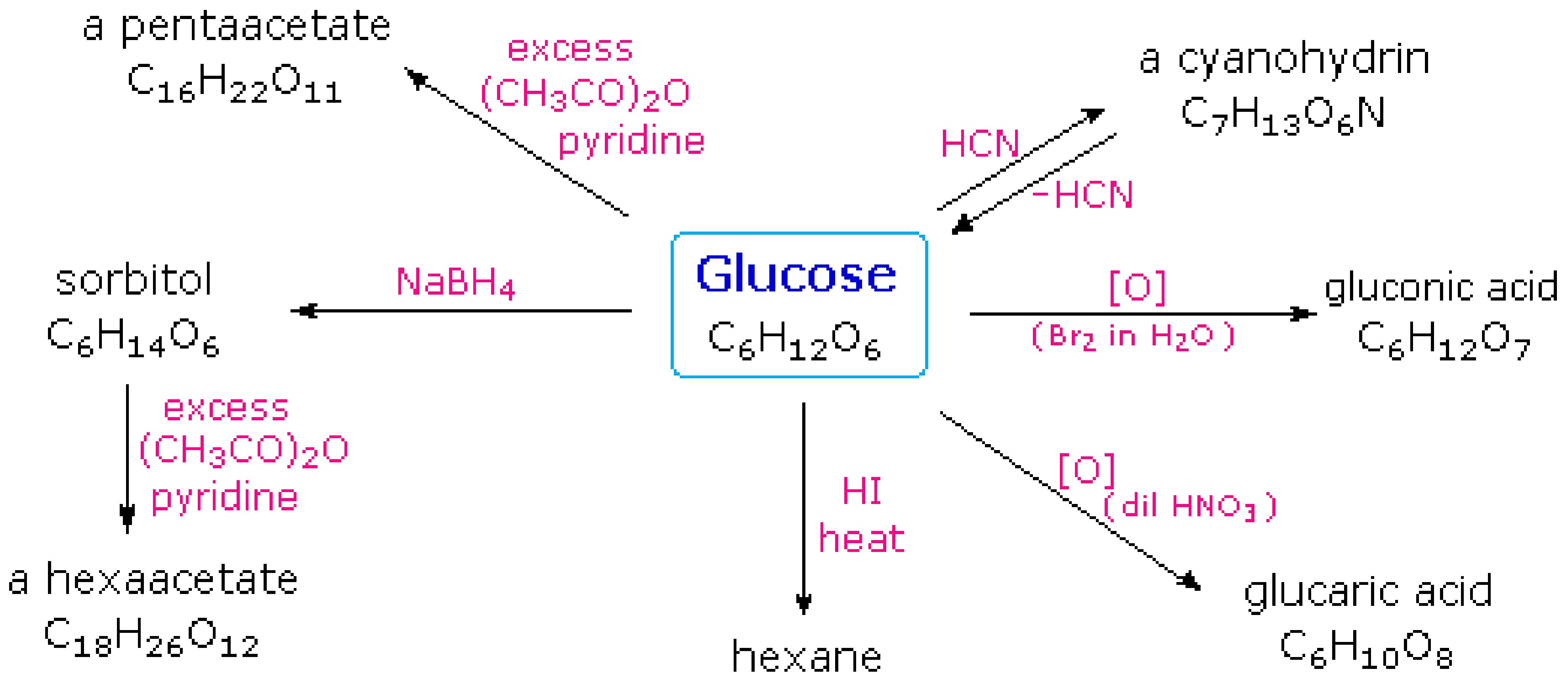
Tollen's Reagent: Ammoniacal Silver Nitrate
{ Ag_2O----------- Ag}
Fehling Solution: Alkaline Copper Sulphate
{ CuO----------------- Cu_2O (Red ppt.) }

Gluconic Acid

Strong Oxidation :



Saccharic/ Glucaric Acid

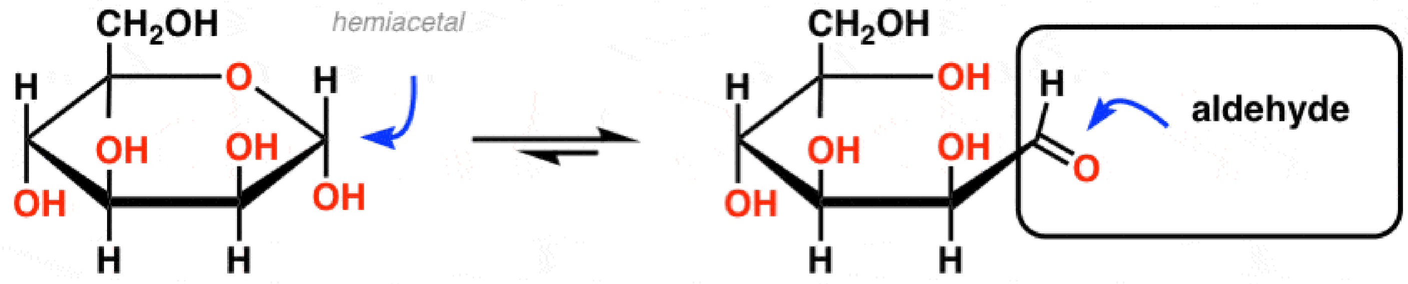

a pentaacetate
$C_{16}H_{22}O_{11}$
excess
$(CH_3CO)_2O$
pyridine
a cyanohydrin
$C_7H_{13}O_6N$
HCN
-HCN
sorbitol
$C_6H_{14}O_6$
$NaBH_4$
Glucose
$C_6H_{12}O_6$
[O]
(Br_2 in H_2O)
gluconic acid
$C_6H_{12}O_7$
excess
$(CH_3CO)_2O$
pyridine
HI
heat
[O]
(dil HNO_3)
a hexaacetate
$C_{18}H_{26}O_{12}$
hexane
glucaric acid
$C_6H_{10}O_8$

Reducing and Non-Reducing Sugars

- The sugar which reduces the Fehling's solution and Tollen's reagent is known as Reducing Sugar
    - Example: Glucose, Fructose
    - Contains free aldehydic or ketonic group
    - Anomeric carbon of the reducing sugars contain OH group
    - Generally, all monosaccharides and some disaccharides are Reducing Sugars

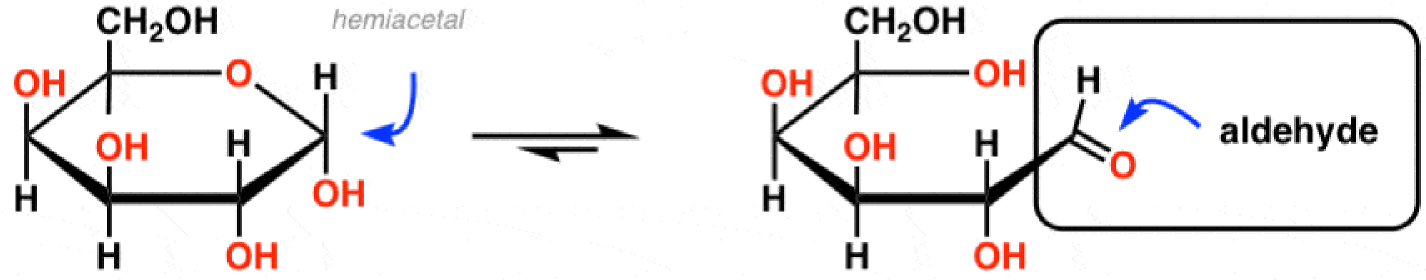
- Sugars, which don't respond to the above mentioned, are non-reducing sugars
    - Example: Sucrose
    - The Anomeric carbon of the Non-Reducing Sugars do not contain OH group

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



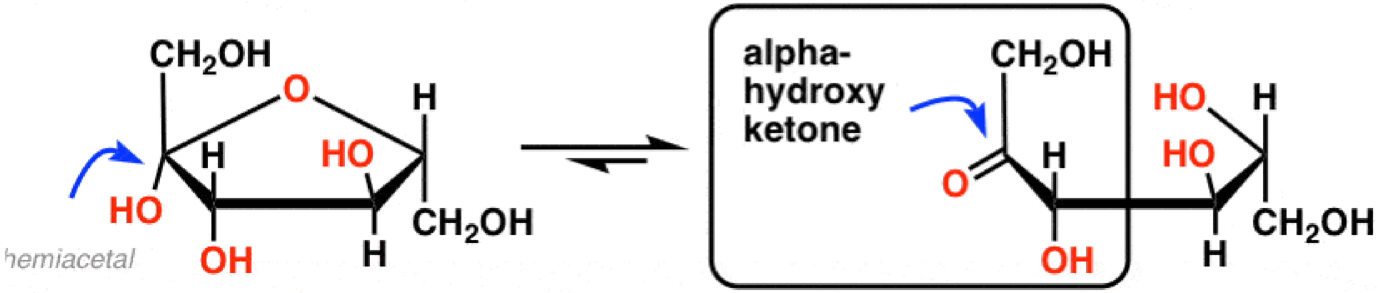
D-Mannose

D-Mannose (open-chain aldehyde)



D-Galactose

D-Galactose (open-chain aldehyde)

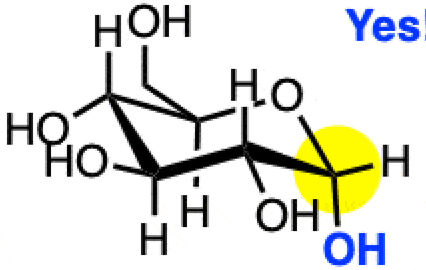


D-Fructose

D-Fructose (keto form)

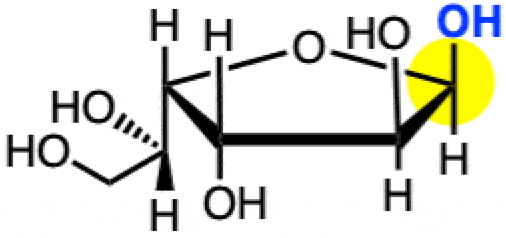
Quiz: Reducing Sugar or Non Reducing Sugar?

A)



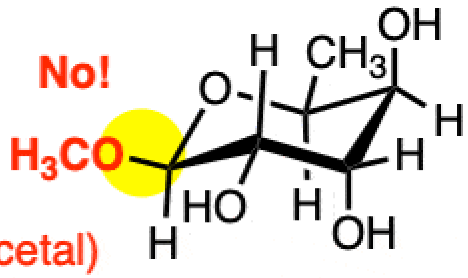
Yes!

B)



Yes!

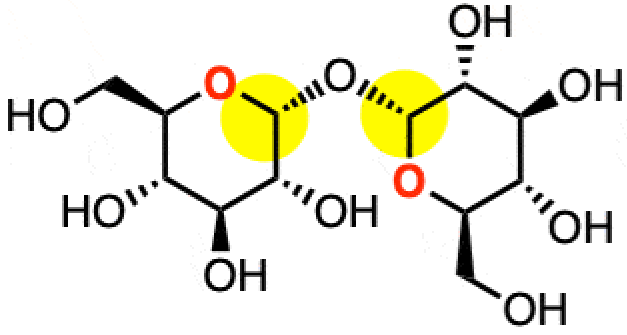
C)



No!

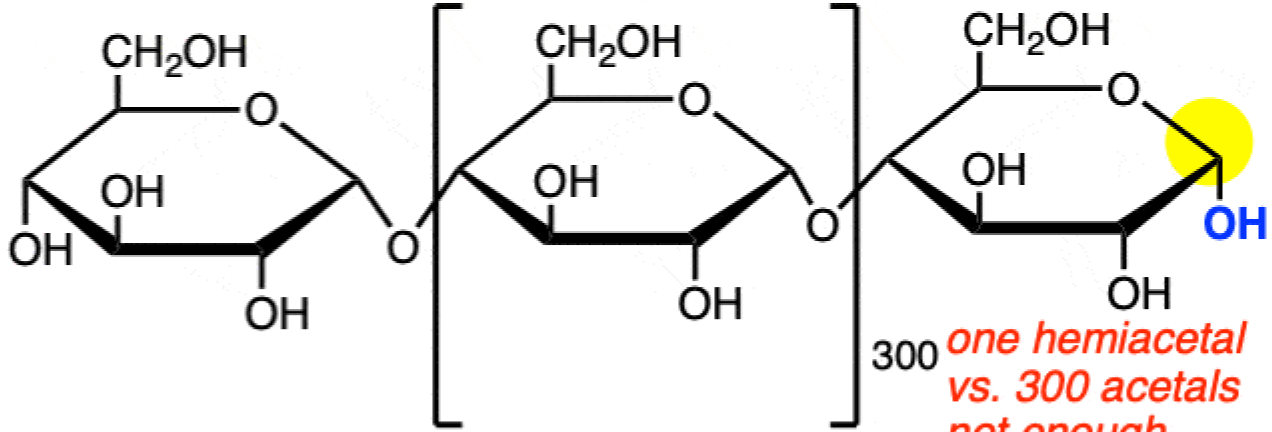
(acetal)

D)



No!

E)



No!

one hemiacetal vs. 300 acetals not enough

Refresh page to flip back

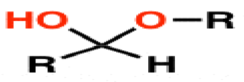
MOC Quiz ID: 2292

Summary

Any sugar* containing a hemiacetal is a reducing sugar.

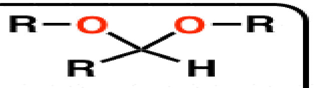
**for our purposes here, "sugar" refers to mono- and di-saccharides, not complex carbohydrates like starch, glycogen, and cellulose*

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

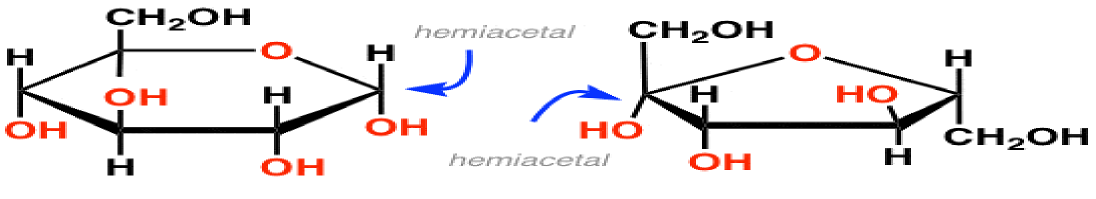


Acetal (Ketal)

- 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:



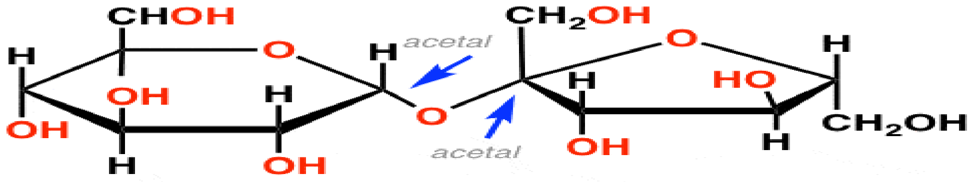
α-D-glucose   D-Fructose

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

A sugar without a hemiacetal is a non-reducing sugar

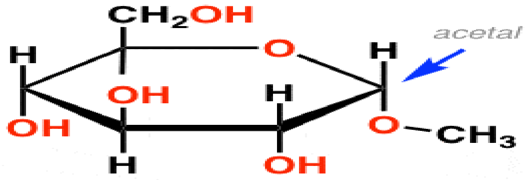
Acetals are "locked" and **not** in equilibrium with a ring-opened form with an aldehyde. They will therefore not react as a reducing agent.

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.

Inversion of Sugars

- A change in the sign of specific rotation of a sugar solution after hydrolysis is known as Inversion of Sugar

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O$$

Sucrose	Glucose	Fructose
(dextro – rotatory)	(dextro – rotatory)	(leavo – rotatory)
$+66.5^{0}$	$+52.5^{0}$	-92^{0}
	(leavo – rotatory)	

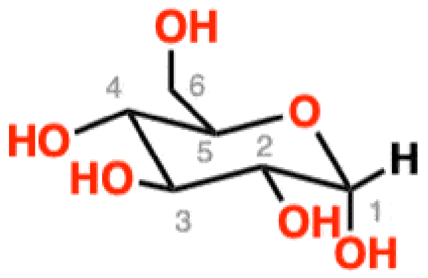
Mutarotation

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

"beta" (β) isomer:



α-D-Glucose

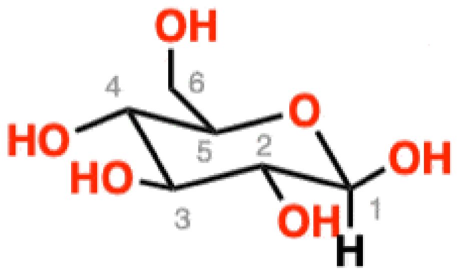
"alpha" (α) isomer:

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*



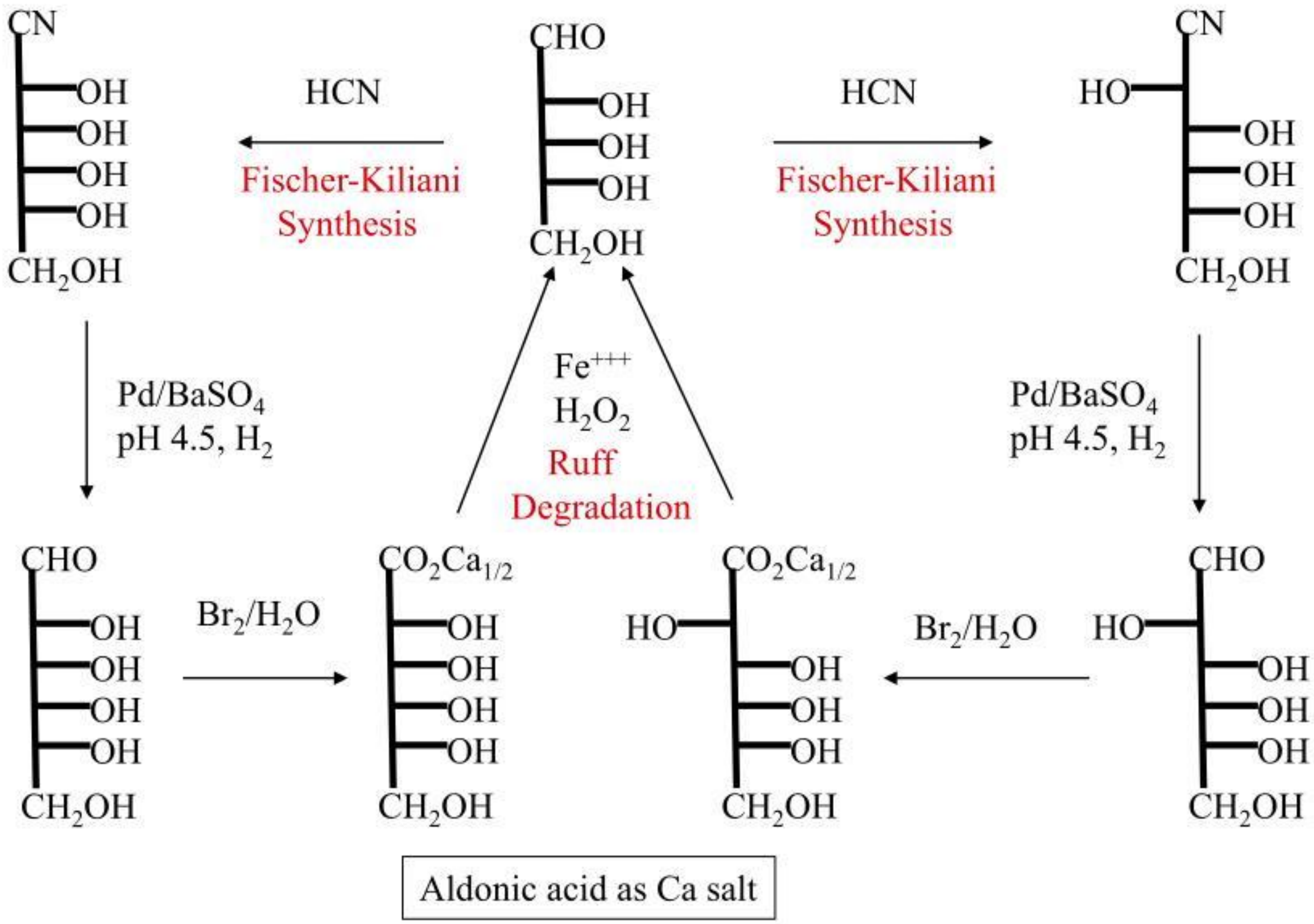
β-D-Glucose

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.

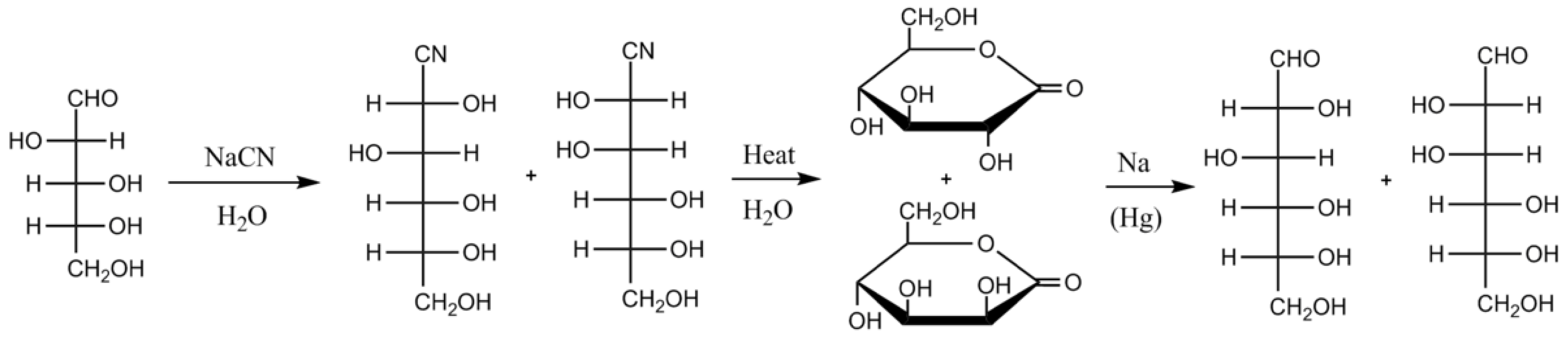
Note: Glycosides do not exhibit mutarotation

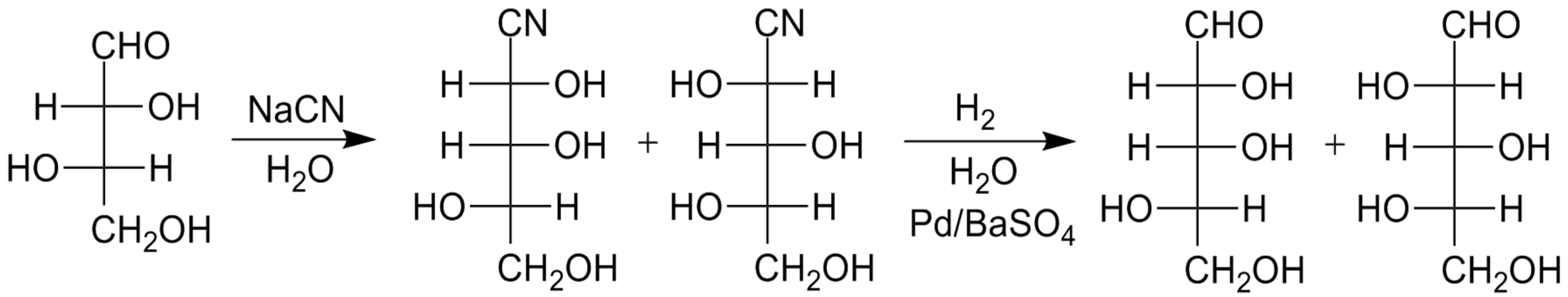
Chain Lengthening and Shortening of Aldoses



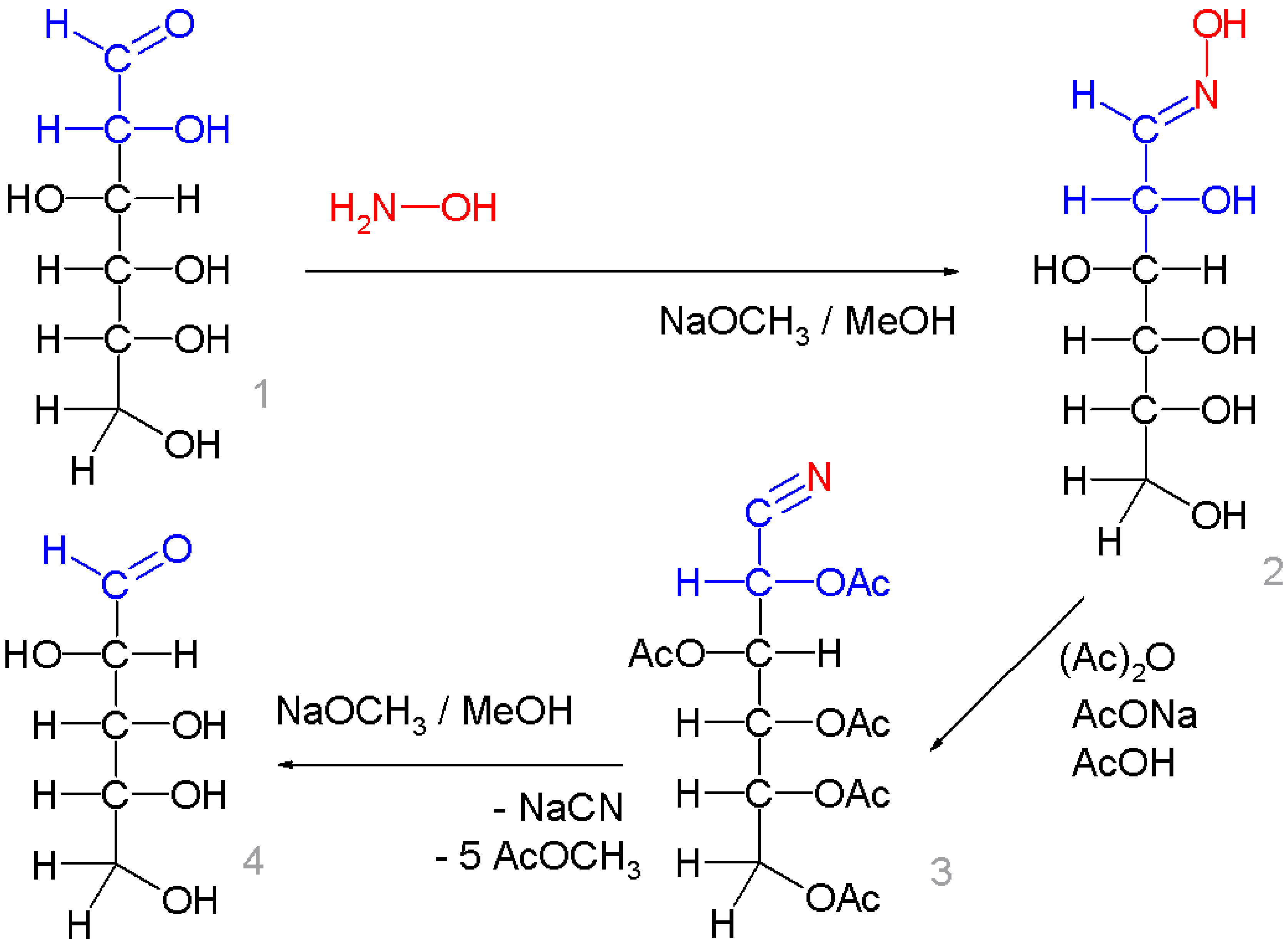
Fenton's Reagent: $Fe^{3+}/\ H_2O_2$

Classic Vs Modern Kiliani-Fischer Synthesis

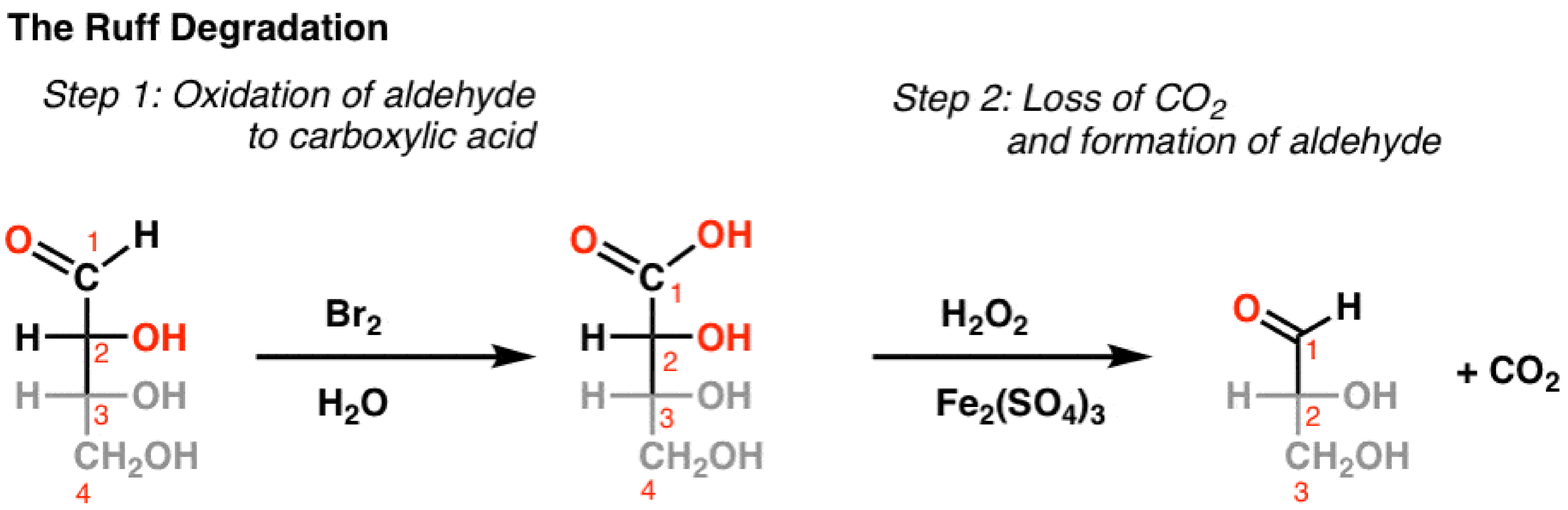




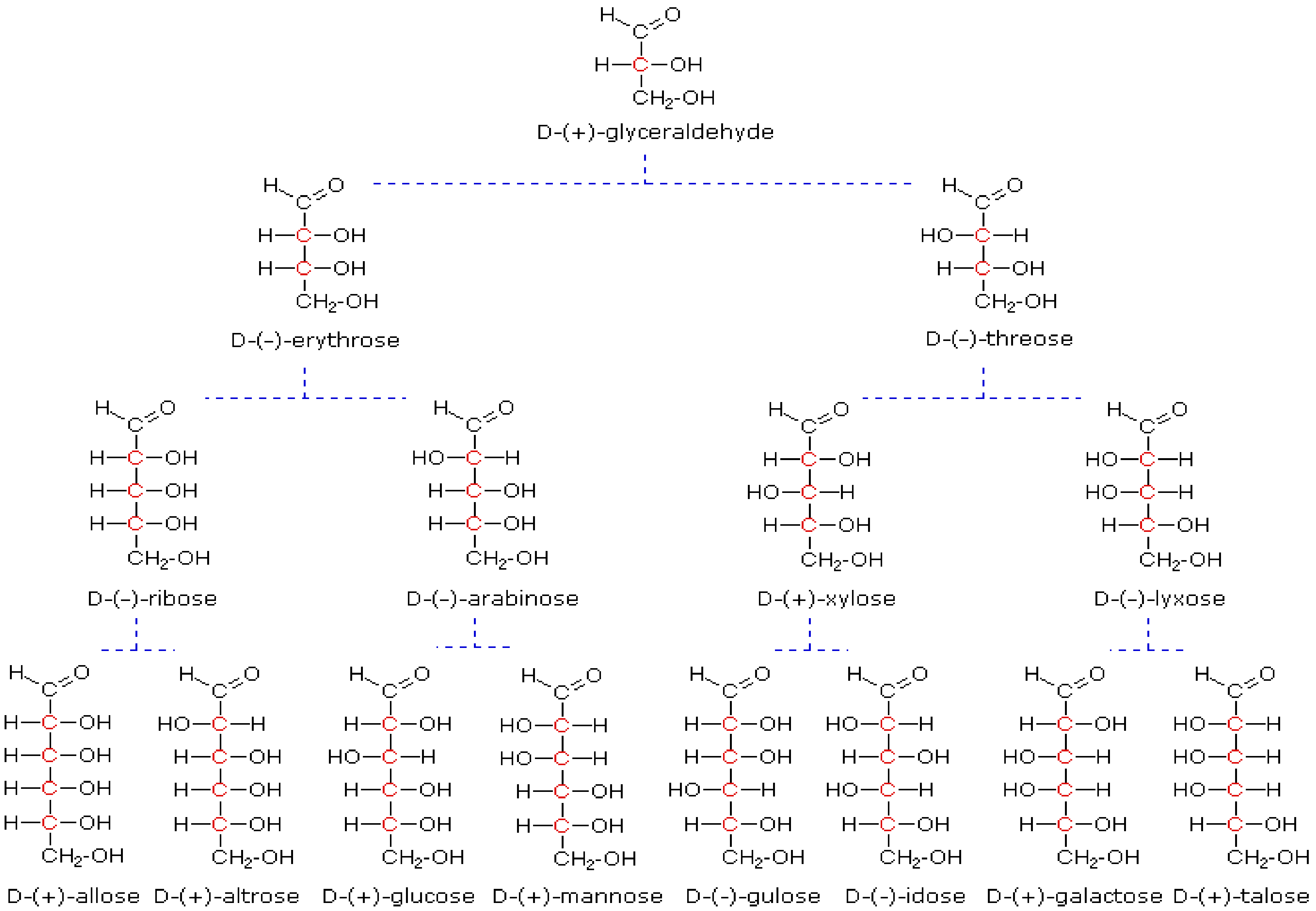
Wohl's Degradation



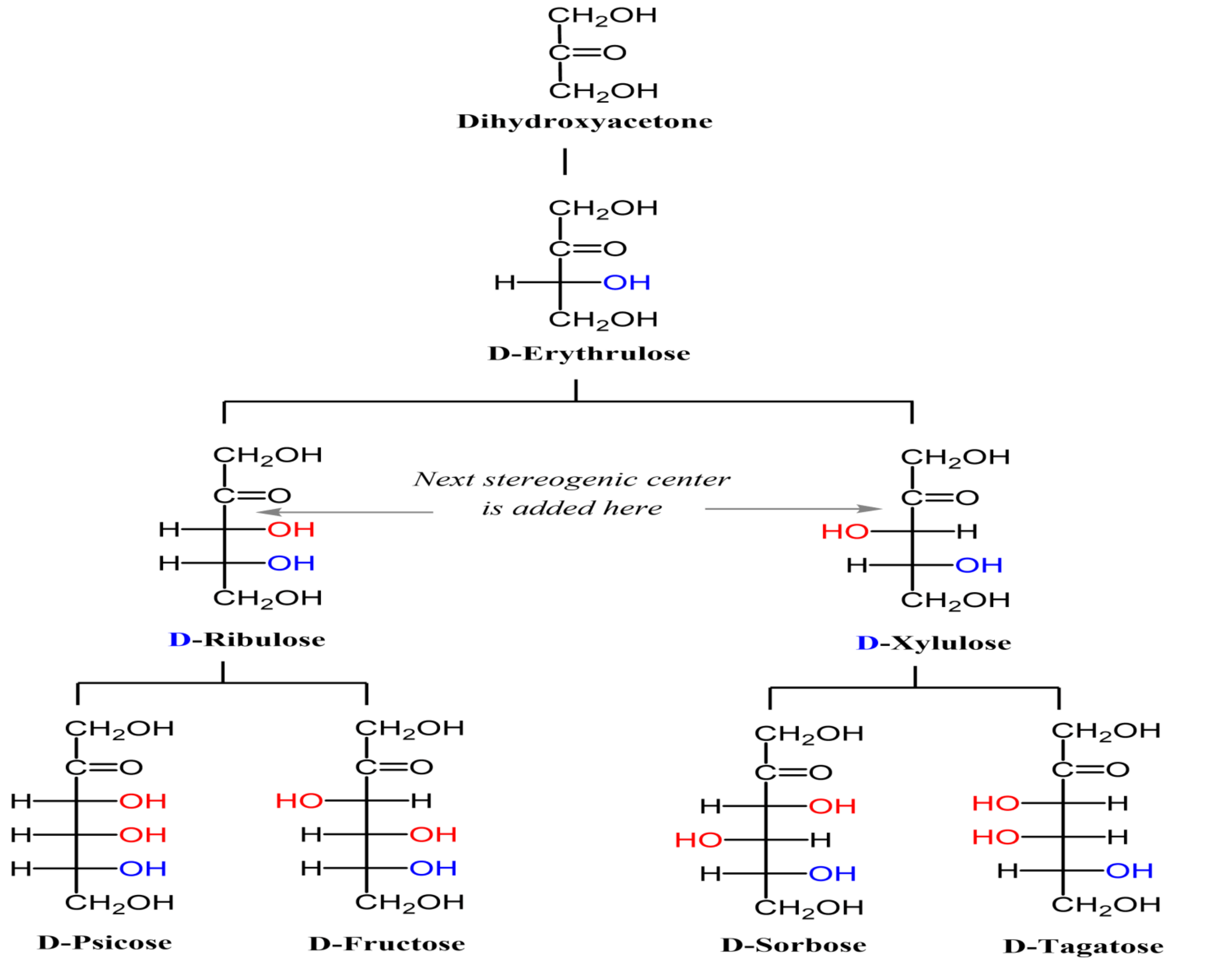
Ruff's Degradation



Family of D-Aldose



Family of D-Ketose



Each chiral center is added below the carbonyl group generating two additional stereoisomers.

References and Suggested Readings

- Carbohydrate Chemistry, by B.G. Davis, A.J. Fairbanks, Oxford University Press.
- Essentials of Carbohydrates, by J.F. Robyt, Springer advanced text in chemistry.
- Organic Chemistry, by I.L. Finar,, Pearson Education.
- https://heecontent.upsdc.gov.in/Home.aspx (For online learning)
- NPTEL official Courses/ YouTube/ related lecture series.
- Books published in Hindi by S. Chand Publication, Pragati Publication, Krishna Publication etc. for B.Sc. Semester 1st Students. (Only Recommended for Hindi Medium Students)