CARBOHYDRATE

"It is the harmonious and synchronous progress of chemical reactions in body which leads to life".

Dr. Suman Adhikari

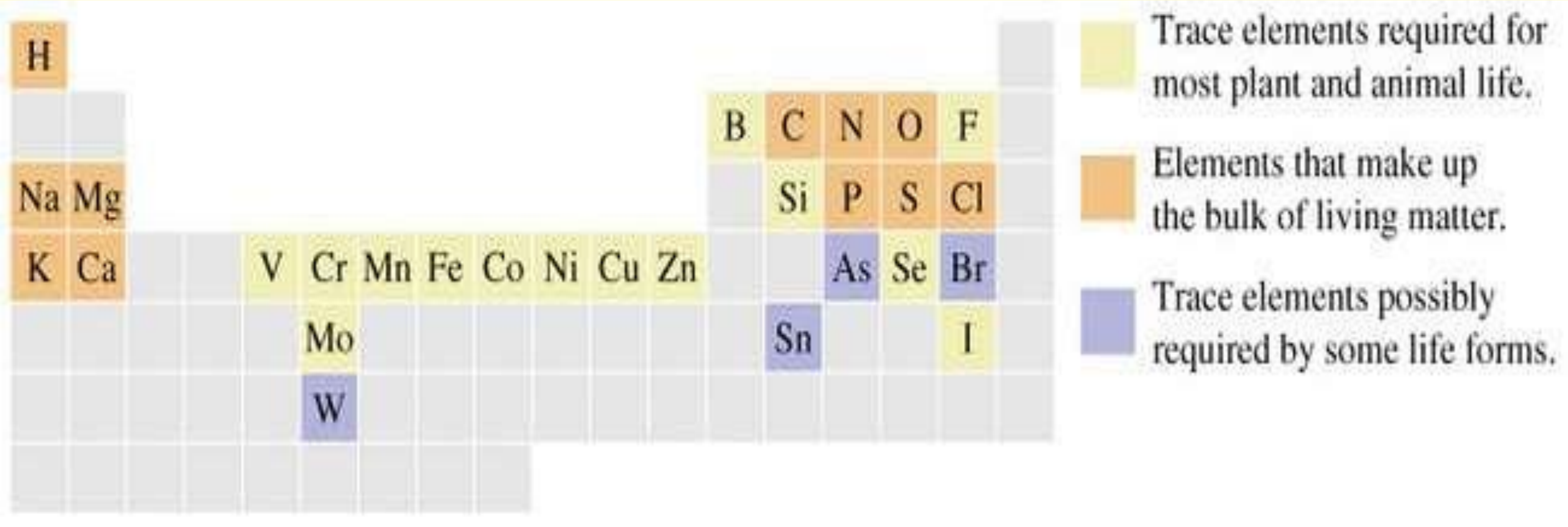
Department of Chemistry,

Govt. Degree college, Dharmanagar

Email: sumanadhi@gmail.com

Phone no.: 9774354025

Chemical Structure of Living Matter:



- 🟨 Trace elements required for most plant and animal life.
- 🟧 Elements that make up the bulk of living matter.
- 🟪 Trace elements possibly required by some life forms.

- *Carbohydrates are important constituents of all living organisms and have a variety of different functions.*

- **carbohydrates have molecular formulas $C_x(H_2O)_y$.**

- Carbohydrates are polyhydroxy aldehydes such as D-glucose, polyhydroxy ketones such as D-fructose, and compounds such as sucrose that can be hydrolyzed to polyhydroxy aldehydes or polyhydroxy ketones.

Classification

- Monosaccharides

  The simplest carbohydrates that cannot be hydrolysed further to give simpler unit of polyhydroxy aldehyde or ketone is called a monosaccharide. E,g Glucos.

- Oligosaccharides

  An oligosaccharide yields 3–10 monosaccharide units on hydrolysis. *E,g Sucrose.*

- Polysaccharides

  Polysaccharides are hydrolyzed to more than 10 monosaccharide units.

  Starch and cellulose.

Reducing sugar and Non Reducing Sugar

The carbohydrates may also be classified as either reducing or nonreducing sugars. All those carbohydrates which reduce Fehling’s solution and Tollens’ reagent are referred to as reducing sugars. All monosaccharides whether aldose or ketose are *reducing sugars.*

Tollen’s: $Ag^+ \rightarrow Ag$ (silver mirror)

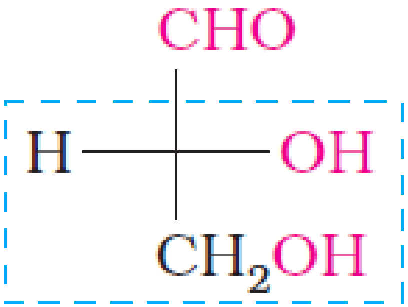
Fehling’s or Benedict’s: Cu^{3+} (blue) → Cu^{2+} (red ppt)

These are reactions of aldehydes and alpha hydroxyketones.

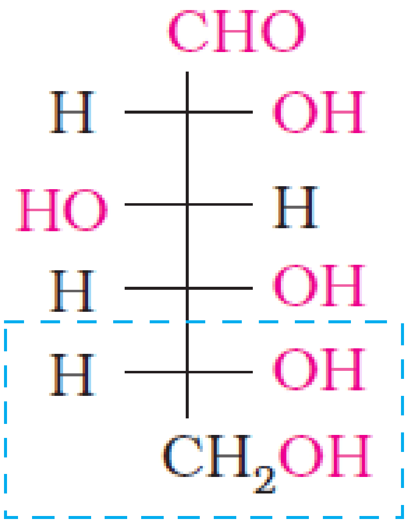
Most disaccharides are reducing sugars.

Sucrose (table sugar), a disaccharide, is <u>not</u> a reducing sugar.

All those compounds which can be chemically correlated to (+) isomer of glyceraldehyde are said to have D-configuration whereas those which can be correlated to (–) isomer of glyceraldehyde are said to have L—configuration. As in (+) glucose, —OH on the lowest asymmetric carbon is on the right side which is comparable to (+) glyceraldehyde, so it is assigned D-configuration.



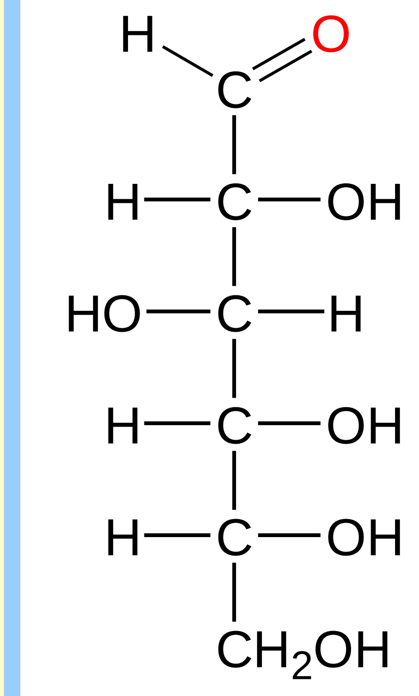
D– (+) – Glyceraldehyde



D–(+) – Glucose

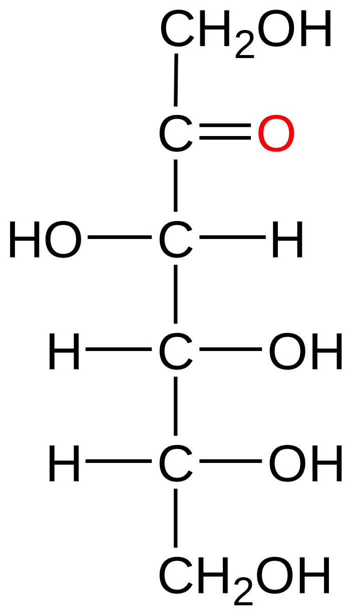
Monosaccharides

Aldoses (e.g., glucose) have an aldehyde group at one end.



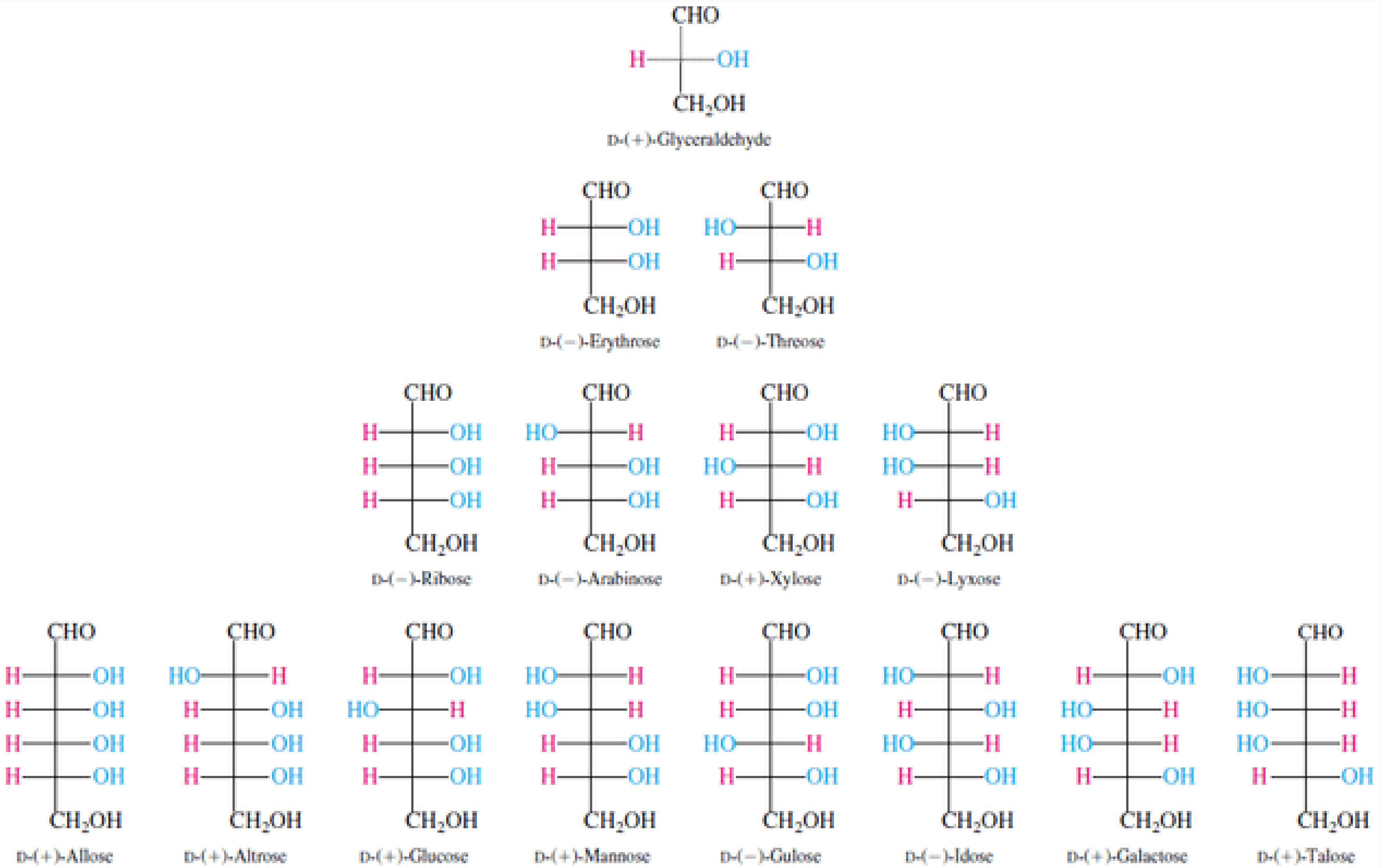
D-glucose

Ketoses (e.g., fructose) have a keto group, usually at C2.



D-fructose

Carbohydrate Family



D-(+)-Glyceraldehyde

D-(−)-Erythrose

D-(−)-Threose

D-(−)-Ribose

D-(−)-Arabinose

D-(+)-Xylose

D-(−)-Lyxose

D-(+)-Allose

D-(+)-Altrose

D-(+)-Glucose

D-(+)-Mannose

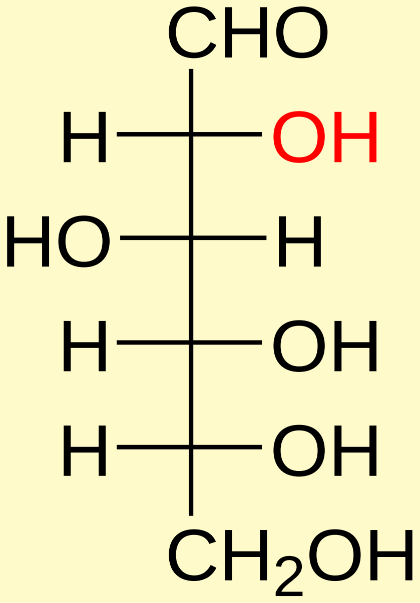
D-(−)-Gulose

D-(−)-Idose

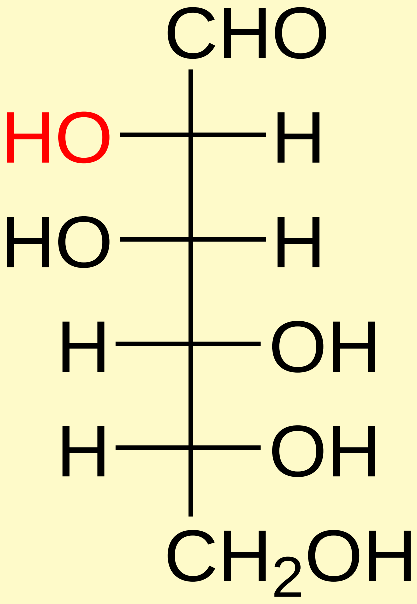
D-(+)-Galactose

D-(+)-Talose

Epimers : stereoisomers that differ only in configuration about one chiral center.



D-glucose



D-mannose

epimers

EPIMERIZATION

- The sugars α-glucose and β-glucose are epimers.
- Epimerisation is a chemical process where an epimer istransformed into its chiral counterpart. It can happen in condensed tannins depolymerisation reactions. Epimerisation can be spontaneous(generally
a slow process), or catalyzed by enzymes, e.g.the epimerization between the sugarsN-acetylglucosamine andN-acetylmann

Preparation of glucose

From sucrose (cane sugar): sucrose is boil with dilute HCl or H_2SO_4 in alcoholic solution, glucose and fructose are obtained in equal amounts,

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

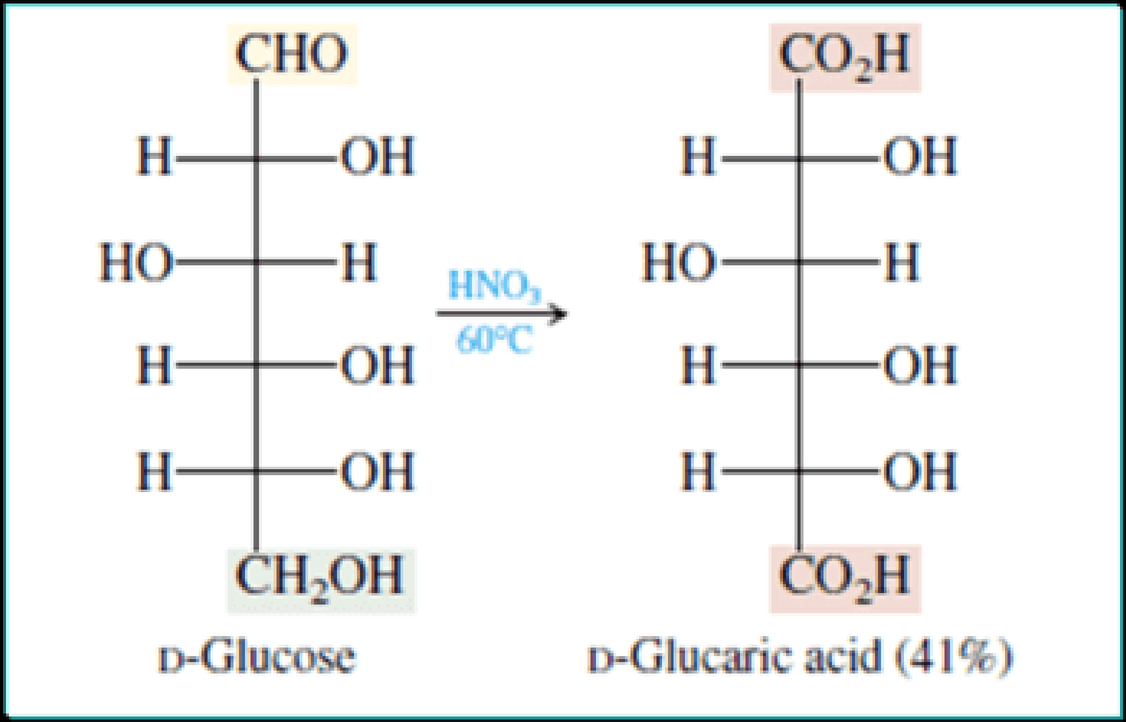
Form starch: Hydrolysis of starch

$$(C_6H_{12}O_5)_n + nH_2O \xrightarrow{H^+} (C_6H_{12}O_6)_n$$

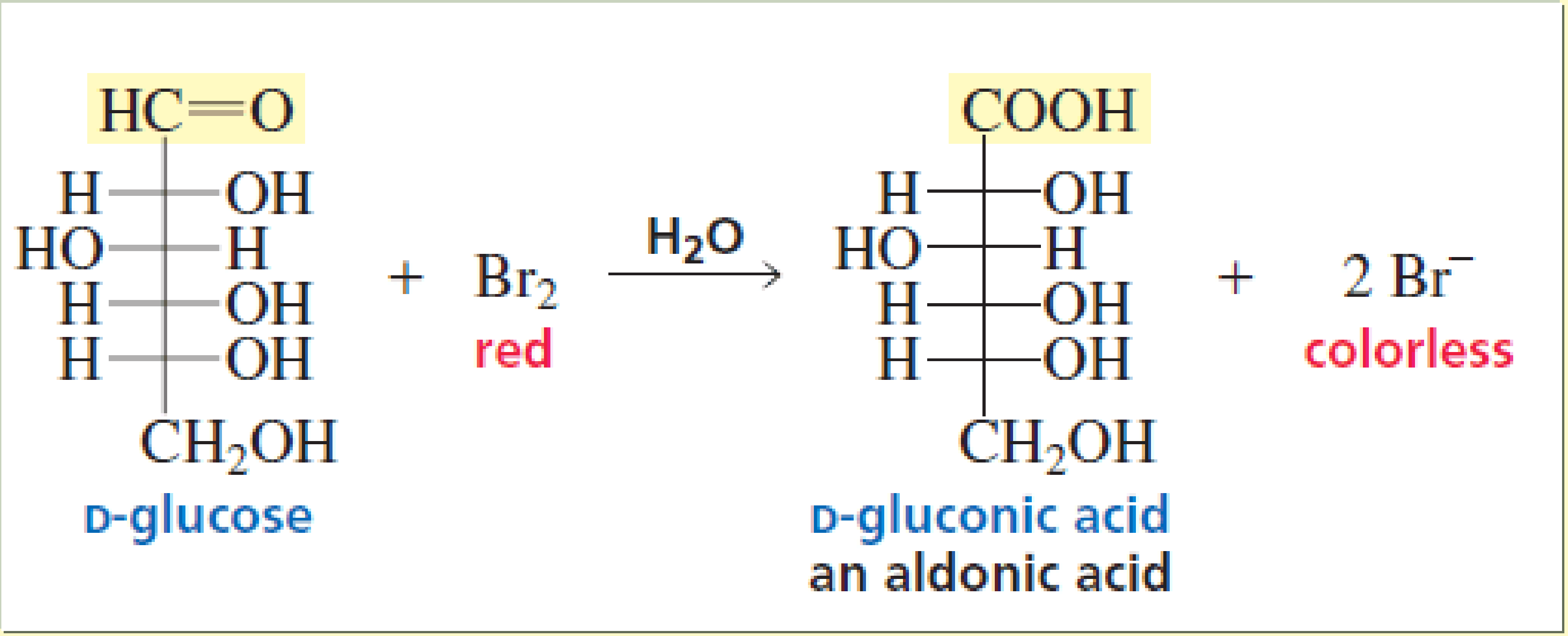
Reaction of glucose

Oxidation:

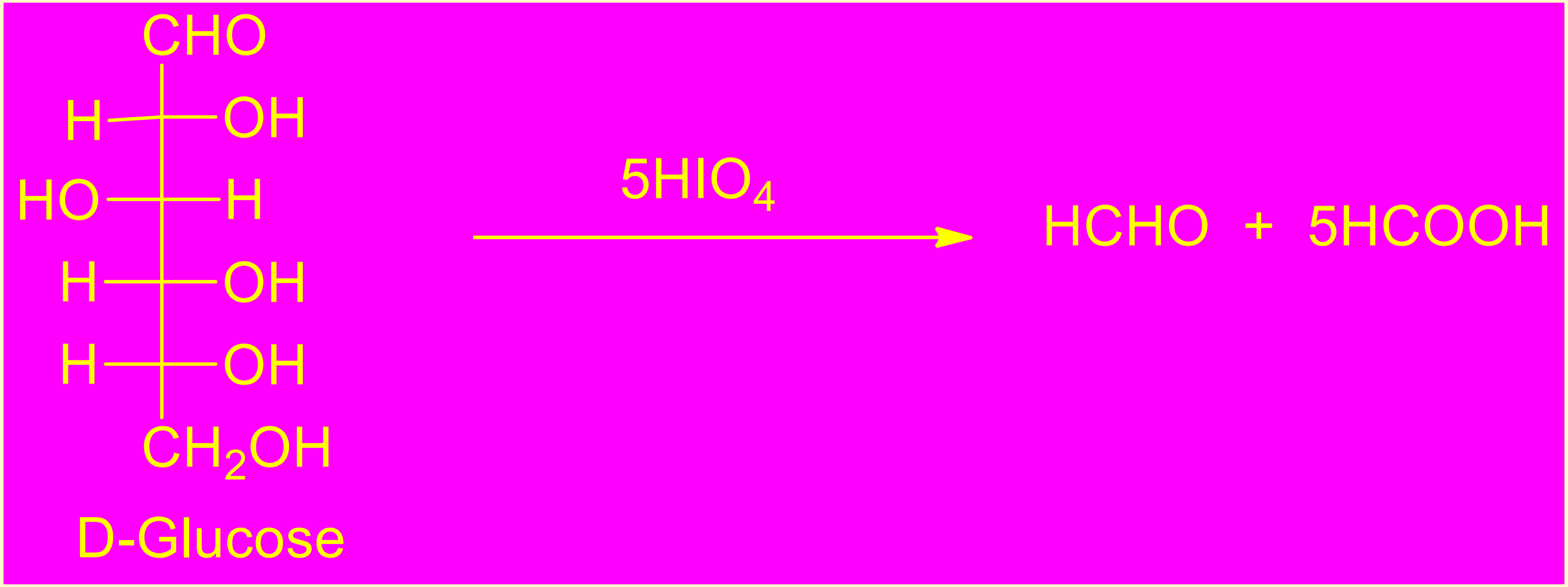
i) On oxidation with nitric acid glucose produces glucaric acid



ii) On oxidation with bromine water glucose produces gluconic acid. Bromine when it is added to the sugar is a mild oxidizing agent and easily oxidizes the aldehyde group, but it cannot oxidize ketones or alcohols.



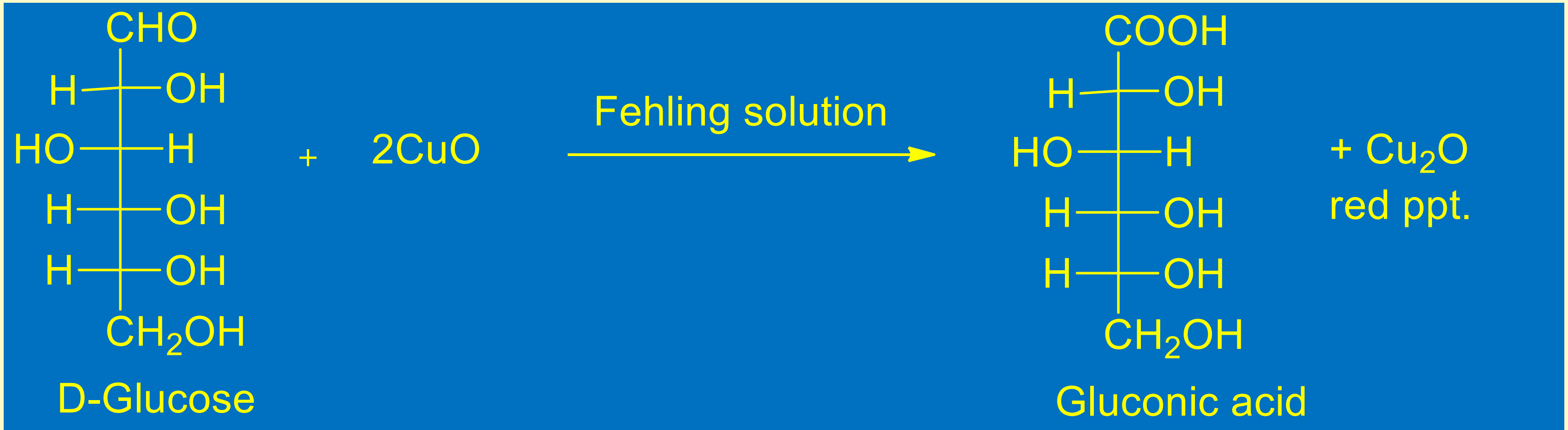
ii) On oxidation with periodic acid (strong oxidising agent) glucose produces 1 molecule formaldehyde and 5 molecules formic acid.

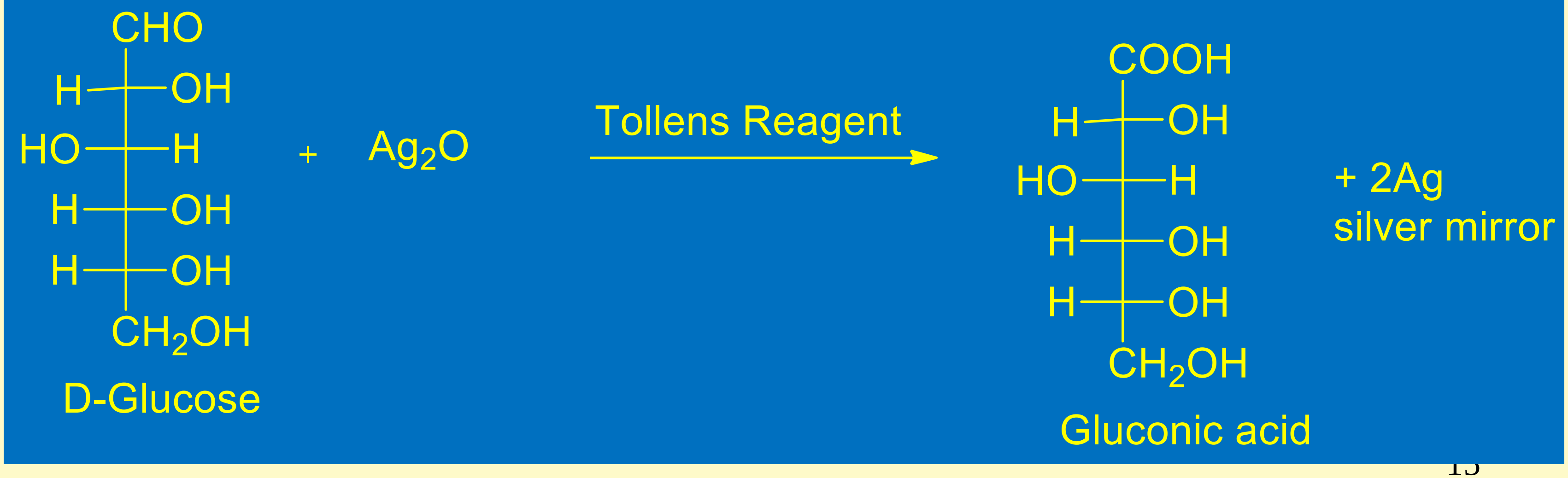


$$\text{D-Glucose} \xrightarrow{5HIO_4} HCHO + 5HCOOH$$

D-Glucose

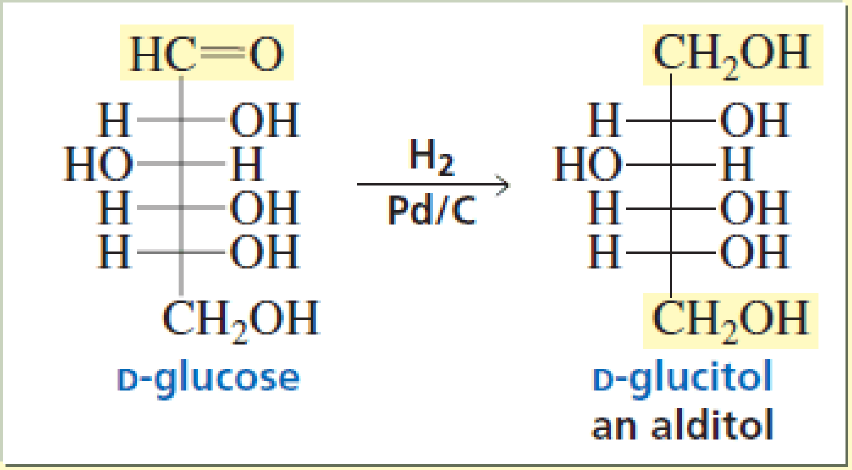
Reaction of glucose as a reducing agent:



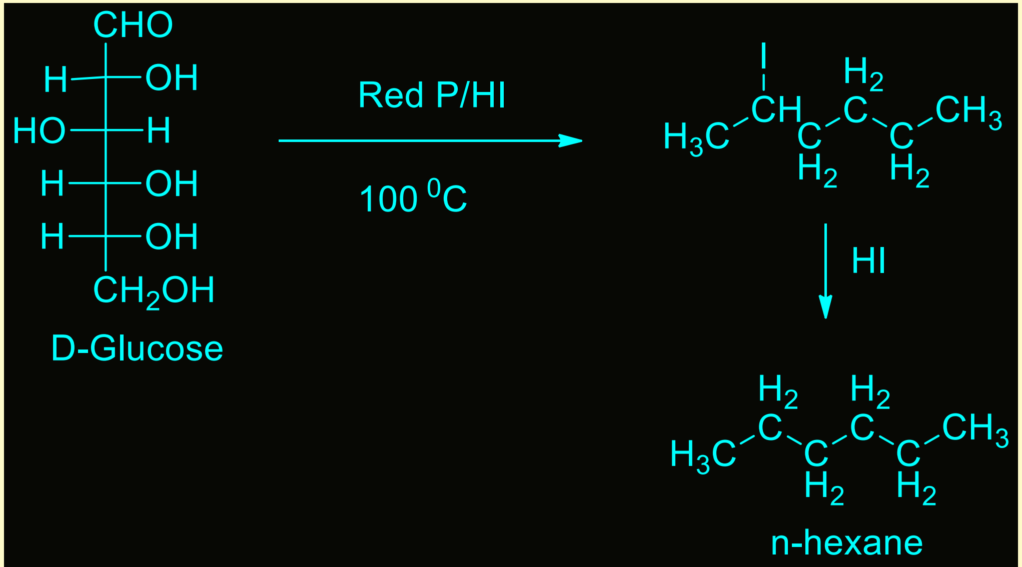


Reduction:

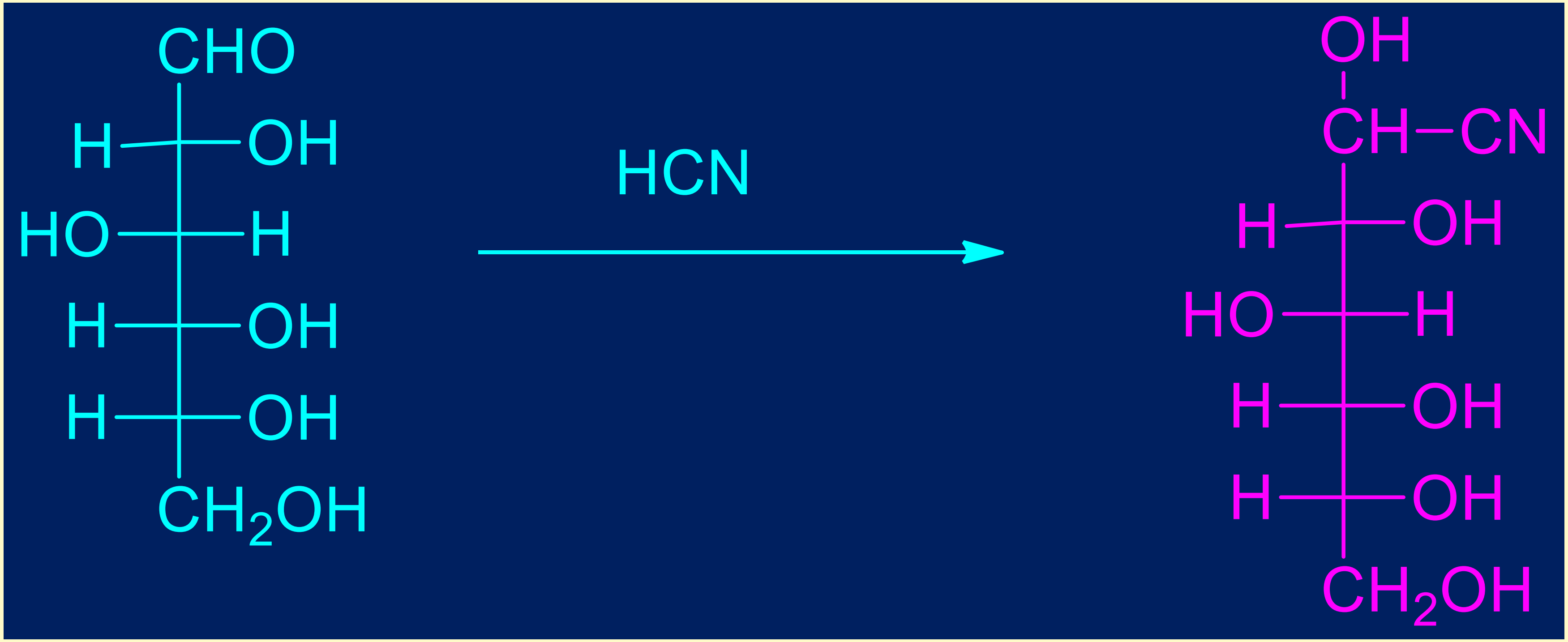
i) On reduction with Na-Hg and water or NaBH4 or H2/Ni or H2 and Pd/C glucose produces glucitol or sorbitol



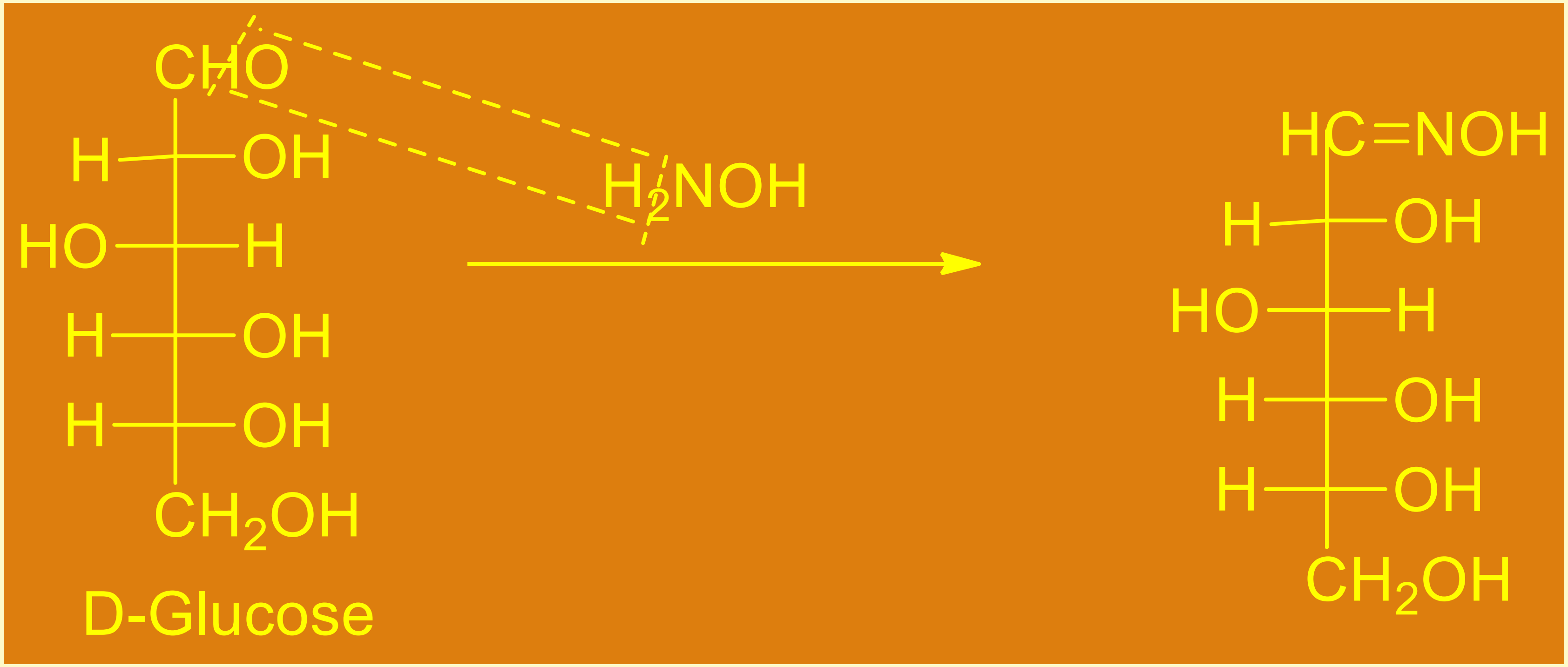
ii) On reduction with Red P and HI glucose produces n-hexane



Reaction with HCN



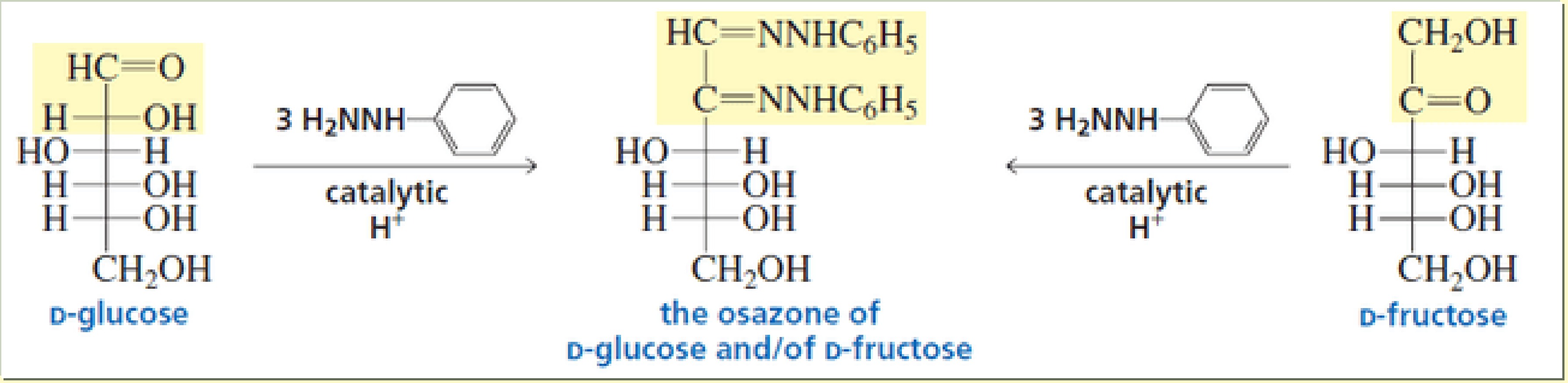
Reaction with Hydroxyl amine



D-Glucose

Osazone Formation

Aldoses and ketoses, react with three equivalents of phenylhydrazine, forming osazones. One equivalent functions as an oxidizing agent and is reduced to aniline and ammonia. The number-1 and number-2 carbons of ketoses react with phenylhydrazine, too. Consequently, D-fructose, D-glucose, and D-mannose all form the same osazone.



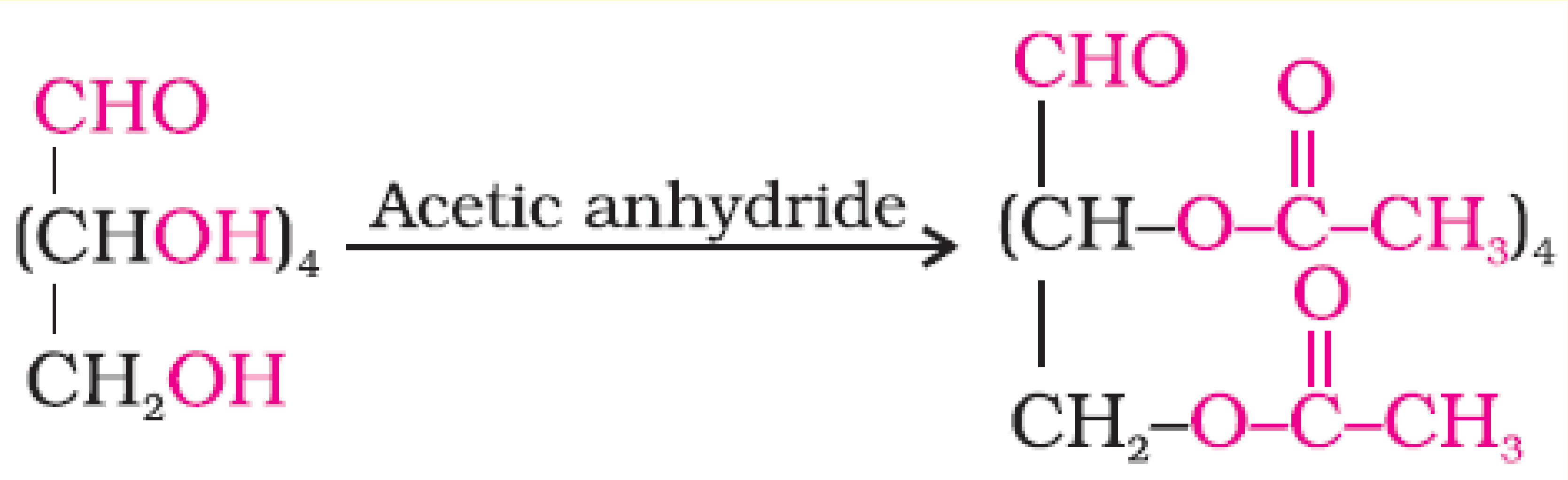
D-glucose

the osazone of D-glucose and/of D-fructose

D-fructose

Reaction with Acetic Anhydride

Acetylation of glucose with acetic anhydride gives glucose pentaacetate which confirms the presence of five –OH groups. Since it exists as a stable compound, five –OH groups should be attached to different carbon atoms.



$$\begin{array}{c}\mathrm{CHO}\\ | \\ (\mathrm{CHOH})_4\\ | \\ \mathrm{CH_2OH}\end{array}\xrightarrow{\text{Acetic anhydride}}\begin{array}{l}\mathrm{CHO}\\ | \\ (\mathrm{CH{-}O{-}}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}CH_3})_4\\ | \\ \mathrm{CH_2{-}O{-}}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}CH_3}\end{array}$$

Cyclic Structure of Glucose

The structure of glucose explained most of its properties but the following reactions and facts could not be explained by this structure.

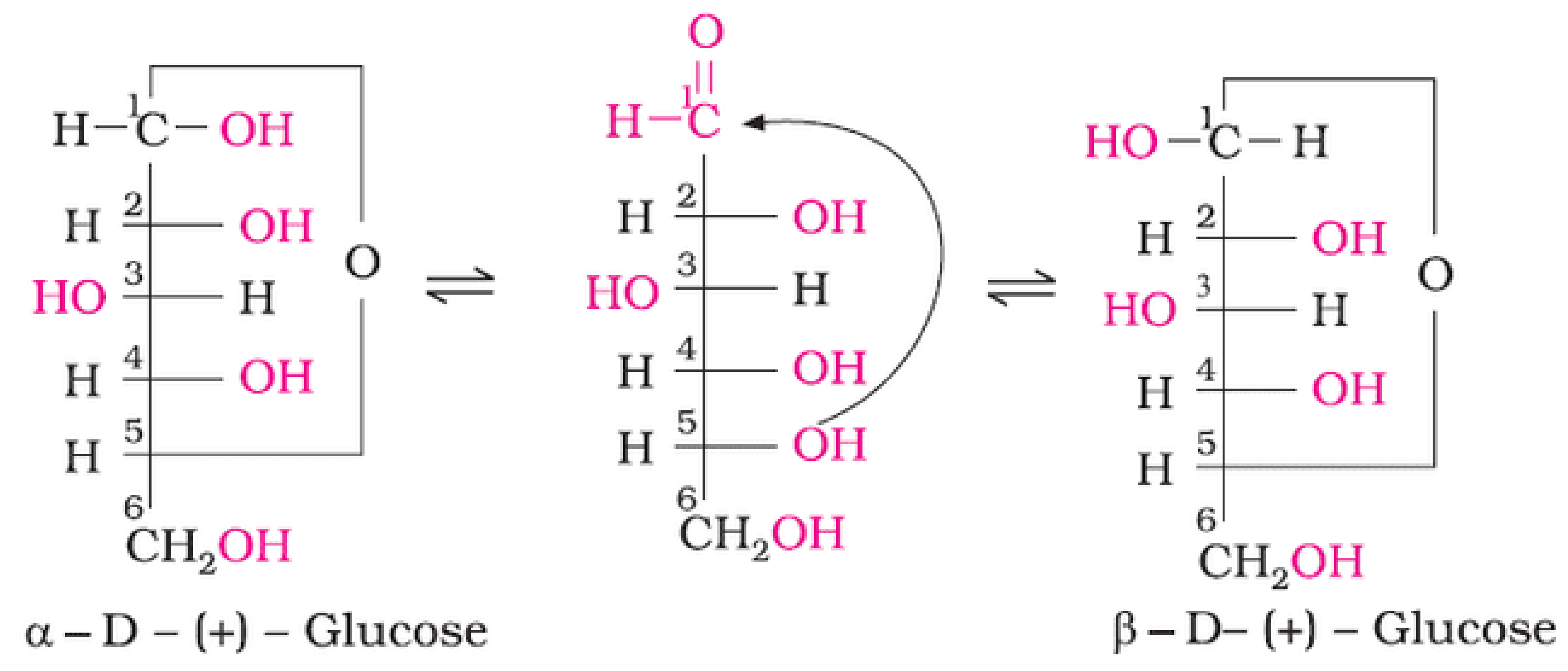
1. Despite having the aldehyde group, glucose does not give 2,4-DNP test, Schiff's test and it does not form the hydrogensulphite addition product with NaHSO3.

2. The pentaacetate of glucose does not react with hydroxylamine indicating the absence of free —CHO group.

3. Glucose is found to exist in two different crystalline forms which are named as α and β. The α-form of glucose (m.p. 419 K) is obtained by crystallisation from concentrated solution of glucose at 303 K while the β-form (m.p. 423 K) is obtained by crystallisation from hot and saturated aqueous solution at 371 K.

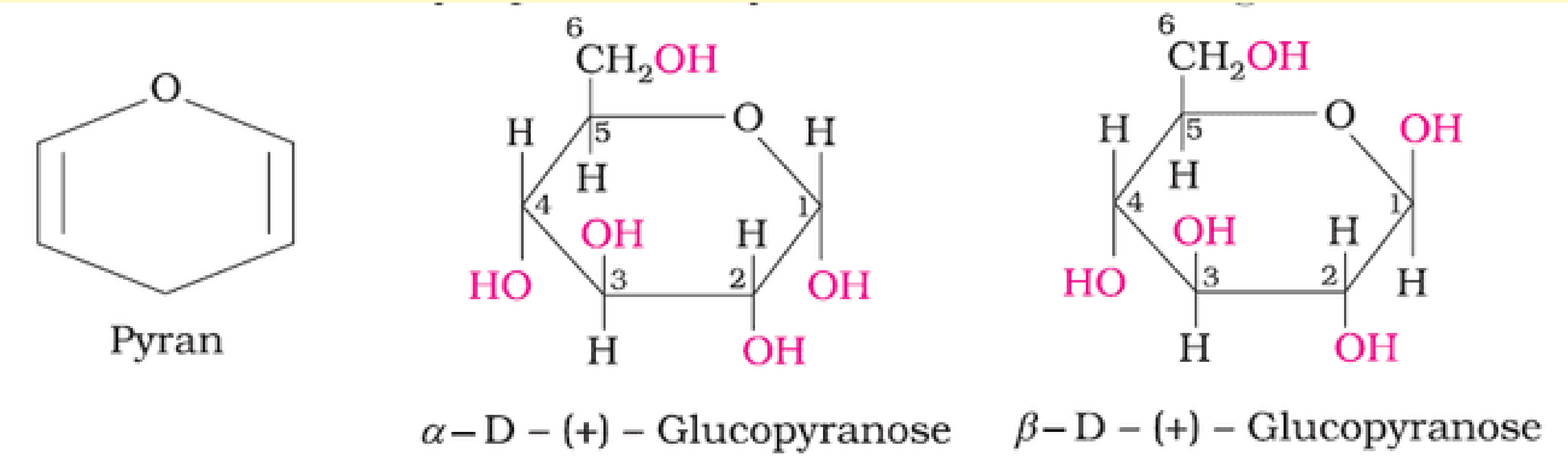
This behaviour could not be explained by the open chain structure for glucose. It was proposed that one of the —OH groups may add to the —CHO group and form a cyclic hemiacetal structure. It was found that glucose forms a six-membered ring in which —OH at C-5 is involved in ring formation. This explains the absence of —CHO group and also existence of glucose in two forms as shown below.

These two cyclic forms exist in equilibrium with open chain structure.

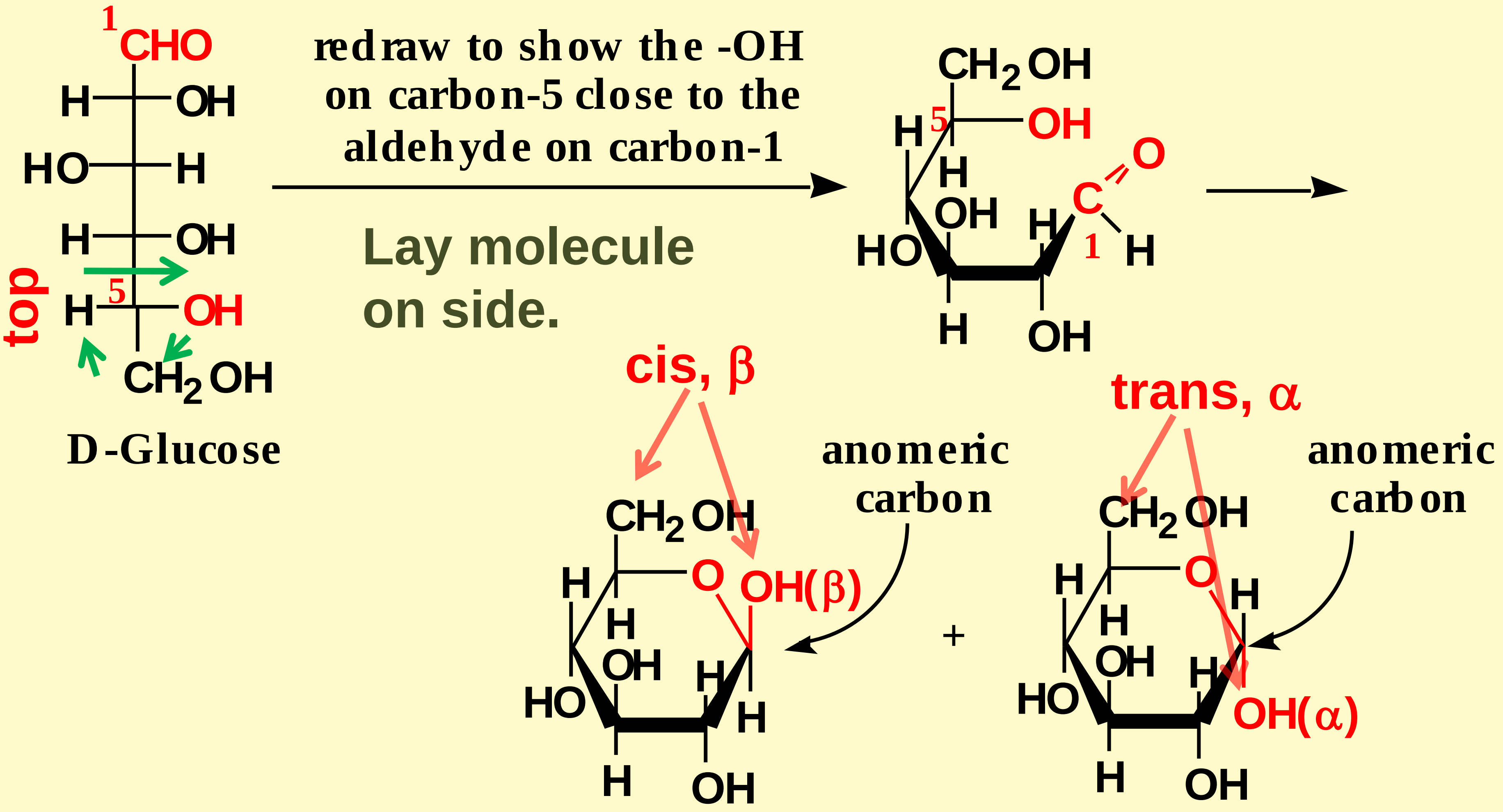


Pyranose structure &Anomeric Carbon

The two cyclic hemiacetal forms of glucose differ only in the configuration of the hydroxyl group at C1, called *anomeric carbon*. Such isomers, i.e., α-form and β-form, are called **anomers**. The six membered cyclic structure of glucose is called **pyranose structure** (α– or β–), in analogy with pyran. Pyran is a cyclic organic compound with one oxygen atom and five carbon atoms in the ring. The cyclic structure of glucose is more correctly represented by Haworth structure as given below.



Haworth Projections



redraw to show the -OH on carbon-5 close to the aldehyde on carbon-1

Lay molecule on side.

D-Glucose

cis, β

trans, α

anomeric carbon

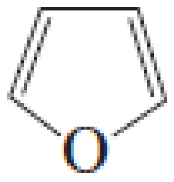
anomeric carbon

β-D-Glucopyranose
(β-D-Glucose)

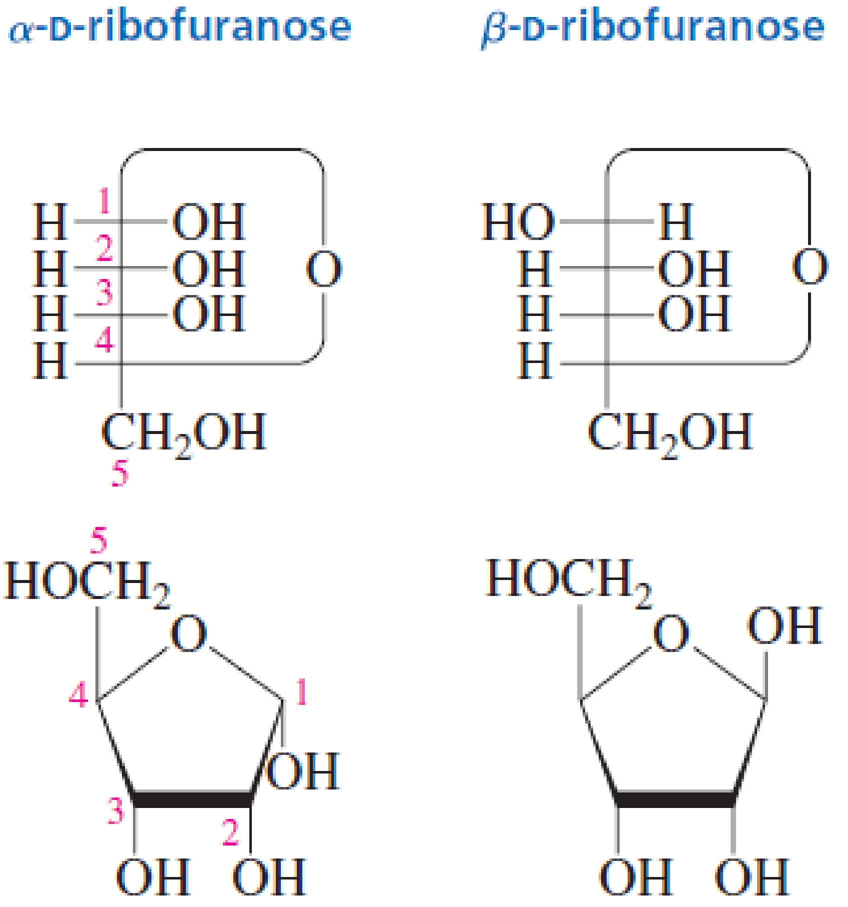
α-D-Glucopyranose
(α-D-Glucose)

Furanose structure

Five membered-ring sugars are called **furanoses**. The Haworth projection of a D-furanose is viewed edge on, with the ring oxygen away from the viewer. The anomeric carbon is on the right-hand side of the molecule, and the primary alcohol group is drawn *up* from the back left-hand corner.



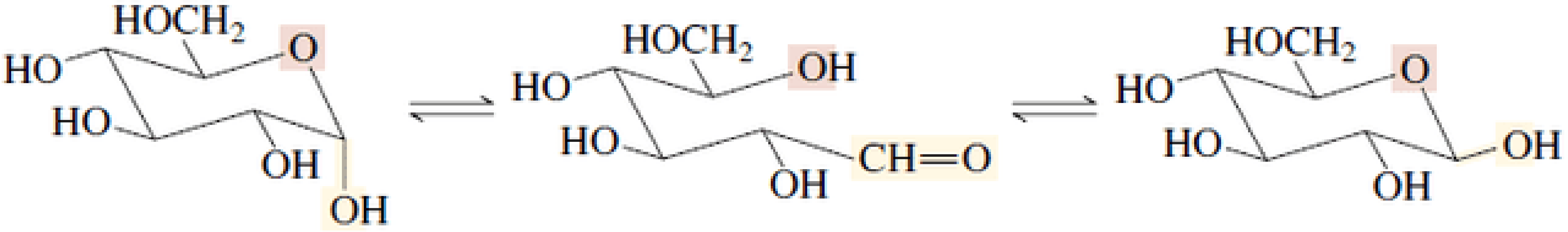
furan



α-D-ribofuranose β-D-ribofuranose

Mutarotation

When crystals of pure α -D-glucose are dissolved in water, the specific rotation gradually changes from +112.2 to +52.7. When crystals of pure β-D-glucose are dissolved in water, the specific rotation gradually changes from +18.7 to +52.7. This change in rotation occurs because, in water, the hemiacetal opens to form the aldehyde and, when the aldehyde recyclizes, both α -D-glucose and β-D-glucose can be formed. Eventually, the three forms of glucose reach equilibrium concentrations. The specific rotation of the equilibrium mixture is +52.7 this is why the same specific rotation results whether the crystals originally dissolved in water are α -D-glucose or β-D-glucose. A slow change in optical rotation to an equilibrium value is known as **mutarotation**.

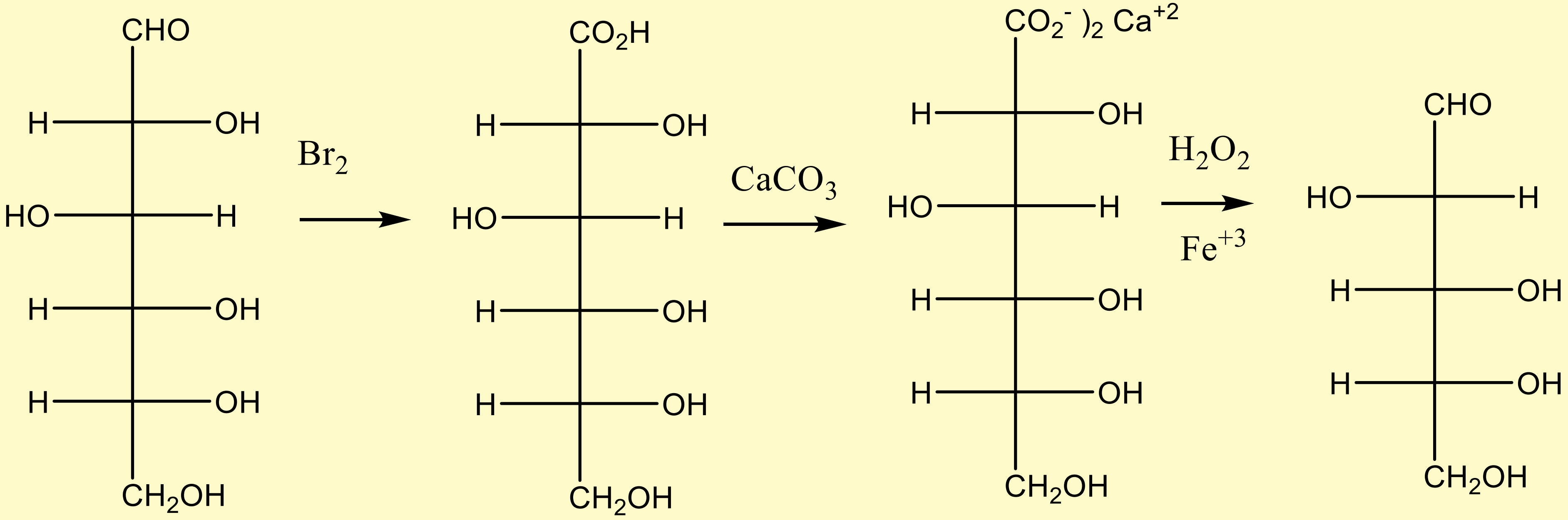


α-D-Glucopyranose
(mp 146°C;
$[\alpha]_D$ +112.2°)

Open-chain form
of D-glucose

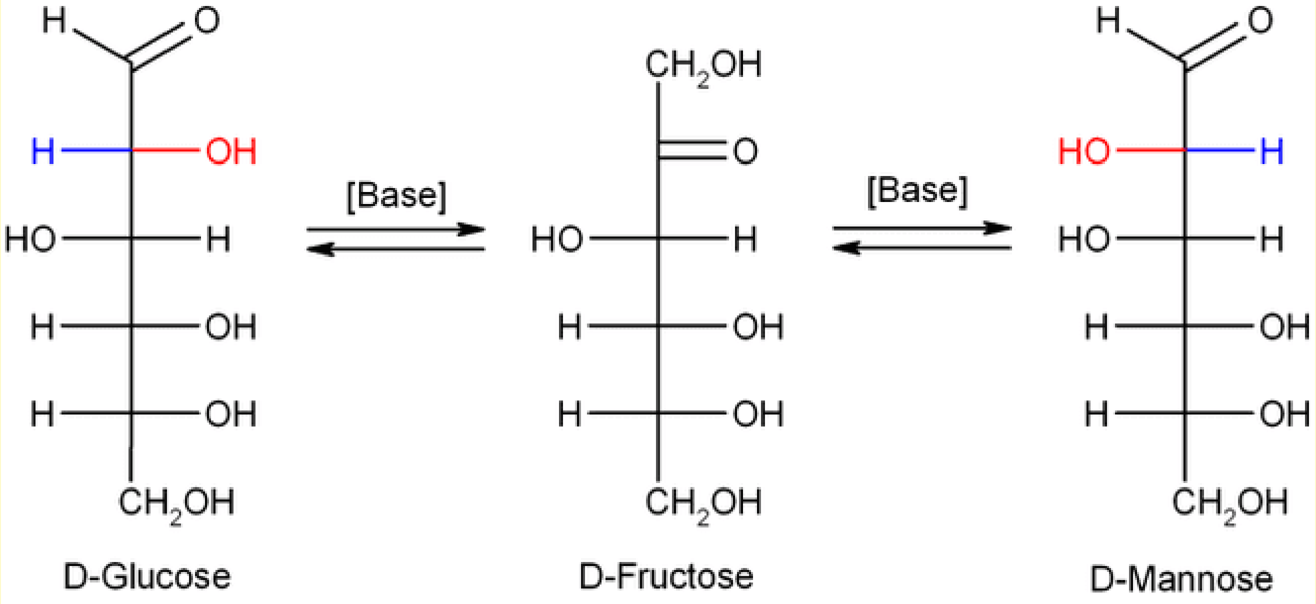
β-D-Glucopyranose
(mp 148–155°C;
$[\alpha]_D$ +18.7°)

Ruff Degradation shortening of chain

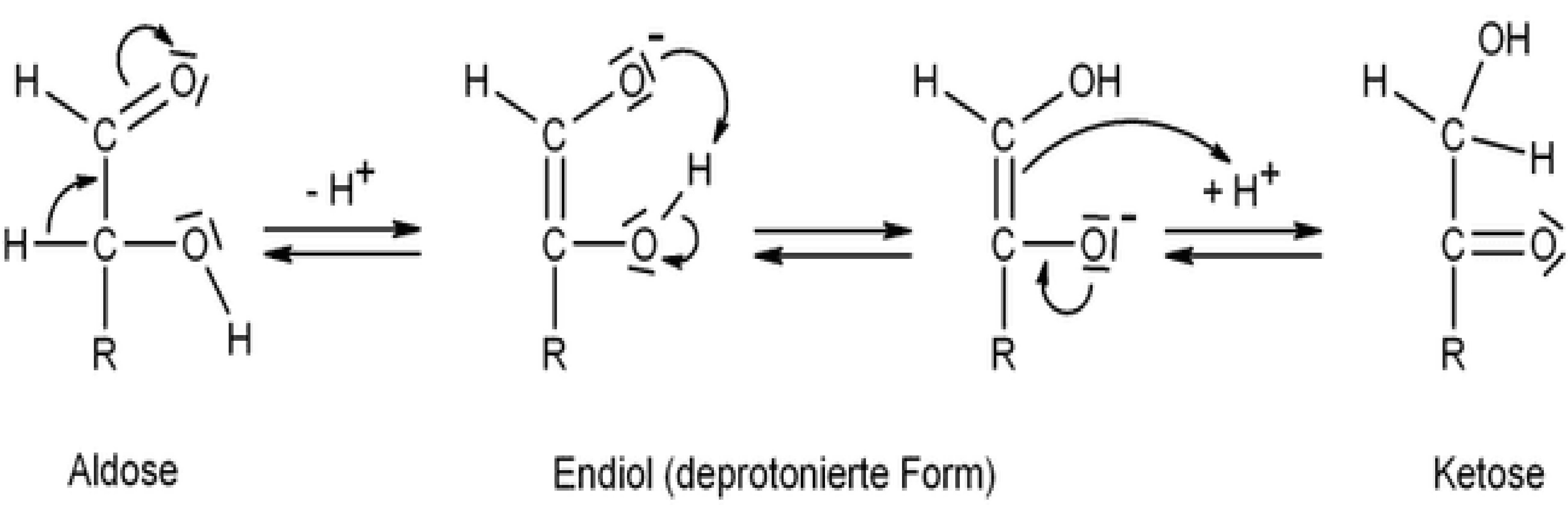


Interconversion of aldoses and ketoses
Or
Lobry de Bruyn-van Ekenstein transformation

Lobry de Bruyn–Alberda–van Ekenstein transformation is the base or acid catalyzed transformation of an aldose into the ketose isomer or vice versa.



Mechanism



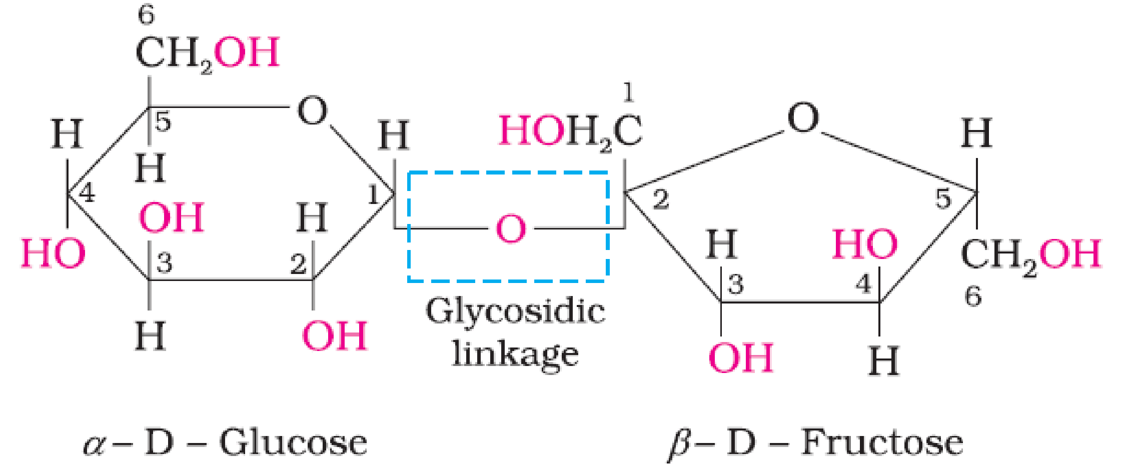
Disaccha
ride

Sucrose

One of the common disaccharides is **sucrose** which on hydrolysis gives equimolar mixture of D-(+)-glucose and D-(-) fructose.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{D-(+)-Glucose}}{C_6H_{12}O_6} + \underset{\text{D-(–)-Fructose}}{C_6H_{12}O_6}$$

These two monosaccharides are held together by a glycosidic linkage between C1 of α-glucose and C2 of β-fructose. Since the reducing groups of glucose and fructose are involved in glycosidic bond formation, sucrose is a non reducing sugar.



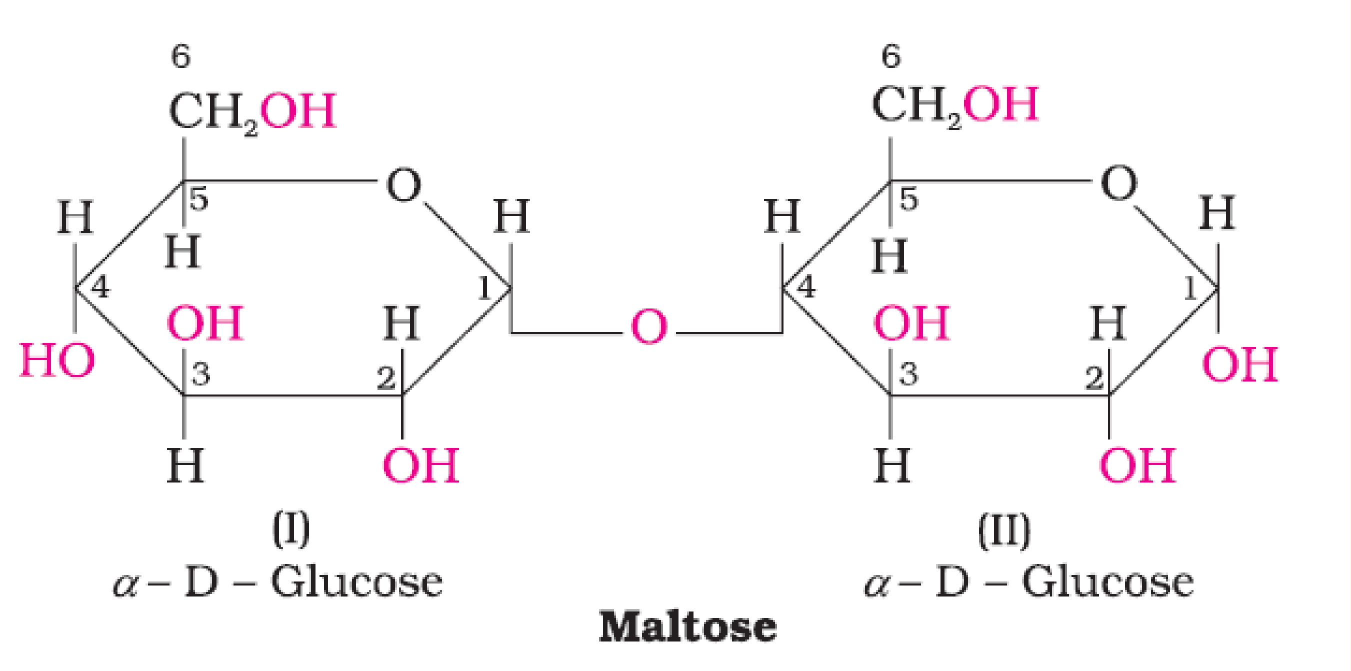
Sucrose

Why Sucrose is called invert sugar?

Sucrose is dextrorotatory but after hydrolysis gives dextrorotatory glucose and laevorotatory fructose. Since the laevorotation of fructose (–92.4°) is more than dextrorotation of glucose (+52.5°), the mixture is laevorotatory. Thus, hydrolysis of sucrose brings about a change in the sign of rotation, from dextro (+) to laevo (–) and the product is named as **invert sugar**.

Maltose

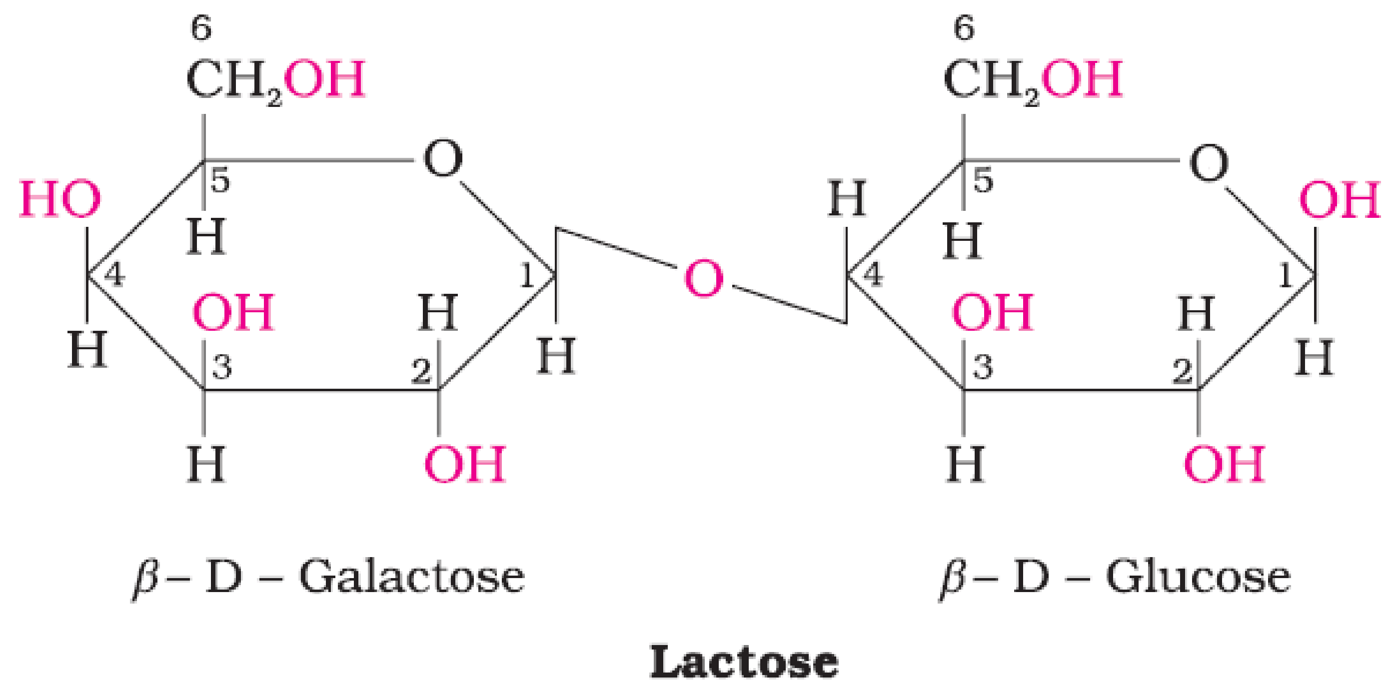
Maltose is composed of two α-D-glucose units in which C1 of one glucose (I) is linked to C4 of another glucose unit (II). The free aldehyde group can be produced at C1 of second glucose in solution and it shows reducing properties so it is a reducing sugar.



Maltose

Lactose:

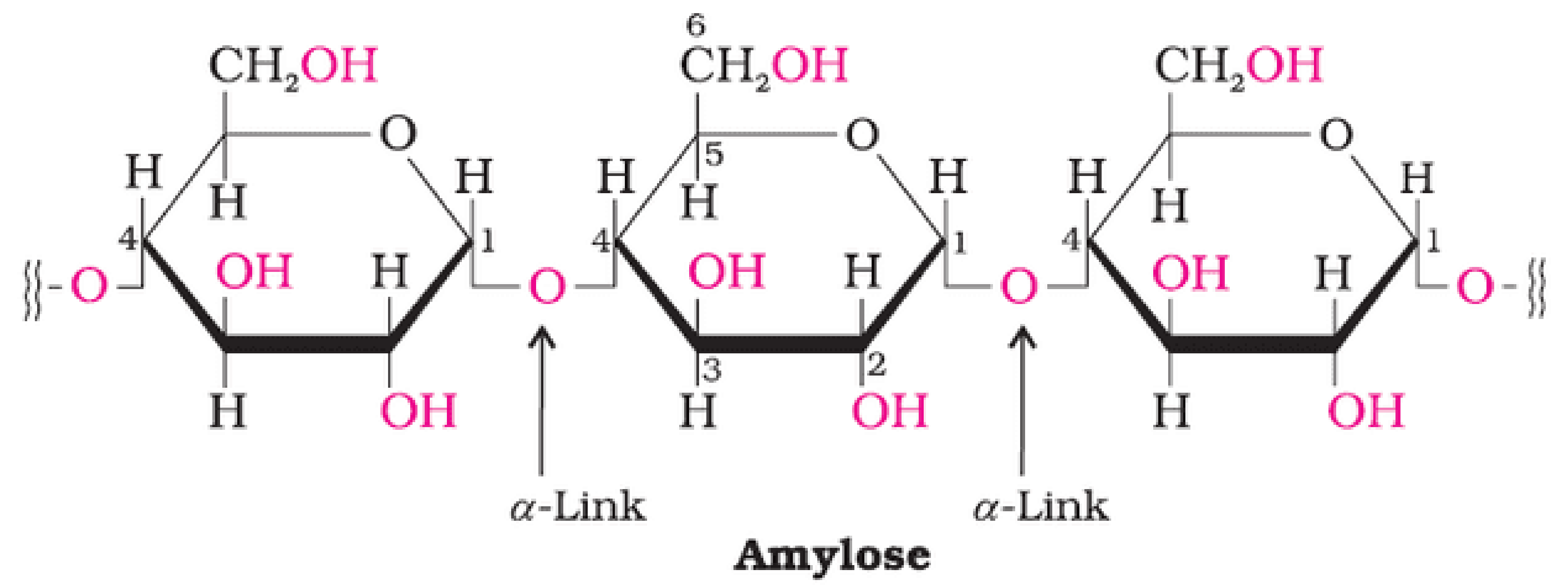
It is more commonly known as milk sugar since this disaccharide is found in milk. It is composed of β-D-galactose and β-D-glucose. The linkage is between C1 of galactose and C4 of glucose. Hence it is also a reducing sugar.



Polysaccharide

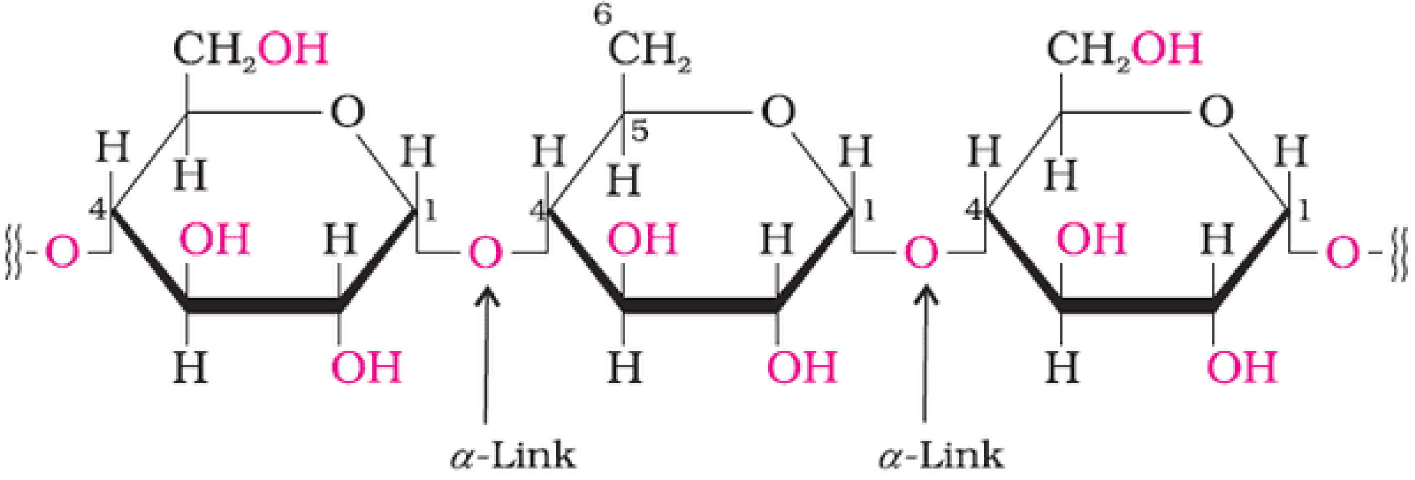
Starch

Starch is the main storage polysaccharide of plants. It is the most important dietary source for human beings. High content of starch is found in cereals, roots, tubers and some vegetables. It is a polymer of α-glucose and consists of two components— **Amylose** and **Amylopectin**. Amylose is water soluble component which constitutes about 15-20% of starch. Chemically amylose is a long unbranched chain with 200-1000 α-D-(+)-glucose units held by C1– C4 glycosidic linkage.



Amylose

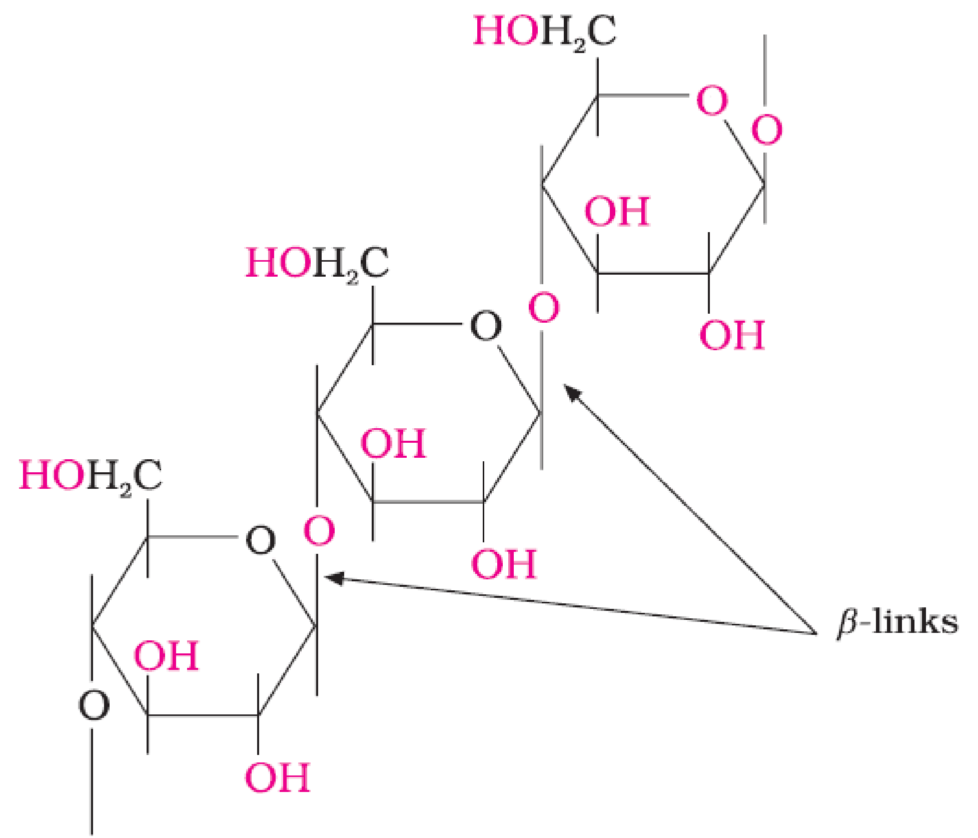
Amylopectin is insoluble in water and constitutes about 80-85% of starch. It is a branched chain polymer of α-D-glucose units in which chain is formed by C1–C4 glycosidic linkage whereas branching occurs by C1–C6 glycosidic linkage.



Amylopectin

Cellulose

Cellulose occurs exclusively in plants and it is the most abundant organic substance in plant kingdom. It is a predominant constituent of cell wall of plant cells. Cellulose is a straight chain polysaccharide composed only of β-D-glucose units which are joined by glycosidic linkage between C1 of one glucose unit and C4 of the next glucose unit.



Cellulose