Carbohydrates

CHE 2112

Carbohydrates

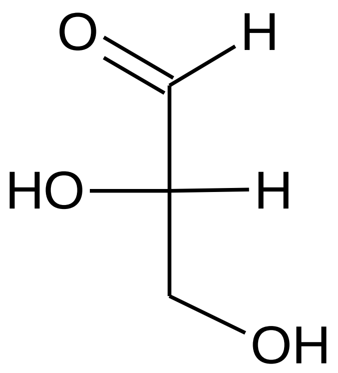
- Are polyhydroxy aldehydes or ketones and their derivatives
- Most conform to empirical formula $(CH_2O)_n$

Classification

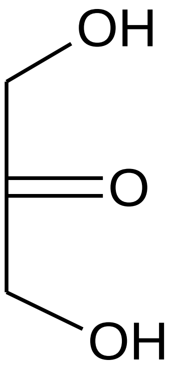
- 3 main groups - monosaccharide, disaccharides & polysaccharides.
- Sometimes 4th group known - oligosaccharides (2 to 10 monosacharides)
- Oligosaccharides include Di, Tri, Tetra, and Penta,….,Deca, - saccharides (*Give an example of each;* Define a legume oligosaccharide and give three examples)

Monosaccharides

- Also called simple sugars
- Simplest carbohydrates
- Are aldehydes or ketones that have 2 or more hydroxyl groups
- Cannot be hydrolysed into simpler form
- Glyceraldehyde and dihydroacetone, with n = 3, are the smallest in this group.



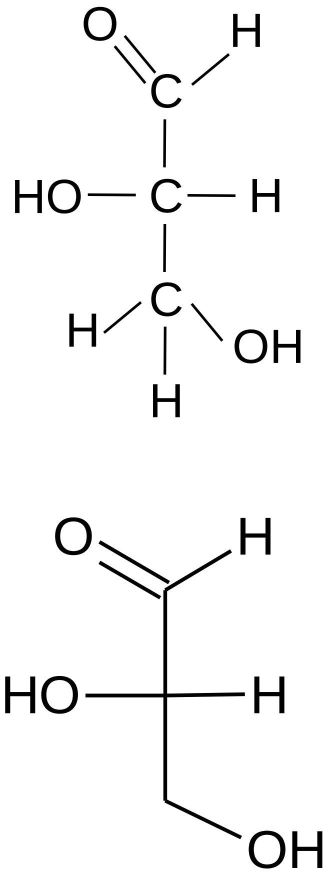
L - Glyceraldehyde



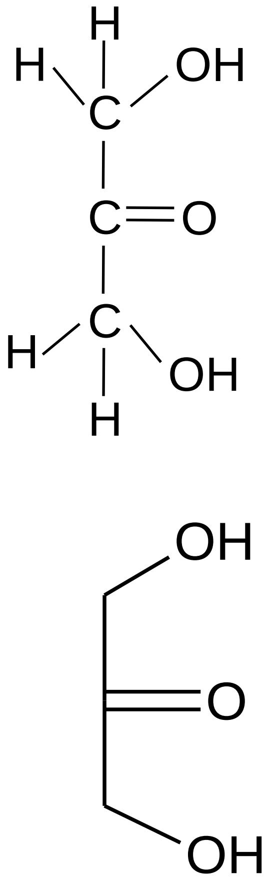
Dihydroxyacetone

- An aldose
- Called an aldose because it is an aldehyde

- A ketose
- Called a ketose because it is a ketone

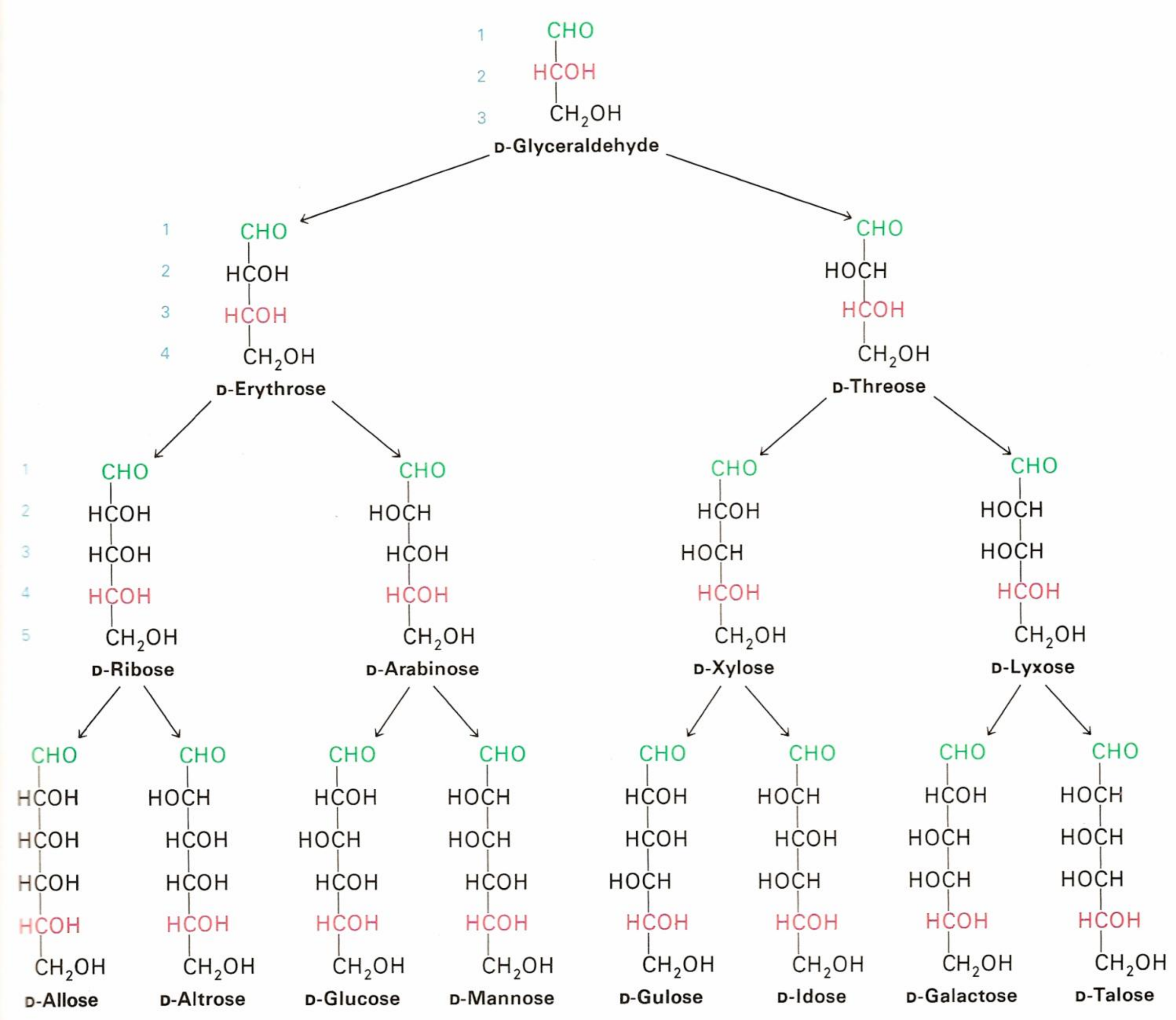


L - Glyceraldehyde



Dihydroxyacetone

- Depending on value of n in $(CH_2O)_n$ or number of carbon atoms monosaccharides can be classified:-
- n = 3 – triose
- n = 4 – tetrose
- n = 5 – pentose
- n = 6 - hexose



Triose

Tetrose

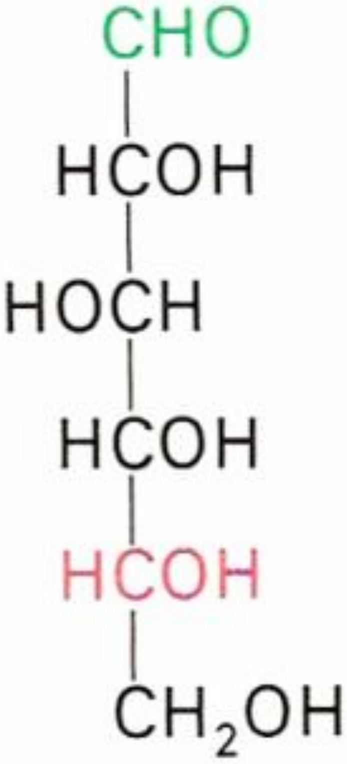
Pentose

Hexose

Monosaccharide Isomerism

1. L and D Isomers (Use glucose as a model)

- Orientation of H and OH around carbon atom adjacent to terminal primary alcohol determines whether the sugar is L or D (refer to preceding slide).
- Most sugars / monosaccharides that occur in mammals are D – isomers.
- Presence of asymmetric carbon makes them optically active.



D-Glucose

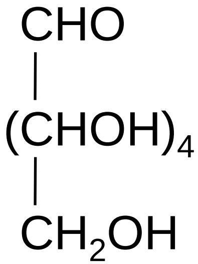
- Are able to rotate a beam of plane polarised light either to he Left or Right

- The left thus levorotatory or designated with a negative sign (-)
- Or to the right thus dextrorotatory or designated with a positive sign (+).
- Therefore a molecule could be designated as either D(-) or D(+) or L(-) or L(+).
- An equal concentration of D and L isomers result in a racemic mixture, which does not rotate plane polarised light, as the 2 isomers cancel each other.

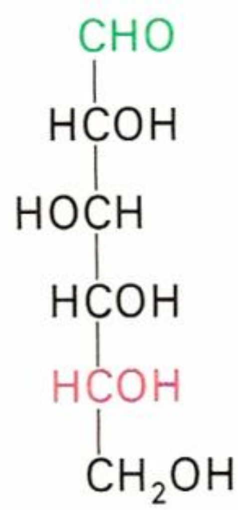
Formulae of Glucose

- Molecular formula can be represented in various ways, revealing different levels of information at a glance

$C_6H_{12}O_6$



$$\begin{array}{l} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}$$



Molecular formula

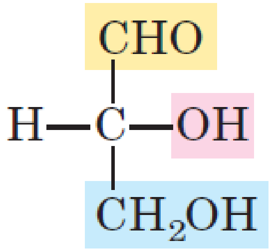
Fittig Baeyer formula

- Functional groups

Fischer Projection formula

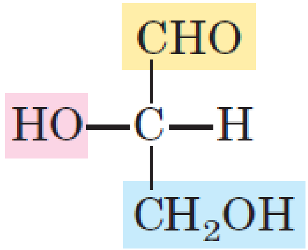
- 4 asymmetric carbons
- Work out total number of isomers (=2^n)

- Fischer projection perspective formula



$$\begin{array}{c}\mathrm{CHO}\\ |\\ \mathrm{H{-}C{-}OH}\\ |\\ \mathrm{CH_2OH}\end{array}$$

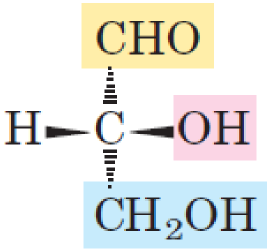
D-Glyceraldehyde



$$\begin{array}{c}\mathrm{CHO}\\ |\\ \mathrm{HO{-}C{-}H}\\ |\\ \mathrm{CH_2OH}\end{array}$$

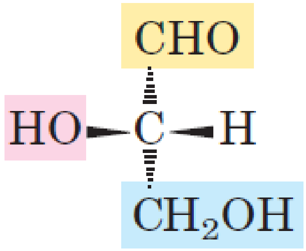
L-Glyceraldehyde

Fischer projection formulas



$$\begin{array}{c}\mathrm{CHO}\\ \vdots\\ \mathrm{H{-}C{-}OH}\\ \vdots\\ \mathrm{CH_2OH}\end{array}$$

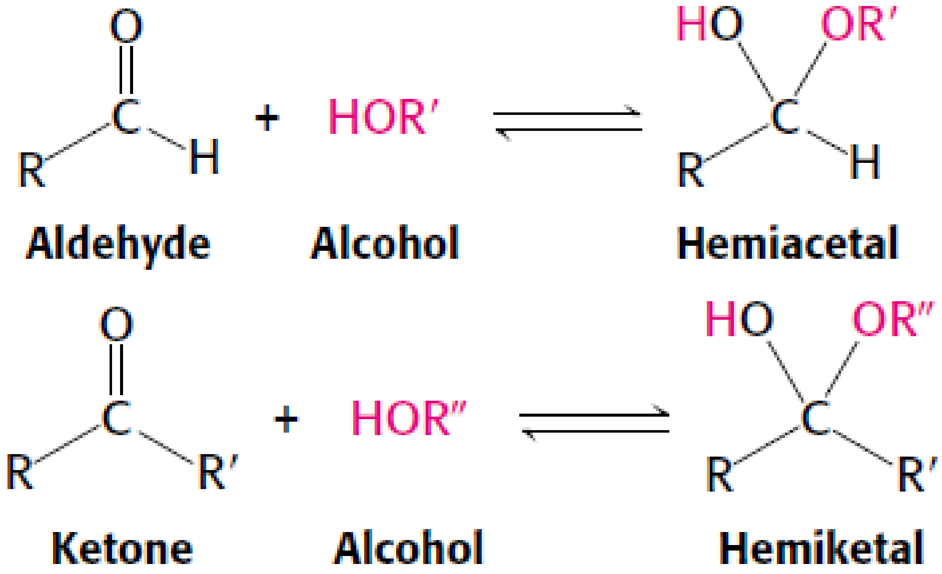
D-Glyceraldehyde



$$\begin{array}{c}\mathrm{CHO}\\ \vdots\\ \mathrm{HO{-}C{-}H}\\ \vdots\\ \mathrm{CH_2OH}\end{array}$$

L-Glyceraldehyde

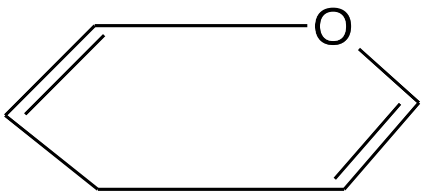
- All these formulae representation fail to explain all the properties of glucose
- Sugars’ aldehyde and ketone groups react with hydroxyl groups to form hemiacetals and hemiketals



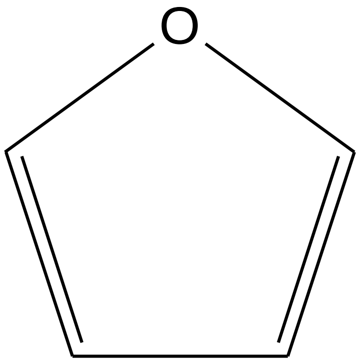
- Sugars with n > 4, aldehyde and ketone groups react with hydroxyl groups intra-molecularly.
- This results in formation of 6-membered rings (pyranose) and 5-membered rings (furanose)
- 7 – membered rings are not possible due to molecular strains not allowing reaction between OH and CHO groups.

2. Pyranose and Furanose ring structures

- Monosaccharide form stable ring structures that are similar to pyran are called pyranose and those similar to furan are called furanose.
- Pyranoses sugars are more stable than furanoses sugars (pyranose formation has a ΔG° than that for furanose)

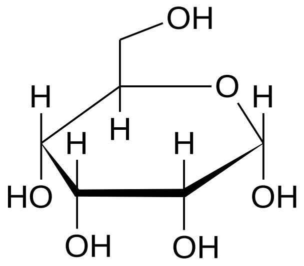


Pyran



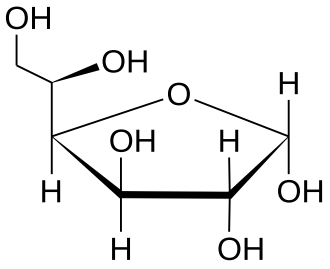
Furan

- These ring structures accounts completely for glucose’s chemical properties



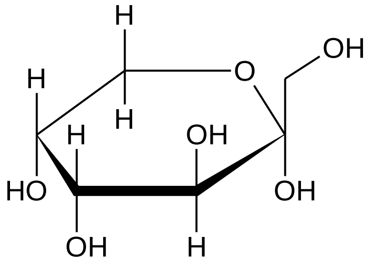
α-D-Glucopyranose

Or α-D-Glucose

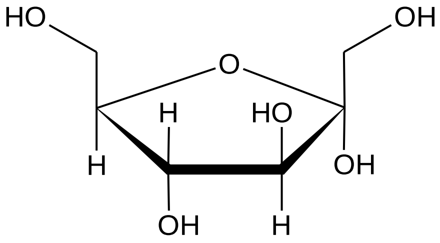


α–D-Glucofuranose

- Ketoses are also able to form ring structures



α–D-Fructopyranose



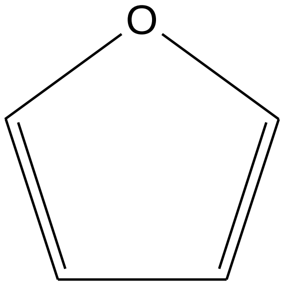
α–D-Fructofuranose

Haworth Perspective Formula

Groups on the right written down while groups on the left are written up, except C_5

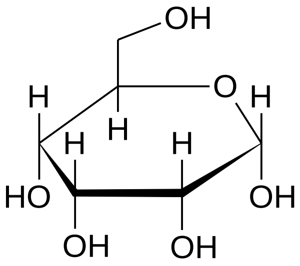
A

Pyran



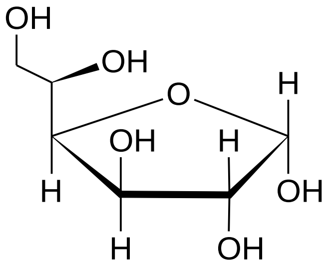
Furan

B



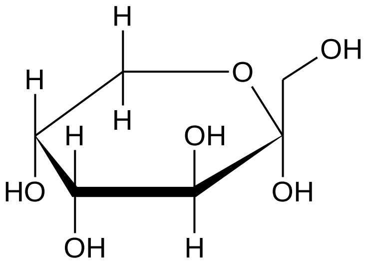
α-D-Glucopyranose

Or α-D-Glucose

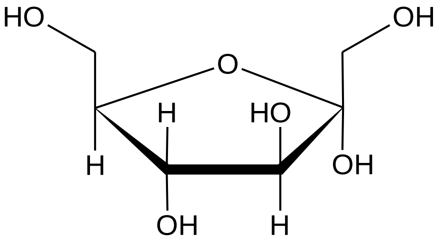


α–D-Glucofuranose

C

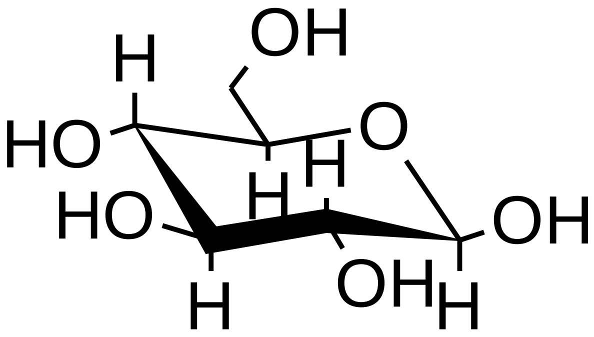


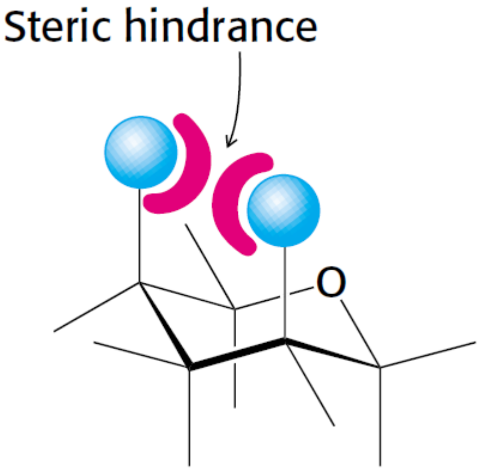
α–D-Fructopyranose



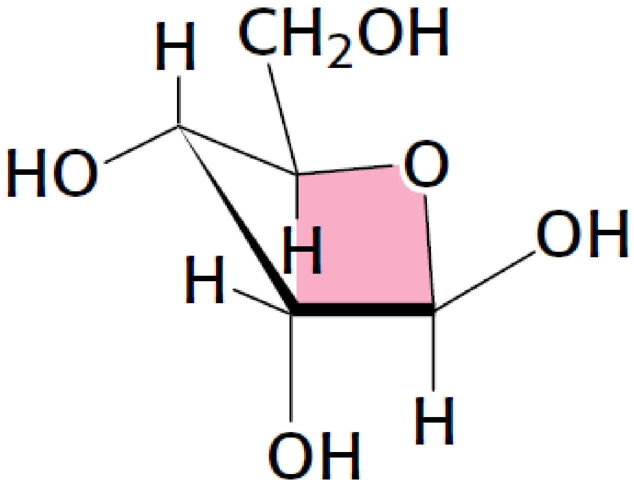
α–D-Fructofuranose

- Glucose solution exhibits 99 % it pyranose form and 1 % furanose form
- Glucose pyranose form has been found to be in the chair conformation with the larger substituents in the equatorial region as the chair conformation is energetically stable/favourable due to less hindrances

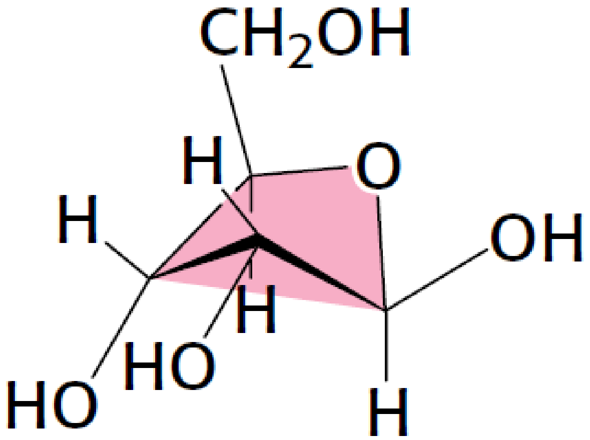




- Envelop confirmation of β –D- ribose
- C_2 – endo and C_3 – endo isomers exist due to changes in configuration at carbon atom 3 and 2.



C₃-endo



C₂-endo

3.α and β anomers (Diastereoisomer)

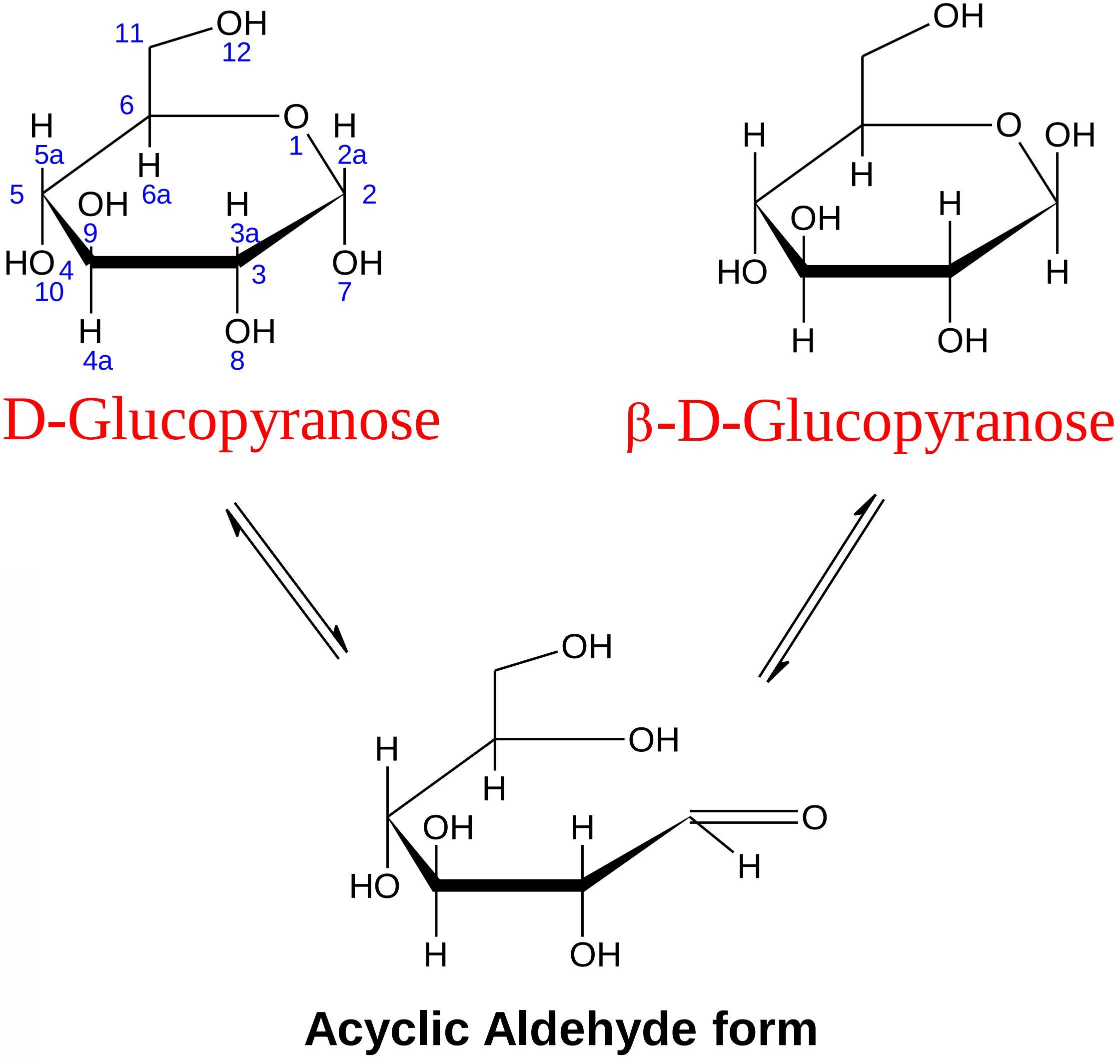
- Cyclisation of linear glucose may result in α and β isomers due to the interchange of H and OH about carbon atom number 1 or anomeric carbon in the cyclic form.
- Isomerisation about carbon atom 1 or anomeric carbon result in a mixture of:-

  63% β-Glucopyranose

  36 % α-Glucopyranose

  1 % represented mainly by α- and β-Glucofuranose
- Inter-conversion or equilibrium result in optical rotation and interchange of H and OH about carbon atom 1 and is called **mutarotation**.

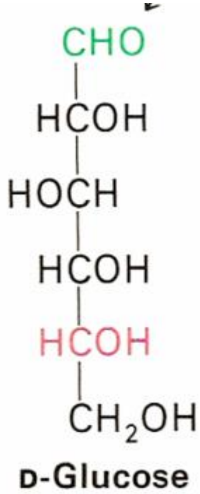
Mutarotation of Glucose



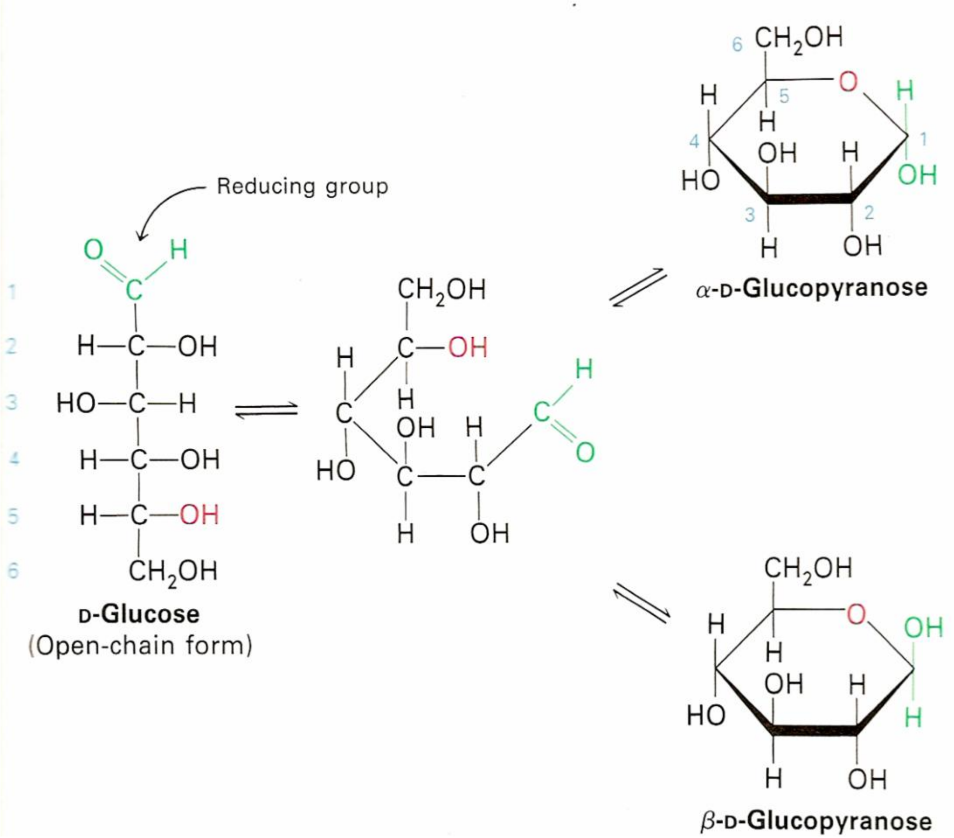
α-D-Glucopyranose

β-D-Glucopyranose

Acyclic Aldehyde form



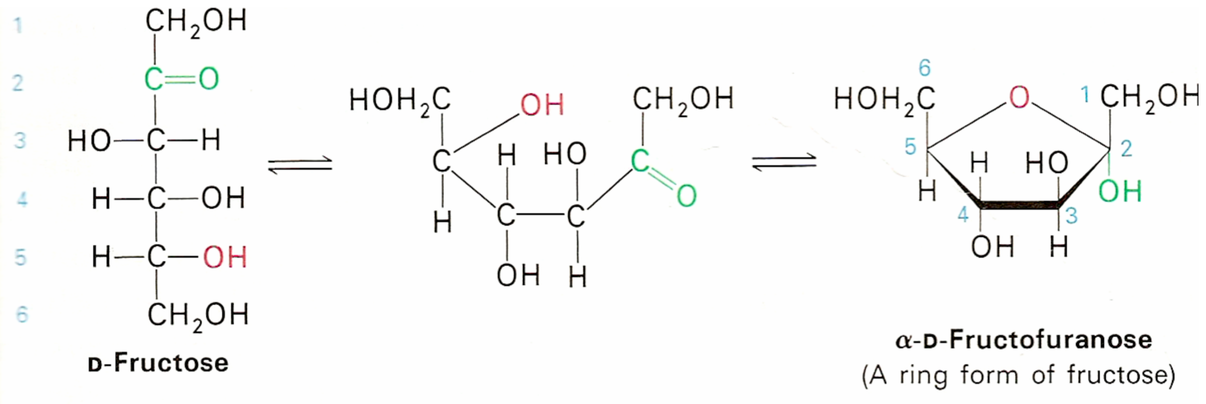
D-Glucose



D-Glucose
(Open-chain form)

α-D-Glucopyranose

β-D-Glucopyranose

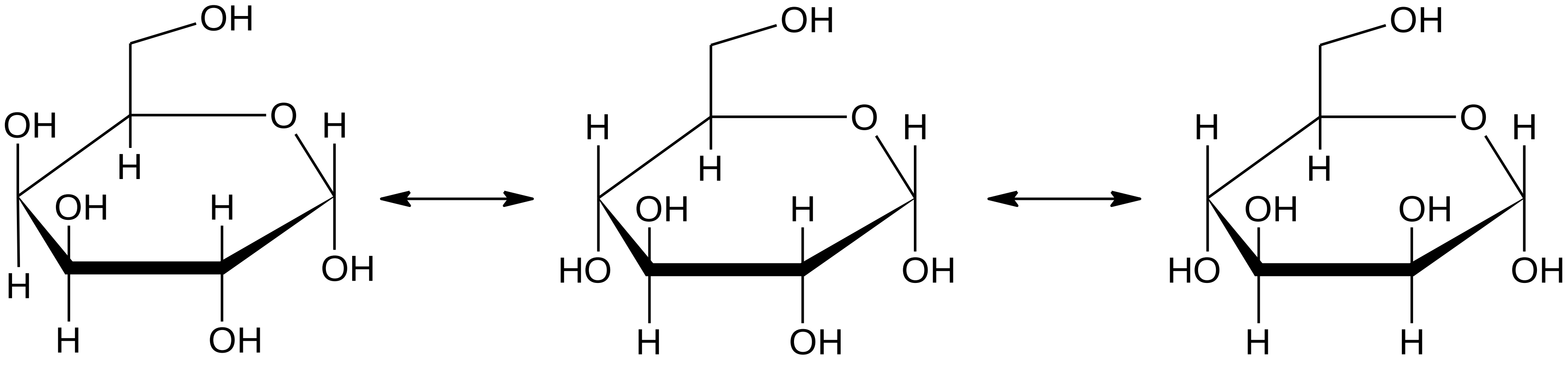


D-Fructose

α-D-Fructofuranose
(A ring form of fructose)

4. Epimers

- Isomers of glucose differing in the position of H and OH at positions 2, 4, and 6 are called epimers.
- Epimers of glucose of biological importance are manose and galactose



α-D-Galactose α-D-Glucose α-D-Manose

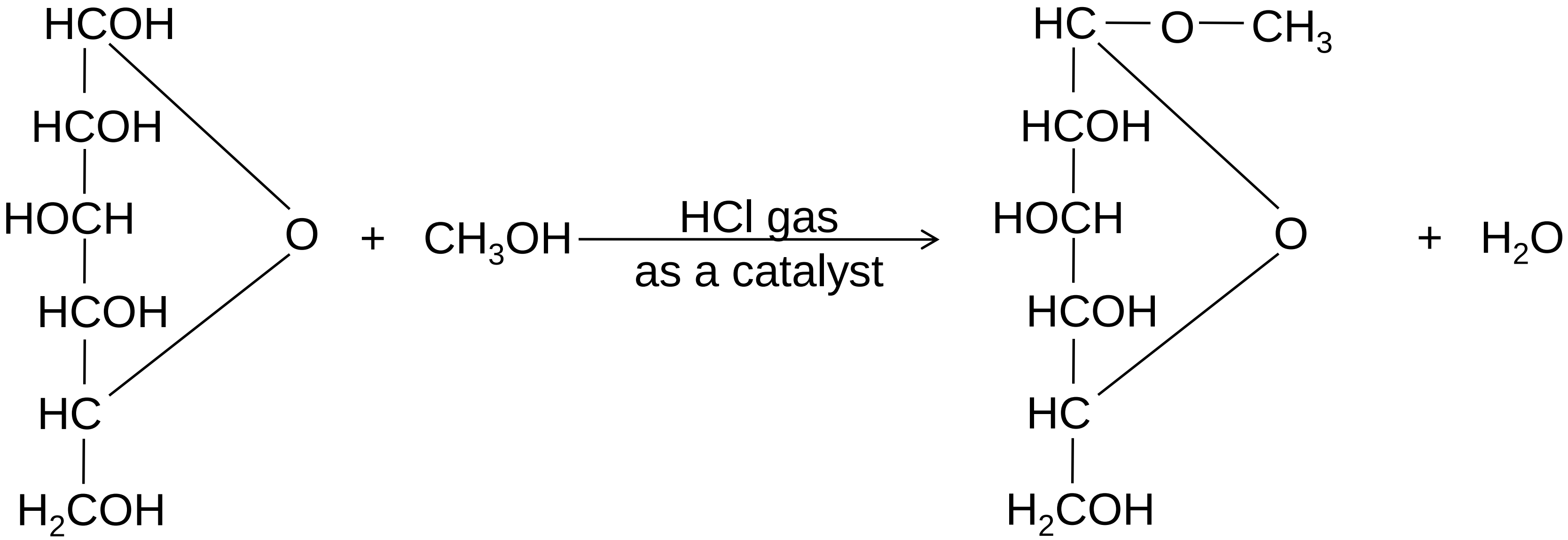
Epimerisation of Glucose

Chemical Properties

- Reactive groups in carbohydrates makes the reactive
- These are glycosidic OH, alcoholic OH and aldehyde (CHO)/ketone(C=O)
- α-form ↔ aldehyde/ketone form ↔ β-form
- Equilibrium shifts in favour of the reacting group

Rxn of Glycosidic OH group

- Reaction with alcohols



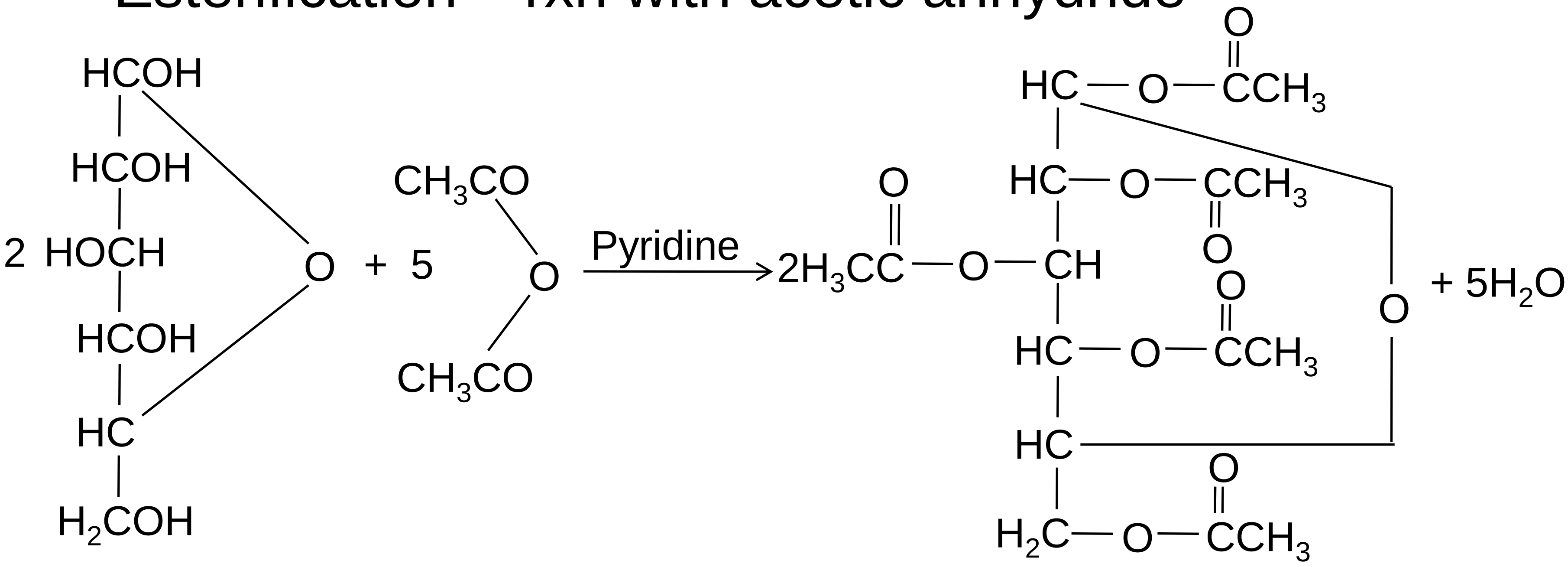
α-D-glucose Methyl alcohol α-methyl-D-glucose

- Glycosidic OH reacts with alcohols to form α – and β-glycosides or acetals
- Glucose forms glucosides and fructose forms fructosides

- Glucosides or glycosides do opt exhibit mutarotation as aldehyde group is in the acetal form
- These are used as medicaments

Rxn of Glycosidic & Alcoholic OH group

- Esterification – rxn with acetic anhydride

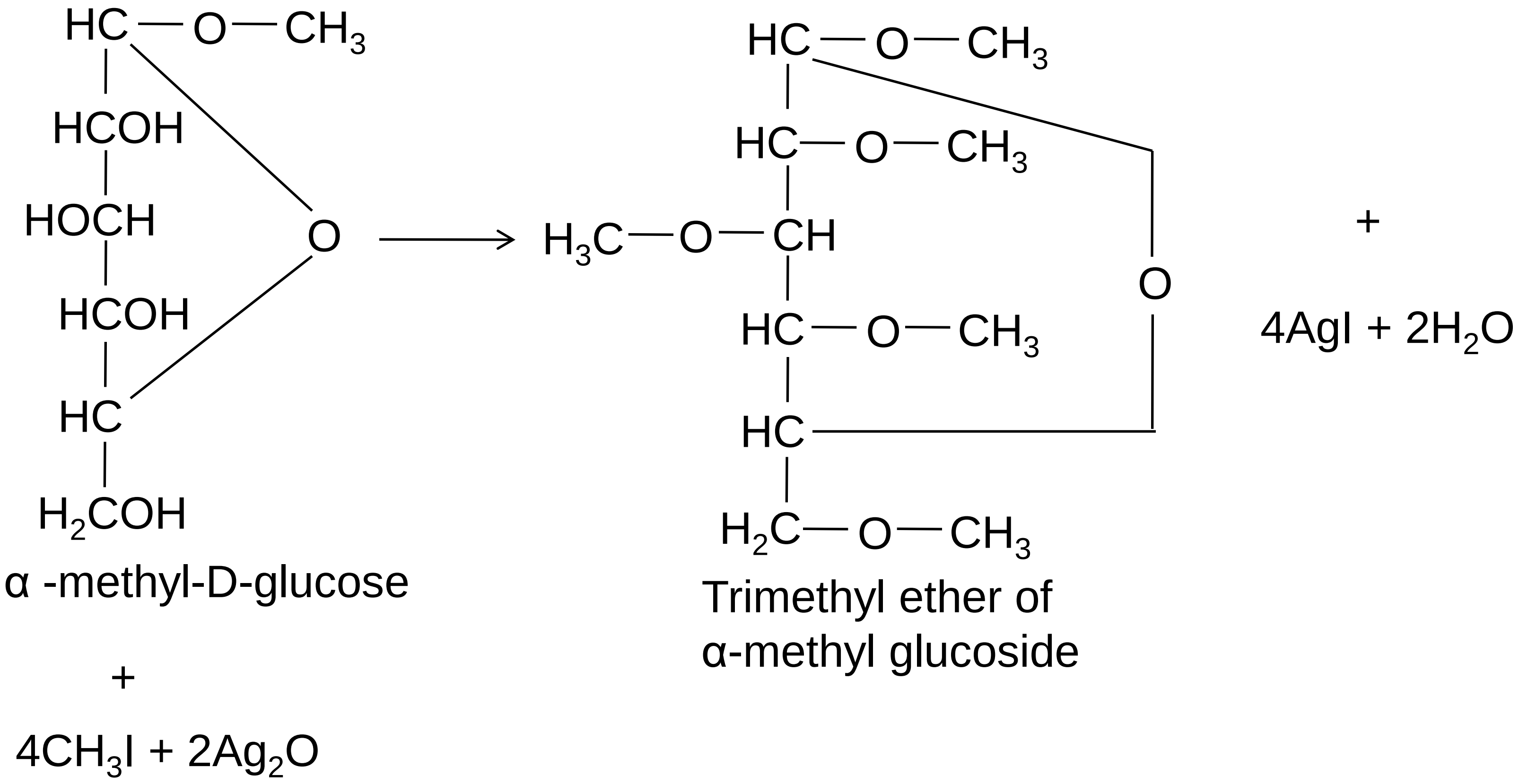


α-D-glucose Acetic anhydride α-D-glucose penta acetate

- Test for presence of alcohol groups in sugars to form esters
- Glucose forms a penta (5 OH groups) acetate derivative

Rxn of Alcoholic OH

- Alcoholic OH of monosaccharides and disaccharides converted to ethers when reacted with methylating agents
- Glycosidic OH group of sugar first protected by R group (methyl group), before methylation



α -methyl-D-glucose

+

$4CH_3I + 2Ag_2O$

Trimethyl ether of
α-methyl glucoside

+

$4AgI + 2H_2O$

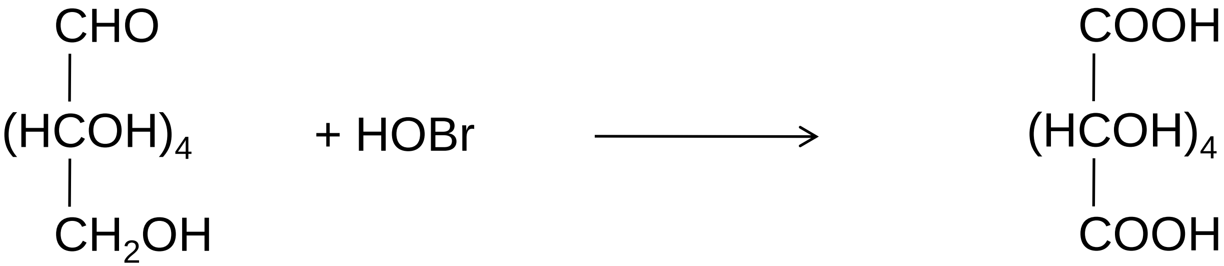
- Rxn used to determine which alcoholic OH groups are free for reaction

Rxns of both Alcoholic OH and CHO/C=O Groups

- Oxidation with Acids
- Cyclic hemiacetal forms of sugars are in equilibrium with a small but finite amount of open chain aldehyde, they can easily be oxidised to carboxylic acids called aldonic acids
- Certain oxidising agents oxidises OH to carboxilc groups

a) Mild Oxidant, HOBr – Only aldehyde group converted to monocarboxylic acids

   - Rxn used to differentiate Aldoses from ketoses



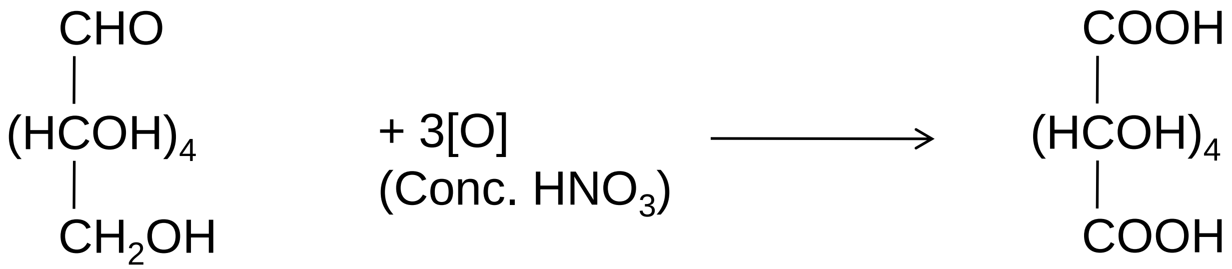
$$\begin{array}{c} CHO \\ | \\ (HCOH)_4 \\ | \\ CH_2OH \end{array} + HOBr \longrightarrow \begin{array}{c} COOH \\ | \\ (HCOH)_4 \\ | \\ COOH \end{array}$$

Glucose

Gluconic acid

b) Strong oxidants, HNO – aldehyde (ketone) and primary OH groups oxidised to dicarboxylic acids

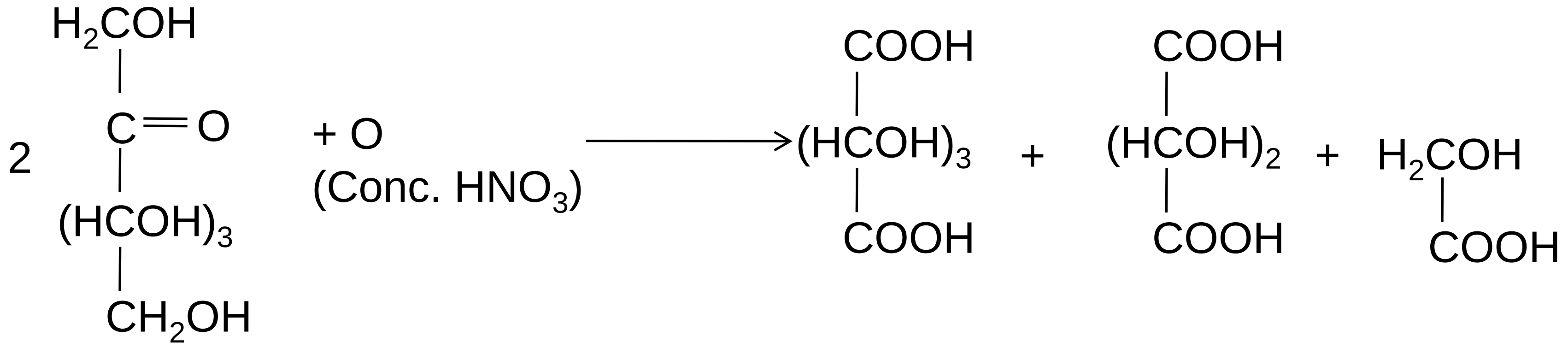
- Aldoses oxidised to same number of carbon atoms while ketoses are oxidised to fewer numbers of carbon products



$$\begin{array}{c}\text{CHO}\\ |\\ (\text{HCOH})_4\\ |\\ \text{CH}_2\text{OH}\end{array} \quad \begin{array}{l}+\ 3[\text{O}]\\ (\text{Conc. HNO}_3)\end{array} \longrightarrow \begin{array}{c}\text{COOH}\\ |\\ (\text{HCOH})_4\\ |\\ \text{COOH}\end{array}$$

Glucose
(An aldose)

Glucaric acid
(Saccharic acid)



$$2\ \begin{array}{c}\text{H}_2\text{COH}\\ |\\ \text{C}{=}\text{O}\\ |\\ (\text{HCOH})_3\\ |\\ \text{CH}_2\text{OH}\end{array} \quad \begin{array}{l}+\ \text{O}\\ (\text{Conc. HNO}_3)\end{array} \longrightarrow \begin{array}{c}\text{COOH}\\ |\\ (\text{HCOH})_3\\ |\\ \text{COOH}\end{array} + \begin{array}{c}\text{COOH}\\ |\\ (\text{HCOH})_2\\ |\\ \text{COOH}\end{array} + \begin{array}{c}\text{H}_2\text{COH}\\ |\\ \text{COOH}\end{array}$$

Fructose
(A ketose)

Trihydroxy
Glutaric acid

Tartaric acid

Glycolic acid

Rxns of CHO/C=O Groups

1. Oxidation with metal hydroxides

- $Cu(OH)_2$, AgOH and $Bi(OH)_3$ oxidise free CHO and C=O of mutarotating monosaccharides and disccharides and get reduced
- AgOH → Ag
- $Bi(OH)_3 \rightarrow Bi$

$Cu(OH)2 \rightarrow Cu_2O$

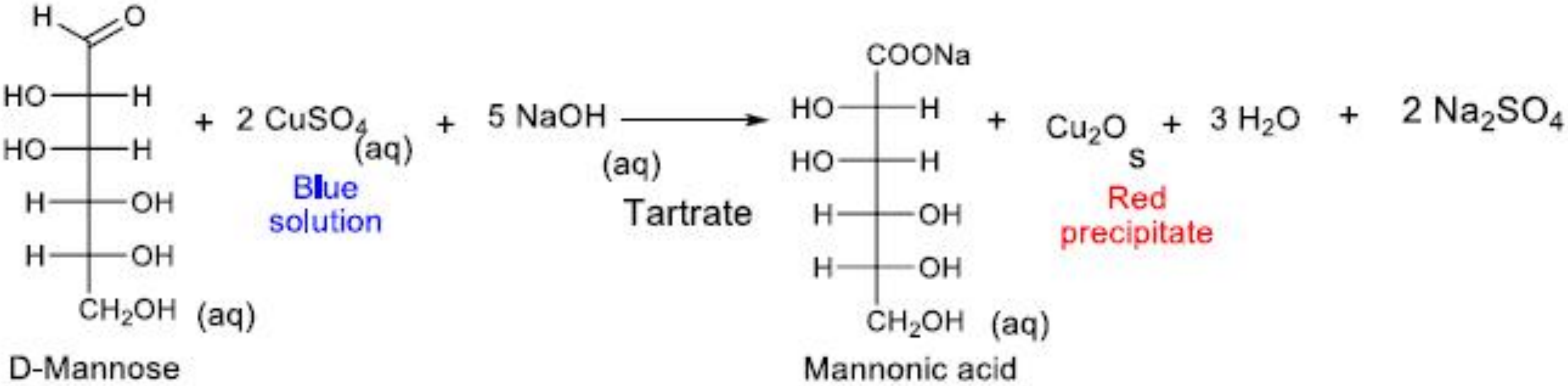
Reducing Sugar + $2Cu^{2+} \rightarrow$ Oxidised Sugar $+2Cu^{+}$

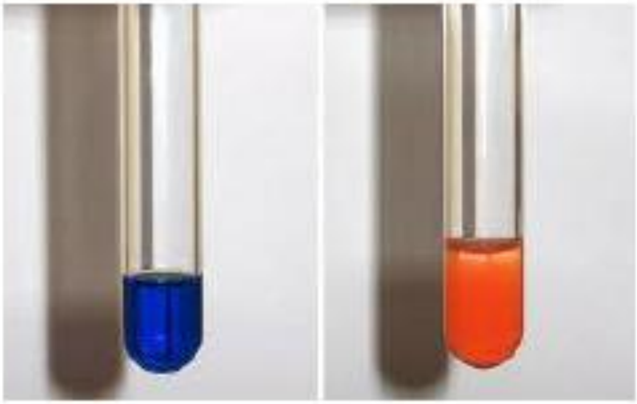
(Blue)

$2Cu^{2+} + 2^{-}OH \rightarrow Cu.OH \rightarrow Cu_2O + H_2O$

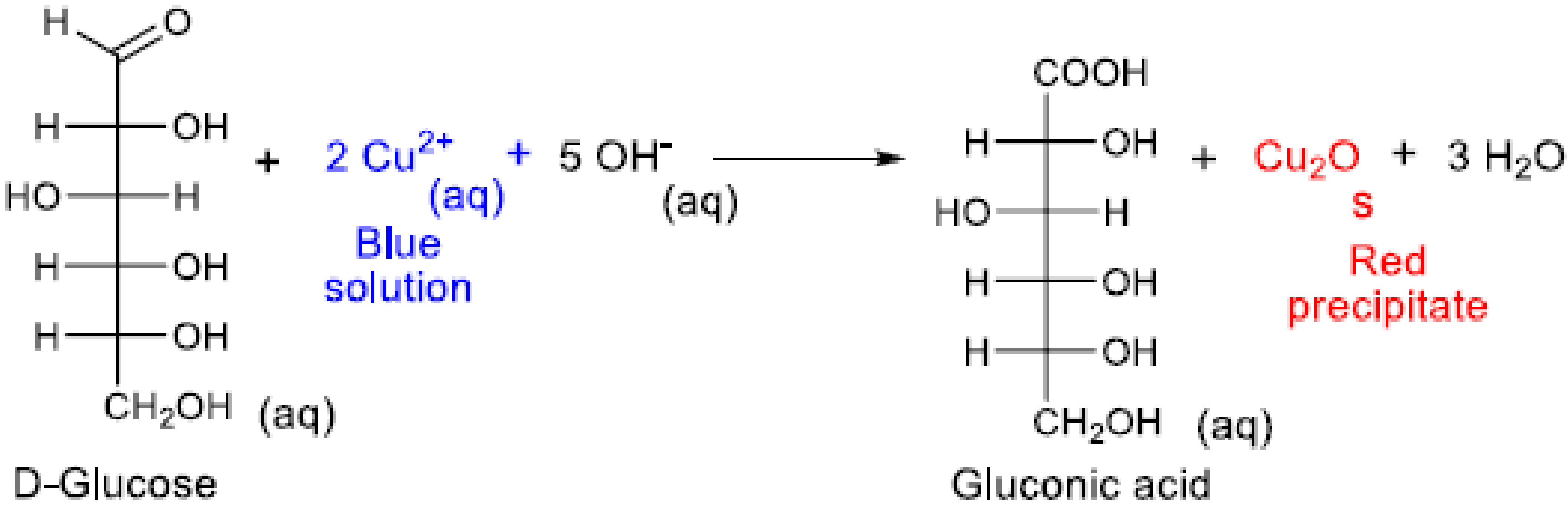
(Yellow) (Red)

- **Fehling’s reagent** (Equimolar of (a) 7% Cu.SO4 & (b) 25% KOH/35% Potassium tartarate) on mixing the two forms a clear blue solution
- Test for reducing sugars
- Solution used in quantitative determination of sugars

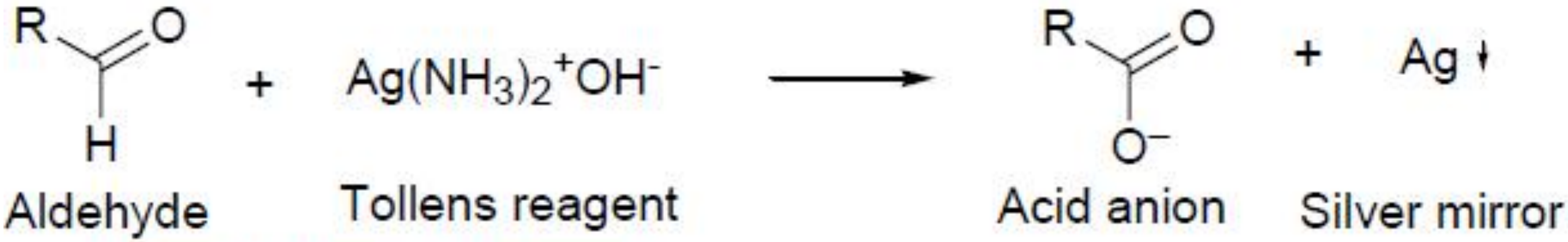

H
O
HO
H
HO
H
H
OH
H
OH
CH₂OH (aq)
D-Mannose
+ 2 CuSO₄ (aq)
Blue solution
+ 5 NaOH (aq)
Tartrate
COONa
HO
H
HO
H
H
OH
H
OH
CH₂OH (aq)
Mannonic acid
+ Cu₂O s
Red precipitate
+ 3 H₂O
+ 2 Na₂SO₄

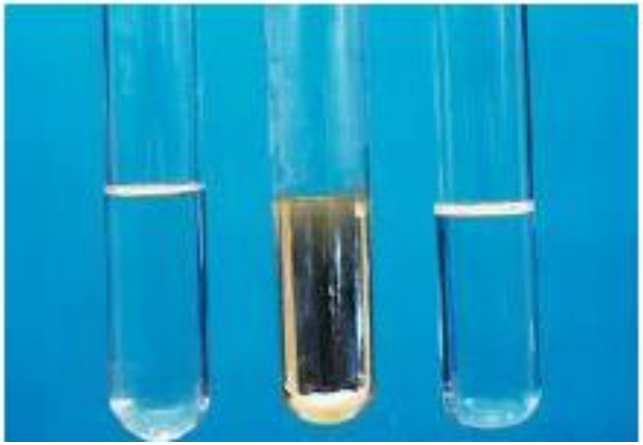


- **Benedict’s Reagent** – (Cu.SO_4, Na_2CO_3 & Sodium citrate
- Variant of Fehling’s reagent
- Qualitative determination of glucose in urine
- Alkaline solution of copper (II) sulphate as its citrate complex oxidizes aliphatic aldehydes, aldoses and ketoses to the corresponding carboxylic acid.
- Reducing sugars give a positive test result because the reduction of the metal is accompanied by oxidation of the sugar – hence called reducing sugars

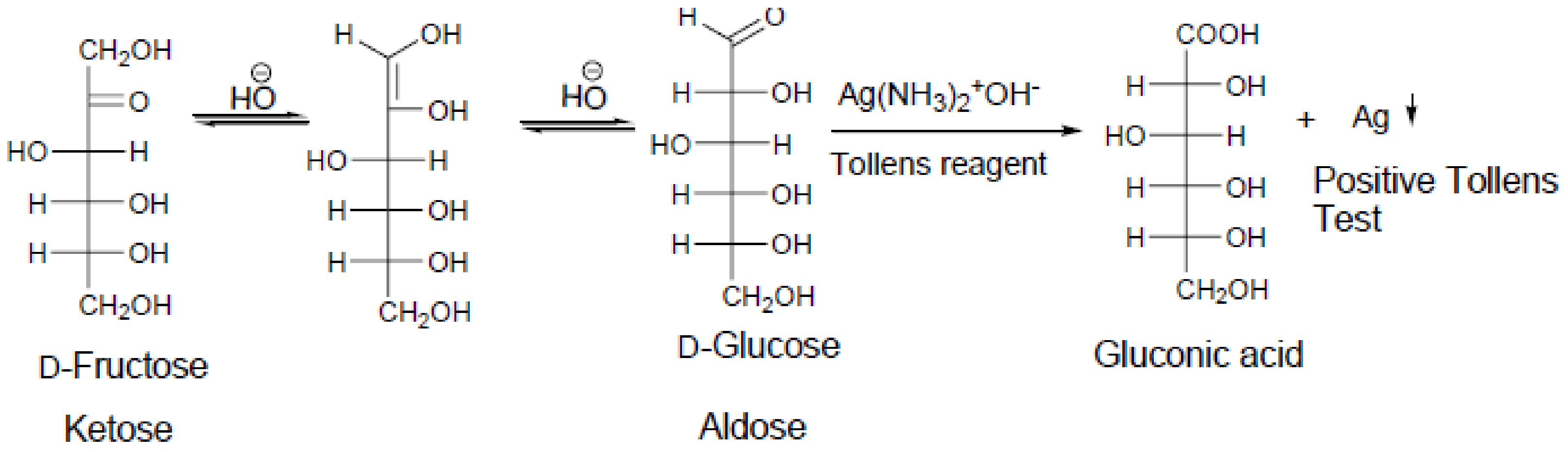

H
O
H
OH
HO
H
H
OH
H
OH
CH$_2$OH (aq)
D-Glucose
+
2 Cu^{2+} (aq)
Blue solution
+
5 OH$^-$ (aq)
COOH
H
OH
HO
H
H
OH
H
OH
CH$_2$OH (aq)
Gluconic acid
+
Cu$_2$O s
Red precipitate
+
3 H$_2$O

- **Tollens reagent -** (silver(1) ammonical hydroxide)
- Oxidizes aldehydes to carboxylate ions.
- Ag(I) complex is soluble in ammonium hydroxide is reduced to metallic silver
- Metallic silver is insoluble in ammonium hydroxide, resulting in formation of a silver mirror on inside of test-tube


R
O
H
+
$Ag(NH_3)_2^+OH^-$
Aldehyde
Tollens reagent
R
O
O^-
+
Ag ↓
Acid anion
Silver mirror



- Tollens test unable to differentiate between aldoses and ketoses but strongly basic solution of Tollens reagent promotes enediol rearrangements
- Basic conditions promotes open-chain form of ketoses being converted to aldoses, which give a +ve Tollens test. Hence Fructose gives a +ve result



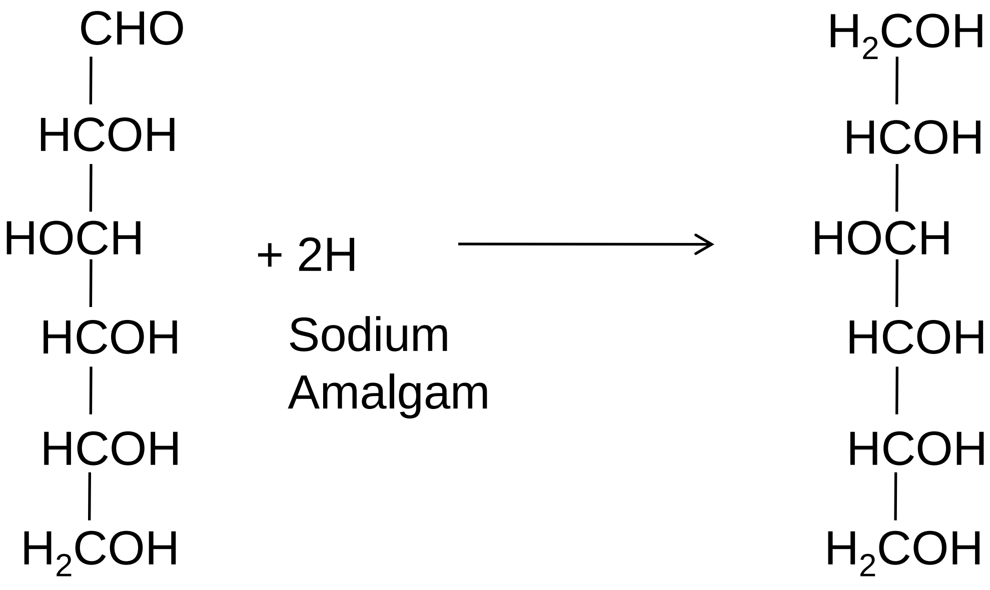
- **Barfoed’s reagent** – (7% Copper acetate & 1% acetic acid)
- Used to different monosaccharides from disaccharides
- Monosaccharides gives a cuprous oxide ppt in dilute acid more quickly than disaccharides
- Monosaccharides are more active reducing agents than disaccharides

- **Molisch test** – (H$_2$SO$_4$ & α-naphthol as a phenol
- Acid hydrolyses acetals and hence the most general of all test for carbohydrates
- Alkali conditions of earlier mentioned testscause fragmentation of sugars to give a mixture of different chain length upon oxidation of the carbohydrate
- Thus earlier test are good for analytical methods than preparative methods

2. Reduction

a) With Sodium amalgam

- Monosaccharides reduced to corresponding alcohol.

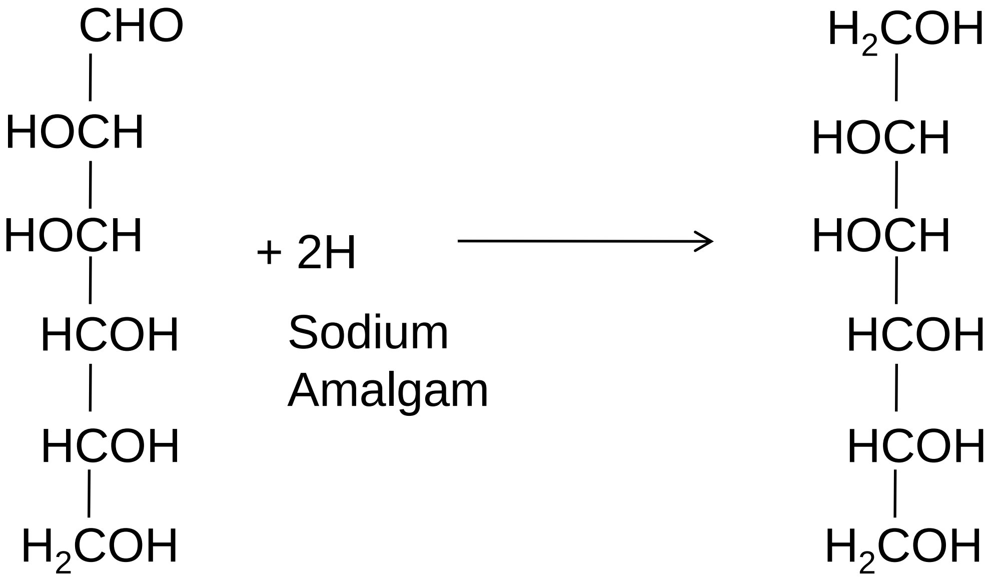


CHO
HCOH
HOCH
HCOH
HCOH
H_2COH
Glucose

+ 2H
Sodium Amalgam

$\longrightarrow$

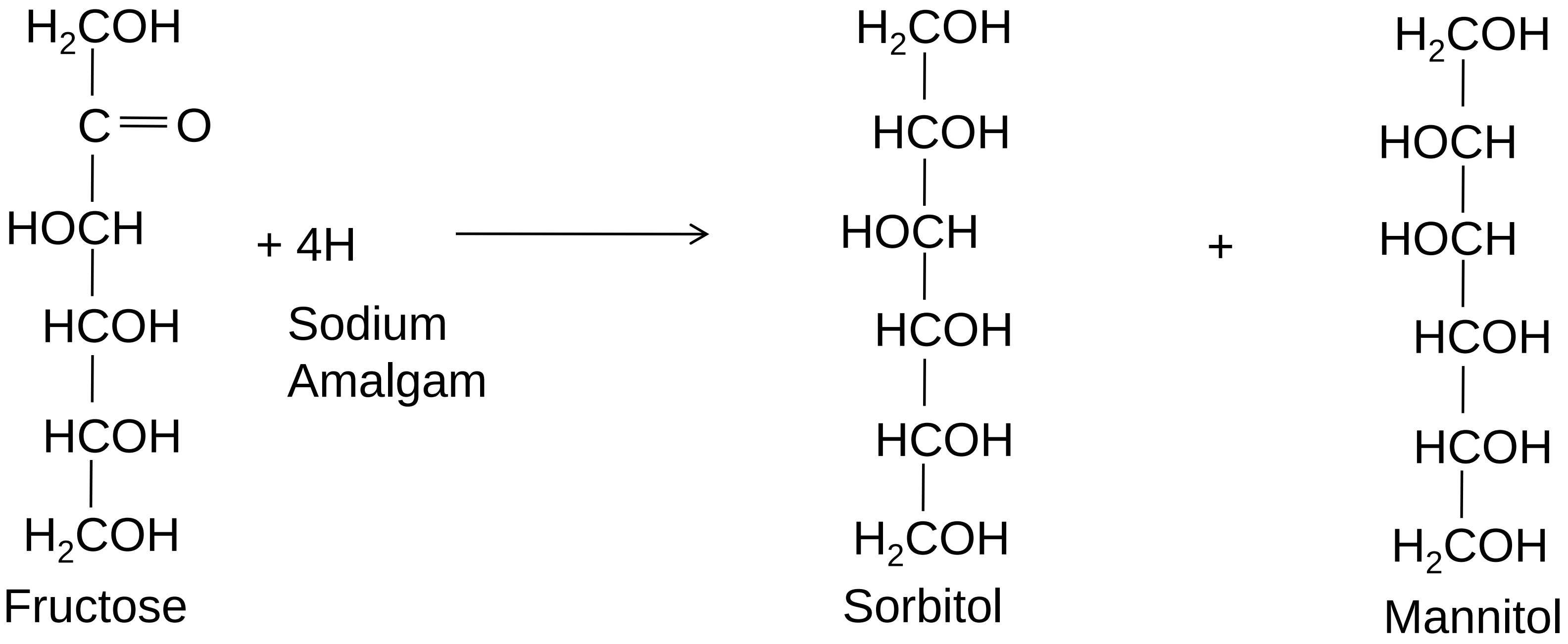
H_2COH
HCOH
HOCH
HCOH
HCOH
H_2COH
Sorbital



$$\begin{array}{c} \mathrm{CHO} \\ | \\ \mathrm{HOCH} \\ | \\ \mathrm{HOCH} \\ | \\ \mathrm{HCOH} \\ | \\ \mathrm{HCOH} \\ | \\ \mathrm{H_2COH} \end{array} + 2\mathrm{H} \xrightarrow[\text{Sodium Amalgam}]{} \begin{array}{c} \mathrm{H_2COH} \\ | \\ \mathrm{HOCH} \\ | \\ \mathrm{HOCH} \\ | \\ \mathrm{HCOH} \\ | \\ \mathrm{HCOH} \\ | \\ \mathrm{H_2COH} \end{array}$$

Mannose

Mannitol



H_2COH
C=O
HOCH
HCOH
HCOH
H_2COH
Fructose

+ 4H
Sodium
Amalgam

$\longrightarrow$

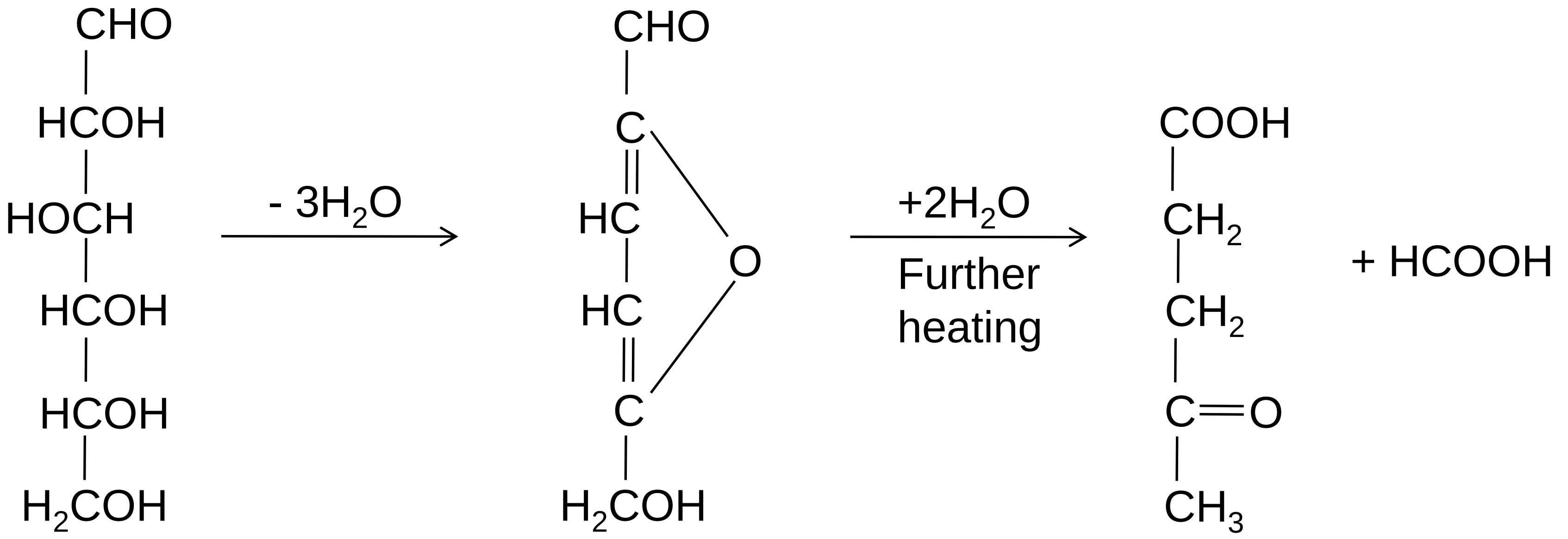
H_2COH
HCOH
HOCH
HCOH
HCOH
H_2COH
Sorbitol

+

H_2COH
HOCH
HOCH
HCOH
HCOH
H_2COH
Mannitol

- Sorbitol and mannitol are used for manufacture of surface active agents and explosives

b) With strong mineral acids

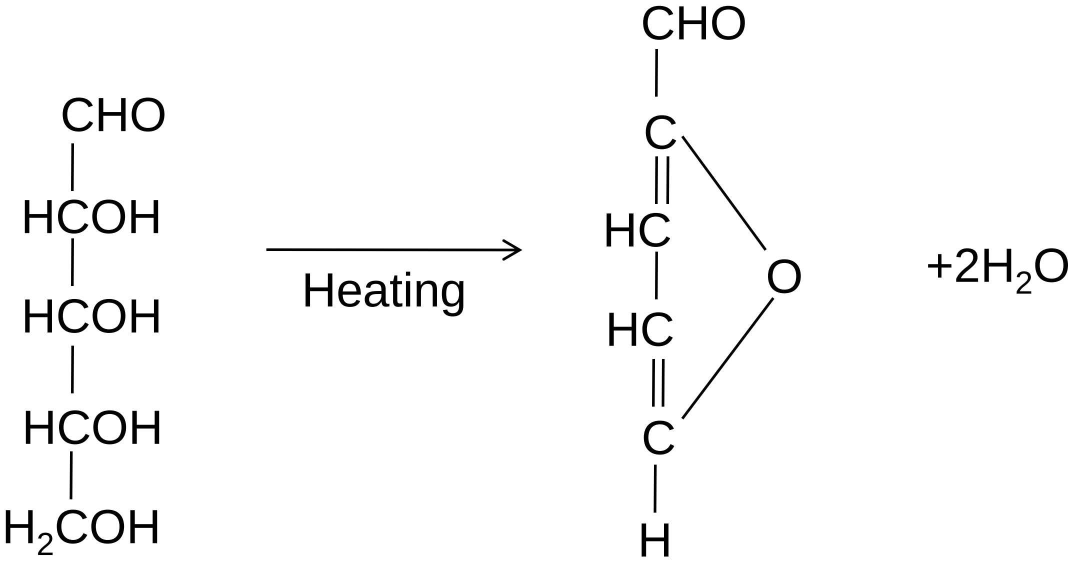


Glucose (Hexose)

5-Hydroxymetylfurfural

Levulinic acid

Formic acid



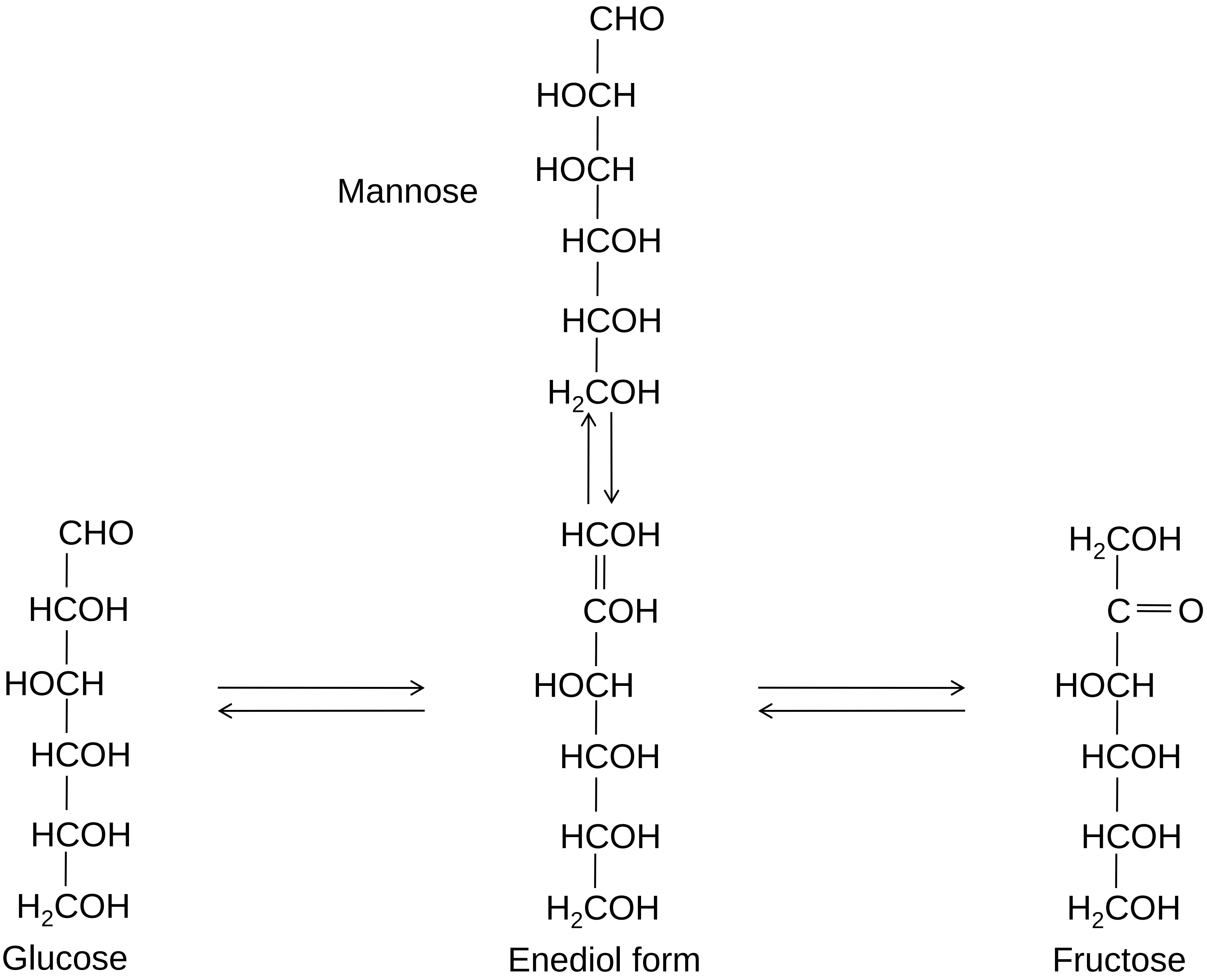
Ribose
Pentose)

Furfural

- Tetroses and Troses do not under this rxn as they have fewer carbon atoms of less than 5 to form a furfural

c) With dilute alkalies

- Lobry De Bruyn-Alberda van Ekenstein transformation/rxn
- In weak alkaline solns of Ca(OH)2 and Ba(OH)2 at temperatures, glucose, mannose and fructose are interconvertable


Mannose
Glucose
Enediol form
Fructose

3. Rxn with Hydrogen cyande (Killiani Synthesis)

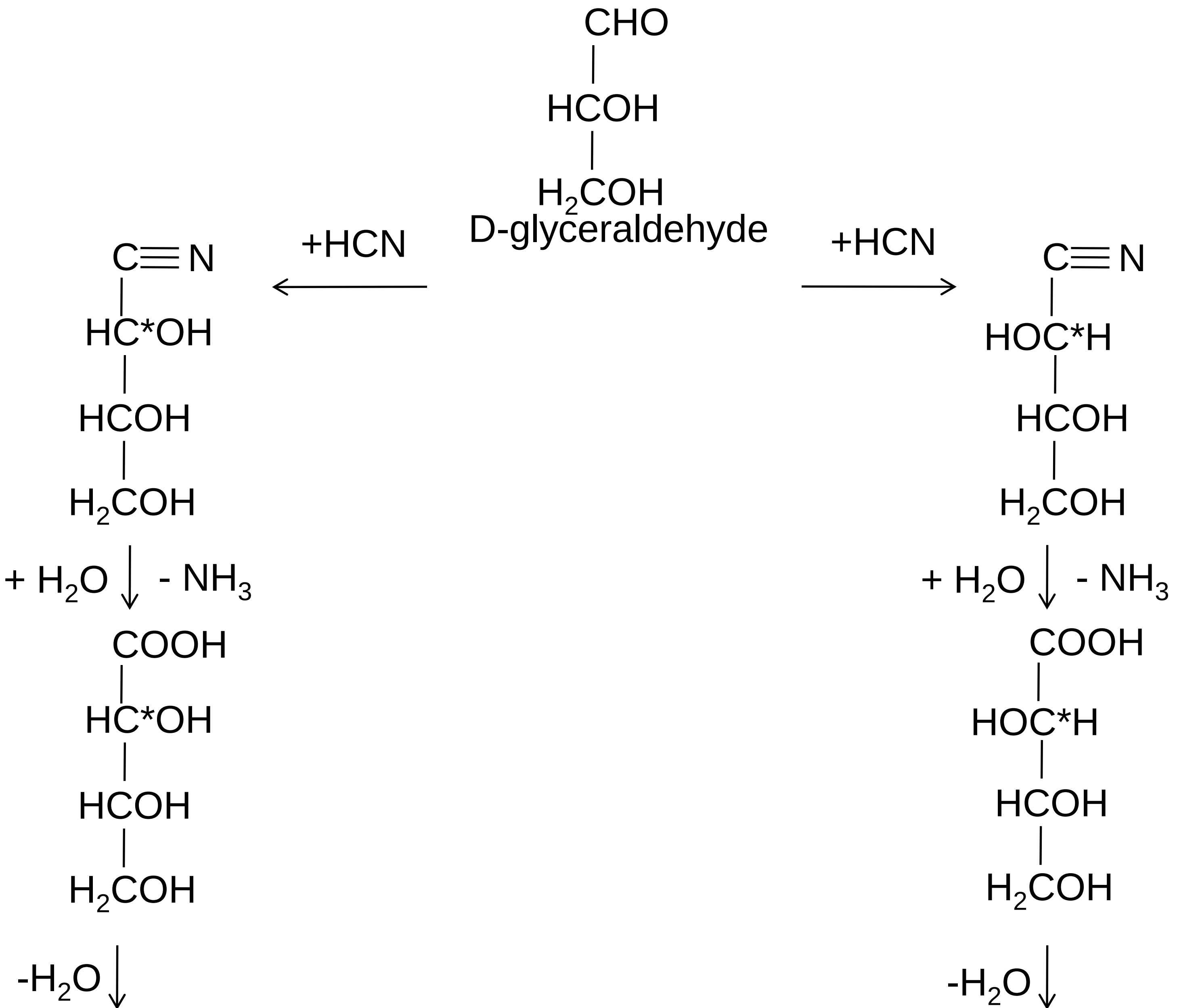
- Method for monosaccharide synthesis by chain elongation of the existing carbohydrate using 4 rxns:-

i. Cyanohydrin formation - Based on addition of HCN to carbonyl carbon of aldehyde or ketone to cyanohydrin

ii. Hydrolysis - Cyanohydrins hydrolysed to carboxylic acids

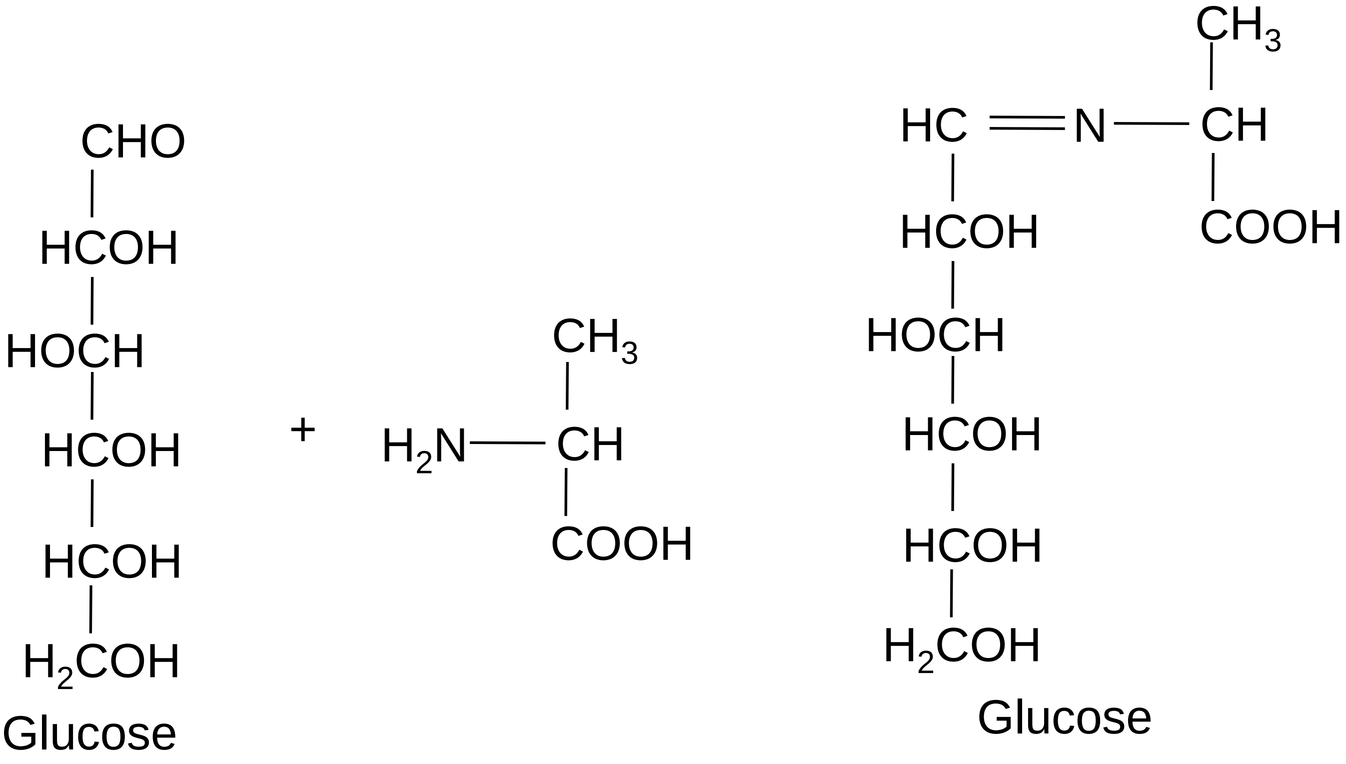
iii. Lactonisation - Carboxylic acids converted to γ-lactones or inner esters

iv. Reduction - Lactones reduced to corresponding aldoses containing 1 more carbon atom than the parent sugar


CHO
HCOH
H2COH
D-glyceraldehyde
+HCN
+HCN
C≡N
HC*OH
HCOH
H2COH
+ H2O
- NH3
COOH
HC*OH
HCOH
H2COH
-H2O
C≡N
HOC*H
HCOH
H2COH
+ H2O
- NH3
COOH
HOC*H
HCOH
H2COH
-H2O

4. Rxn with Ala

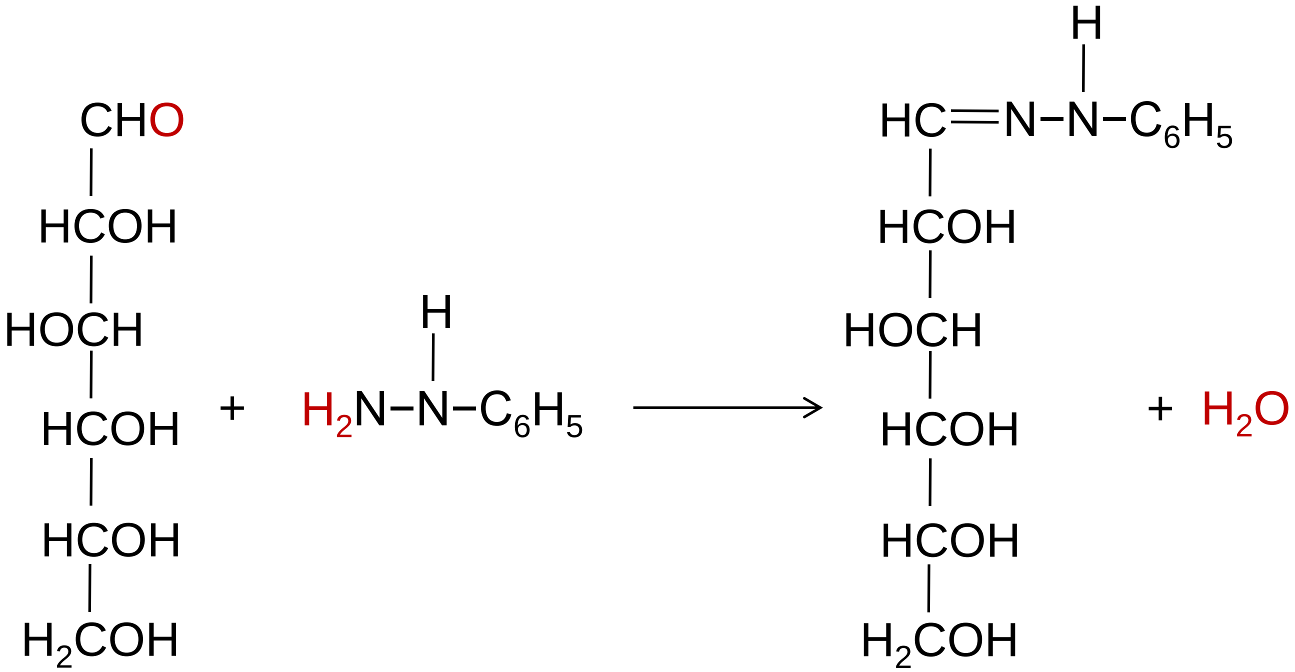
- Formation of schiff bases – Ala reacts with carbohydrates



- Browning of bread during baking and other mixtures of carbohydrates and proteins thought to be due to formation of schiff bases as a result of the rxn between carbohydrate aldehyde group and amine groups of proteins

5. Reaction with Phenyl Hydrazine

- Involves the carbonyl carbon (aldehyde or ketone) and the adjust carbon atom in the monosaccharide
- 3 mole of phenyl hydrazine are required to reduce the monosaccharide to react with aldehydes or ketones

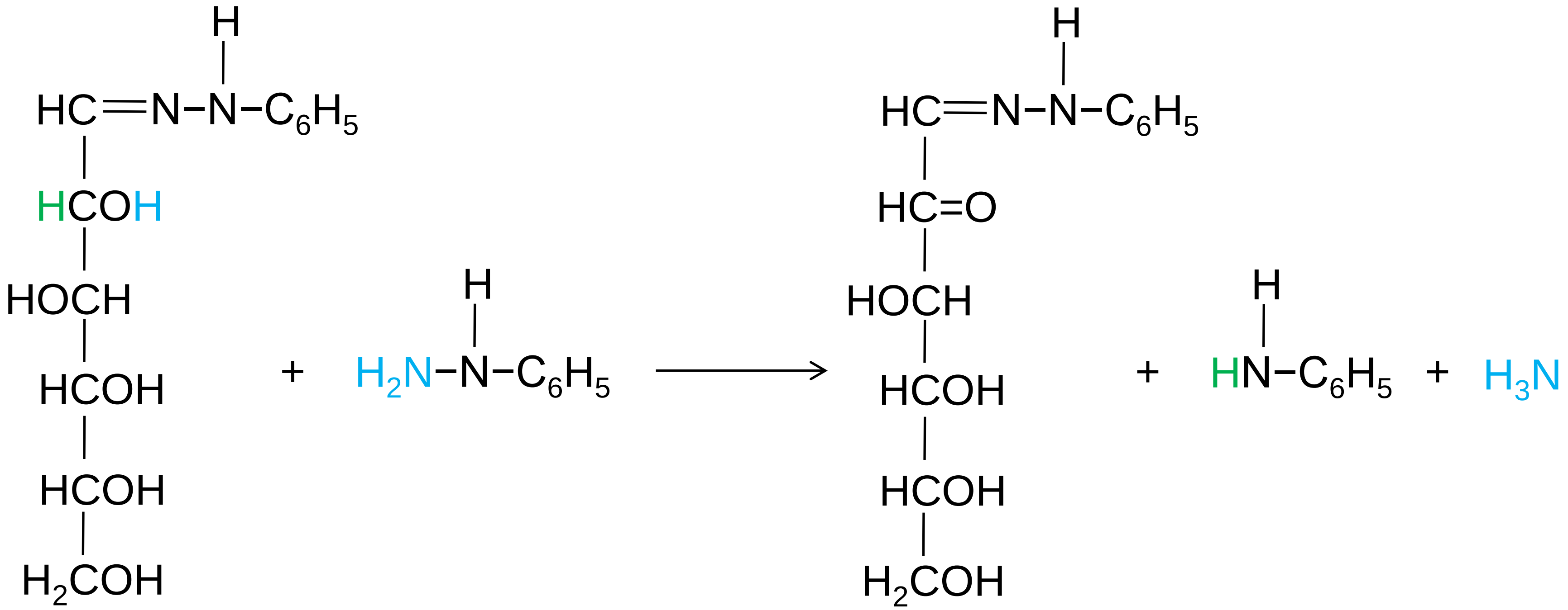


$$\begin{array}{c} CHO \\ | \\ HCOH \\ | \\ HOCH \\ | \\ HCOH \\ | \\ HCOH \\ | \\ H_2COH \end{array} + \begin{array}{c} \quad\; H \\ \quad\; | \\ H_2N-N-C_6H_5 \end{array} \longrightarrow \begin{array}{l} \qquad\qquad\; H \\ \qquad\qquad\; | \\ HC=N-N-C_6H_5 \\ | \\ HCOH \\ | \\ HOCH \\ | \\ HCOH \\ | \\ HCOH \\ | \\ H_2COH \end{array} + H_2O$$

Glucose

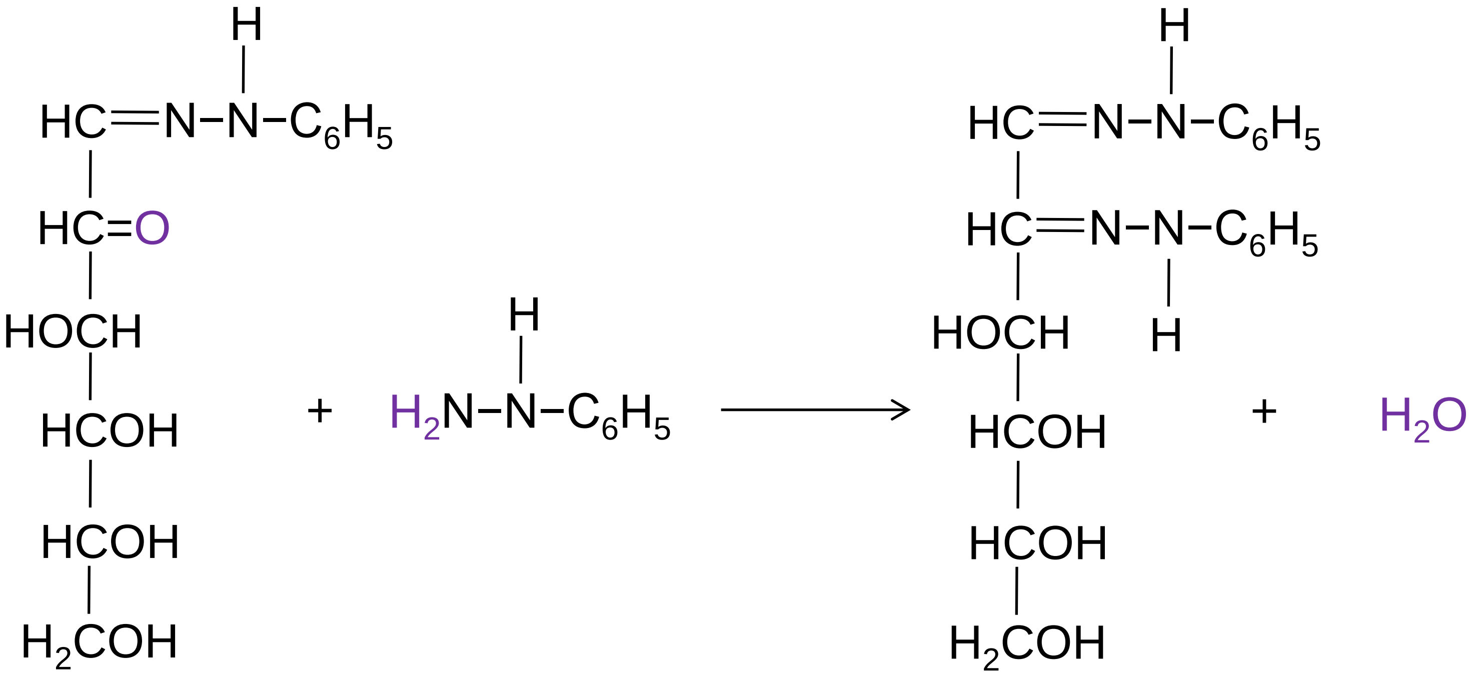
Phenyl hydrazine

Glucose hydrazine



$$\begin{array}{c} HC{=}N{-}\overset{H}{N}{-}C_6H_5 \\ | \\ HCOH \\ | \\ HOCH \\ | \\ HCOH \\ | \\ HCOH \\ | \\ H_2COH \end{array} + H_2N{-}\overset{H}{N}{-}C_6H_5 \longrightarrow \begin{array}{c} HC{=}N{-}\overset{H}{N}{-}C_6H_5 \\ | \\ HC{=}O \\ | \\ HOCH \\ | \\ HCOH \\ | \\ HCOH \\ | \\ H_2COH \end{array} + H\overset{H}{N}{-}C_6H_5 + H_3N$$

Glucose hydrazine Phenyl hydrazine Glucose hydrazone Aniline

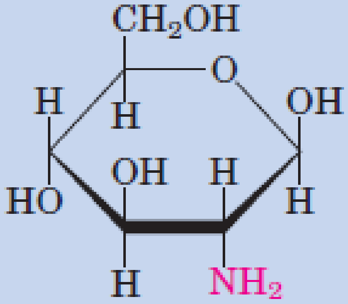


Glucose hydrazone Phenyl hydrazine Glucose osazone

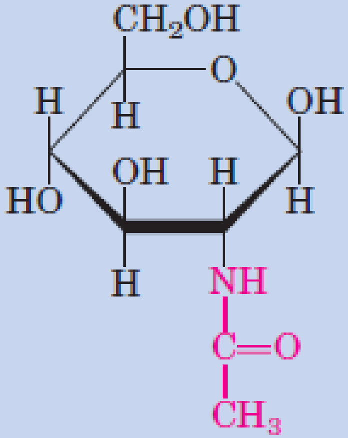
Osazones of mutarotating reducing sugars

- form yellow usually insoluble crystals
- have characteristic melting temperatures
- Hence used for identification of sugars
- Reducing disaccharides form crystals with specific shapes
- Glucose, fructose and mannose form the same osazone hence cannot be differentiated by this reaction

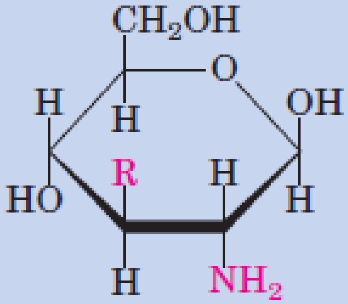
- **Sugar derivatives**
- Hydroxyl group in parent cpd replaced with another substituent, or carbon atom is oxidized to a carboxyl group
- Hydroxyl at C-2 of glucose, galactose & mannose, replaced with an amino group to give glucosamine, galactosamine & mannosamine, respectively
- Amino group is nearly always condensed with acetic acid, as in N-acetylglucosamine



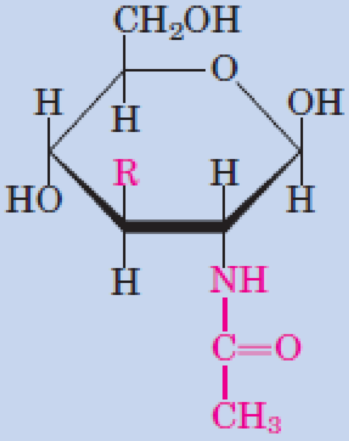
β-D-Glucosamine



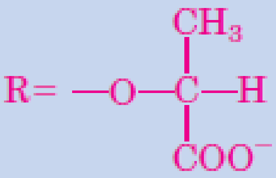
N-Acetyl-*β*-D-glucosamine



Muramic acid



N-Acetylmuramic acid



$$R = -O-\overset{\displaystyle CH_3}{\underset{\displaystyle COO^-}{C}}-H$$

- N-acetylglucosamine forms part of many structural polymers, including those of bacterial cell wall
- Bacterial cell walls also contain a derivative of glucosamine, N-acetylmuramic acid

Functions of monosaccharides

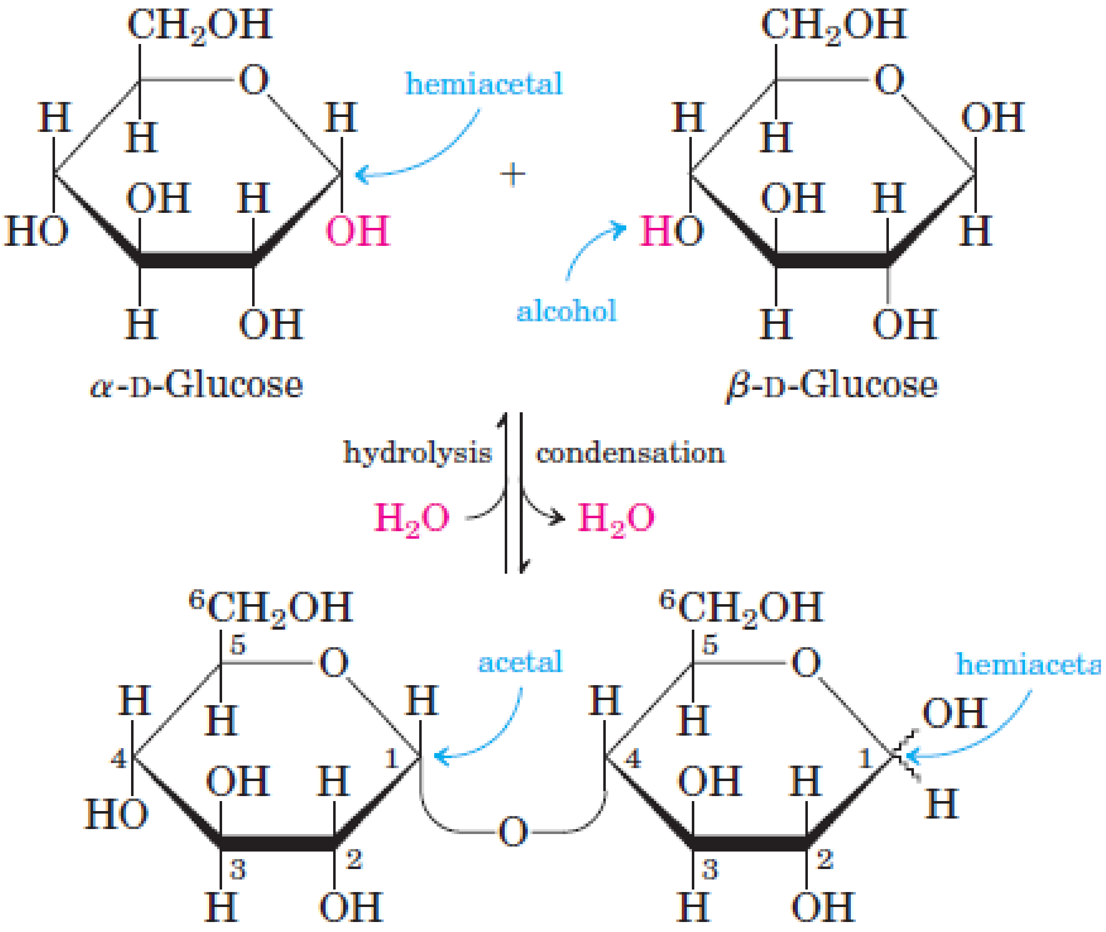
- Important metabolic intermediates both in phosphorylated and unphosphorylated forms, for the generation of energy
- Important constituents of nucleotides, nucleic acids, and many coenzymes e.g. NAD, NADP, flavoproteins. In this case it is mostly the pentoses.
- As glycosides they found in many drugs and spices
- As amino sugars are contained in several antibiotics e.g. erythromycins.

Disaccharides

- Most common among oligosaccharides
- Sugars made up of 2 monosaccharides joined by a glycosidic linkage.
- Three abundant disaccharides - sucrose, lactose and maltose

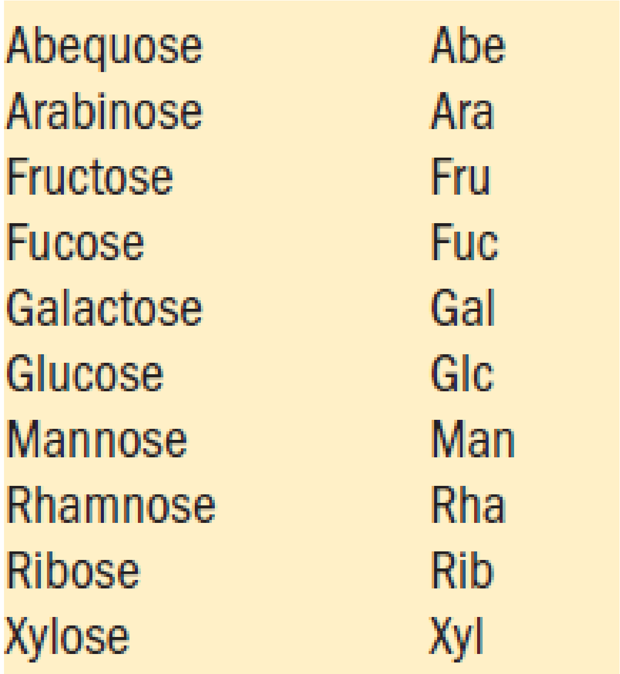
Maltose

- Derived from starch, germinating cereals and malt.
- Made up of 2 glucose molecules joined by α-1, 4 glycosidc linkage



Maltose

α-D-glucopyranosyl-(1→4)-D-glucopyranose

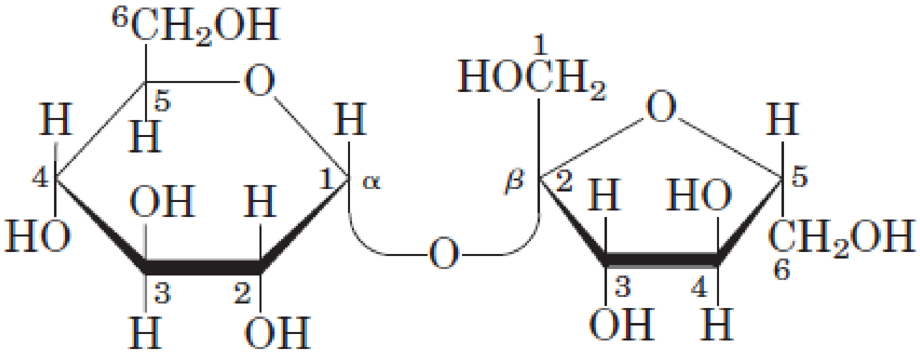


Abequose	Abe
Arabinose	Ara
Fructose	Fru
Fucose	Fuc
Galactose	Gal
Glucose	Glc
Mannose	Man
Rhamnose	Rha
Ribose	Rib
Xylose	Xyl

- Hydrolysed to 2 glucose molecules by maltase found on the outer surface of epithelial cells lining the small intestines.
- It is a reducing sugar

Sucrose

- Found in Cane and beet sugar, sorghum, pineapple and carrot roots
- Made up of α – D-glucose and β –D- fructose
- The two are joined through their anomeric carbon atoms



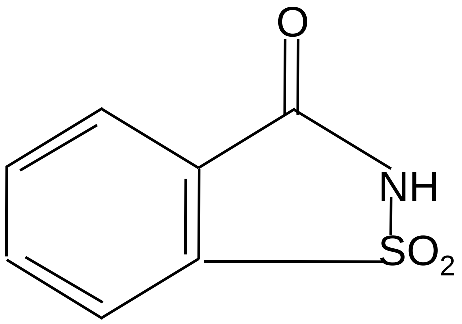
Sucrose
α-D-glucopyranosyl β-D-fructofuranoside
Glc(α1↔2β)Fru

- The aldehyde or ketone group is utilised in the formation of α 1 – 2 glycosidic linkage.
- Absence of anomeric carbon makes sucrose fail to reduce alkaline cupper sulphate, hence it is called a non reducing sugar
- It is hydrolysed to its constituent monosaccharides by sucrase found in the intestinal mucosal cells
- Sucrase is also called invertase because it converts the initial substrate dextrorotatory sucrose to glucose which is dextrorotatory and fructose which is levorotatory

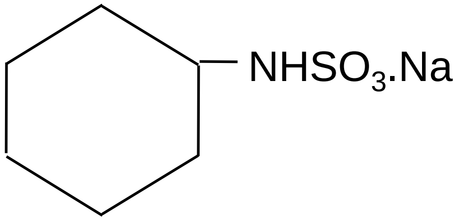
- Sucrase is also called invertase because it converts the initial substrate dextrorotatory sucrose to glucose which is dextrorotatory and fructose which is levorotatory
- Levorotatory fructose predominates and hence changes or inverts the dextrorotatory sucrose to levorotatory.
- Action of sucrase on sucrose results in a mixture of glucose and fructose (or called invert sugar)
- Sweetest of the three common sugars but less so of artificial sweeteners

ARTIFICIAL SWEETENERS

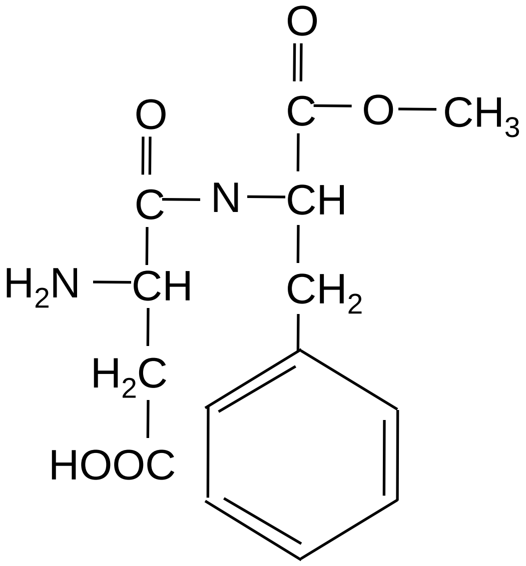
- Are molecules/cpds of different types that stimulate tongue taste buds stimulated by sugars but are of no food value



Sacharin



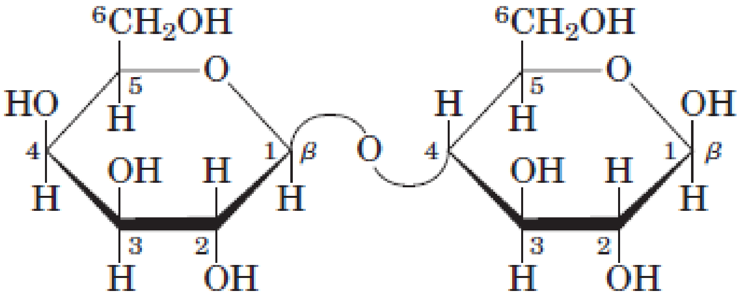
Sucaryl sodium



Aspartame

Sugar/Sweetener	**Relative Sweetness**
Sugars	
Lactose	0.16
D-Galactose	0.32
Maltose	0.32
D-Xylose	0.40
D-Glucose	0.74
Sucrose	*1.00*
Invert sugar	*1.23*
D-Fructose	1.73
Sweetener	
Sucaryl sodium	30
Aspartame	180
Saccharine	400
Monellin	2000

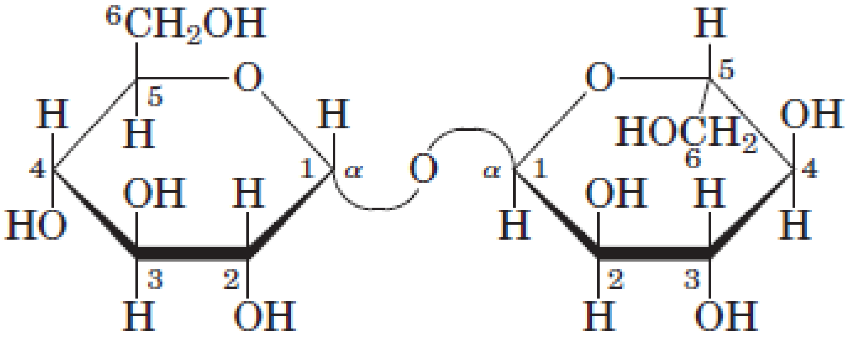
Lactose



Lactose (β form)
β-D-galactopyranosyl-(1→4)-β-D-glucopyranose
Gal(β1→4)Glc

- Found in milk, may occur in urine during pregnancy
- Made up of galactose and glucose joined β -1, 4-glycosidic linkage
- Hydrolysed by lactase found in outer surface of epithelial cells of intestines
- Is a reducing sugar because it has a free anomeric carbon, which would form an aldehyde in a basic solution and is able to reduce alkaline cupper sulphate
- Forms osazones

- Trehalose
- Occurs in yeast, fungi & major component of insect circulating fluid (hemolymph)
- Made up of two α-D-glucose through 1 → 1 glycosidic linkage



Trehalose
α-D-glucopyranosyl α-D-glucopyranoside
Glc(α1↔1α)Glc

- Acid (HCl) hydrolysis yields 2 glucose units
- Non reducing sugar & does not form osazones

Polysaccharides

- Made up of more than 10 monosaccharide (2 – 10 called oligosaccharides).

a. Homopolysaccharides contain only type of monomeric unit, e.g. starch and glycogen.

b. heteropolysaccharides contain two or more different types of monomeric units, e.g. Hyaluronic acid.

Starch

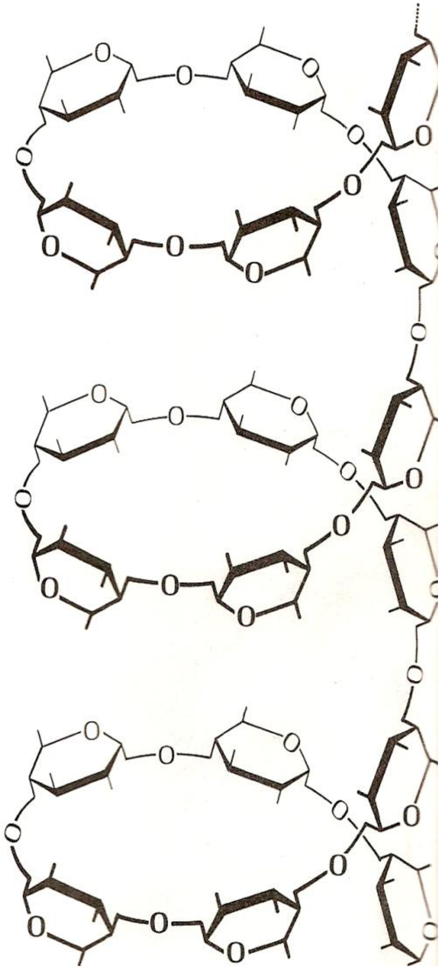
Sources

- Cereals, legumes, potatoes and other vegetables.
- Starch occurs in two types

1**. Amylose** (15 – 20 %)

- Consists of long unbranched chains with all D – glucose units linked through α (1 – 4) glycosidic linkages.
- Chains vary in molecular weights from a few thousands to 500 000.

- Occurs in helical structures which are not truly water soluble but form micelles which are responsible for the blue/purple colour when reacted with iodine.
- Major components of starch can hydrolysed into two different ways

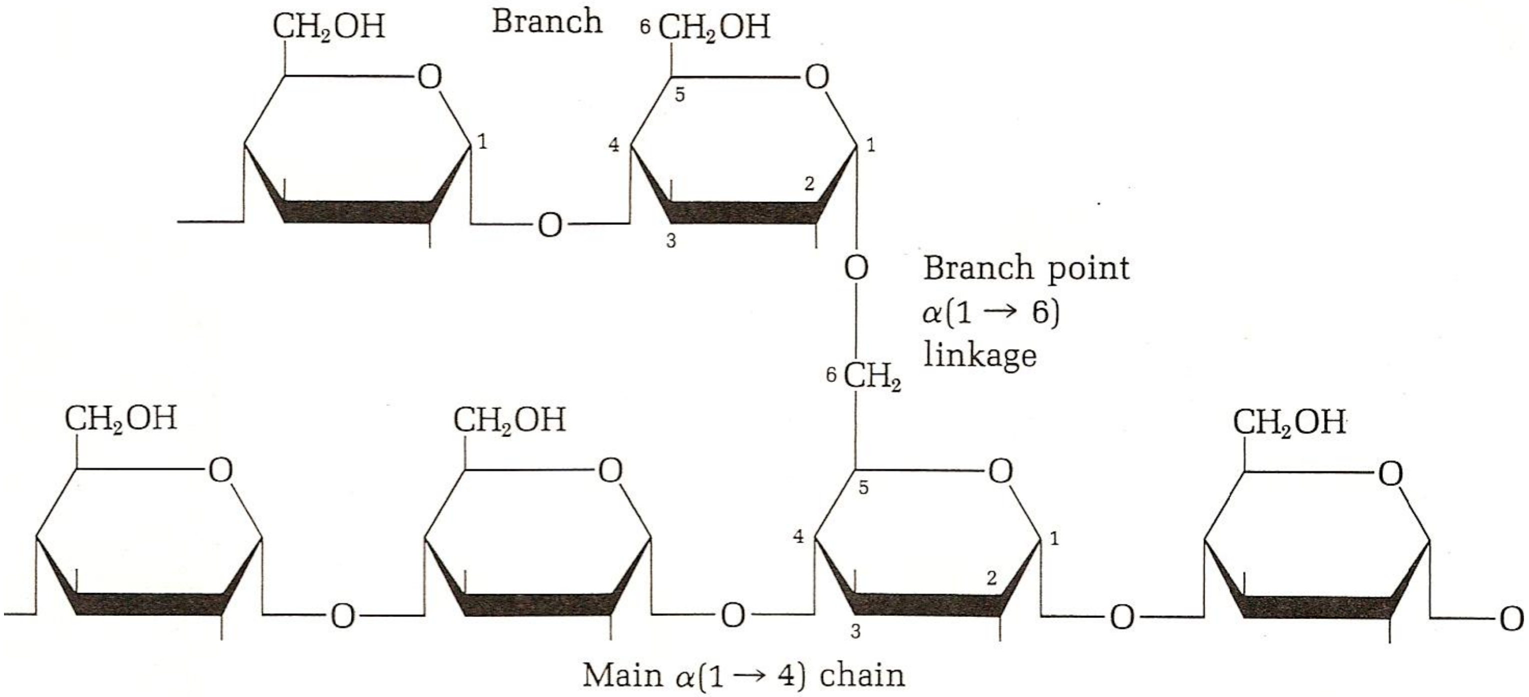


Helical structure of Amylose

- a. Amylose can be hydrolysed by α – amylase [α (1-4)-glucan 4-glucanohydrolase] present in saliva and pancreatic juice and takes part in the hydrolysis of starch in the GIT.
- α – amylase cleaves the α (1-4) linkages at random to yield a mixture of glucose and free maltose only.
- b. Amylose also hydrolysed by β – amylase [α (1-4)-glucan 4-maltohydrolase] which occurs in malt
- It cleave successive maltose from the reducing end and quantitatively.

Amylopectin

- Highly branched
- Branches have an average length of about 24 to 30 glucose residues and this is dependent on species.
- Glucose residues forming the backbone are linked through α (1-4) glycosidic linkages.
- Branch points are through α (1-6) glycosidic linkages

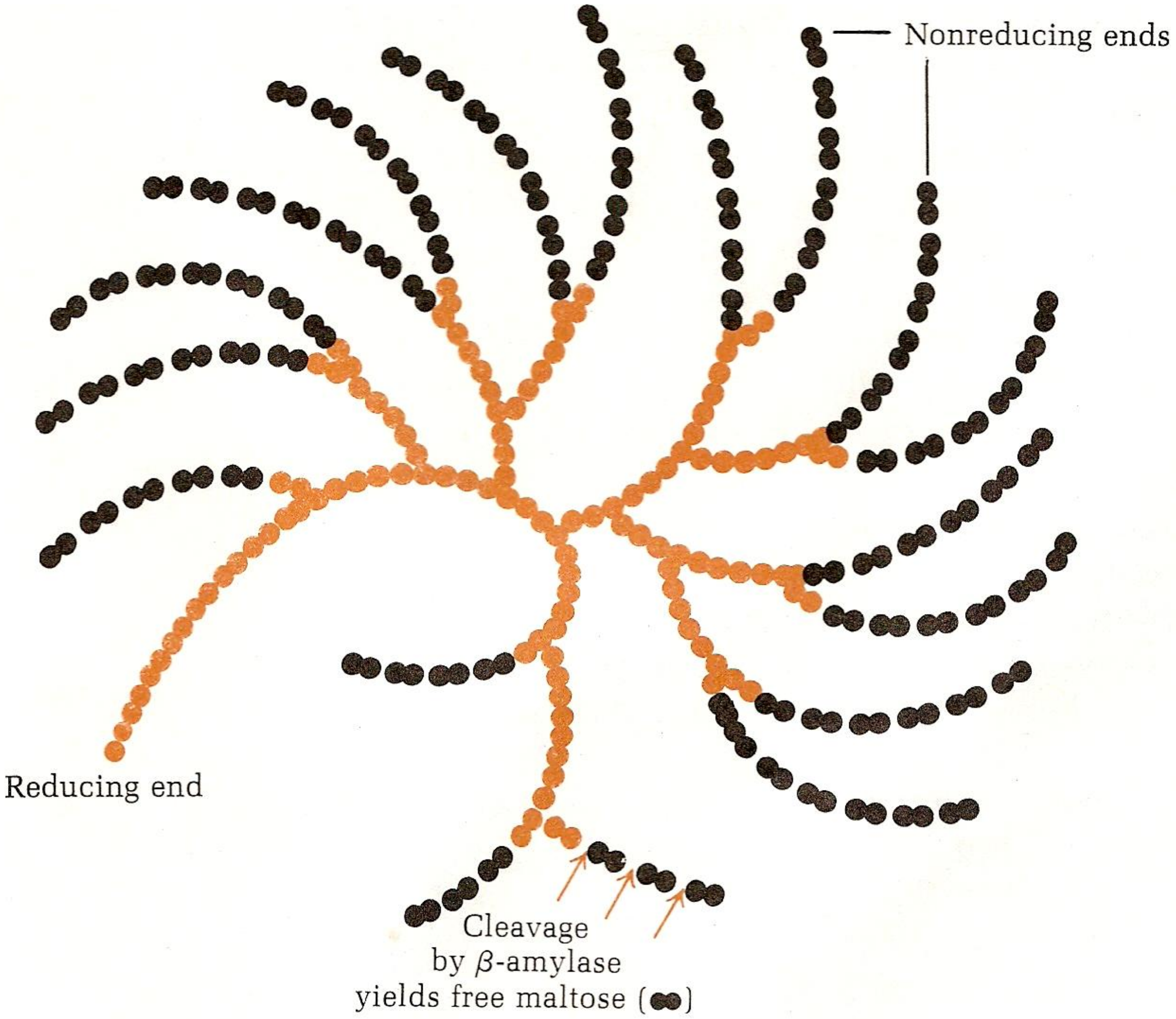


Branch

Branch point $\alpha(1 \rightarrow 6)$ linkage

Main $\alpha(1 \rightarrow 4)$ chain

- Exhaustive end product resulting from the action of β – amylase on starch is a highly branched core called LIMIT DEXTRINS.
- Called limit dextrin because it represents the limit of action of β – amylase on starch, as β – amylase is unable to hydrolyse α (1-6) glycosidic linkages.
- α (1- 6)-glucosidase [α (1- 6)-glucan 6-glucanohydrolase] is a debranching enzyme that is able to hydrolyse the α (1-6) glycosidic linkages at branch points.
- Therefore, amylopectin can be hydrolysed to maltose and glucose through the combined action of β – amylase and α (1- 6)-glucosidase.

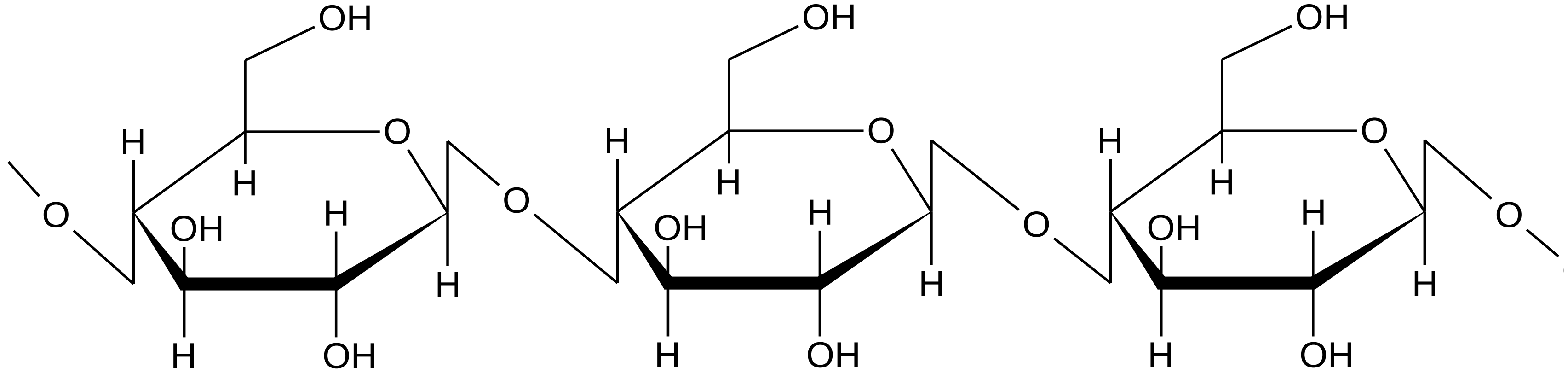

Nonreducing ends
Reducing end
Cleavage
by β-amylase
yields free maltose (●●)

Glycogen

- Stored in animal muscle and liver especially where it may occur up to 70 % of the wet weight.
- Made up of glucose moieties that are linked through α (1-4) glycosidic linkages.
- A compact and highly branched molecule
- Branches occur every 8 to 12 glucose residues.
- Branches increases the solubility of glycogen and create large numbers of terminal residues hence increases rate of synthesis and degradation of glycogen
- Branches occur through α (1-6) glycosidic linkages.
- Hydrolysed by α-amylase into glucose
- β – amylase hydrolyses it into maltose and its action result in limit dextrins.
- Gives a red-violet colour with iodine.

Cellulose

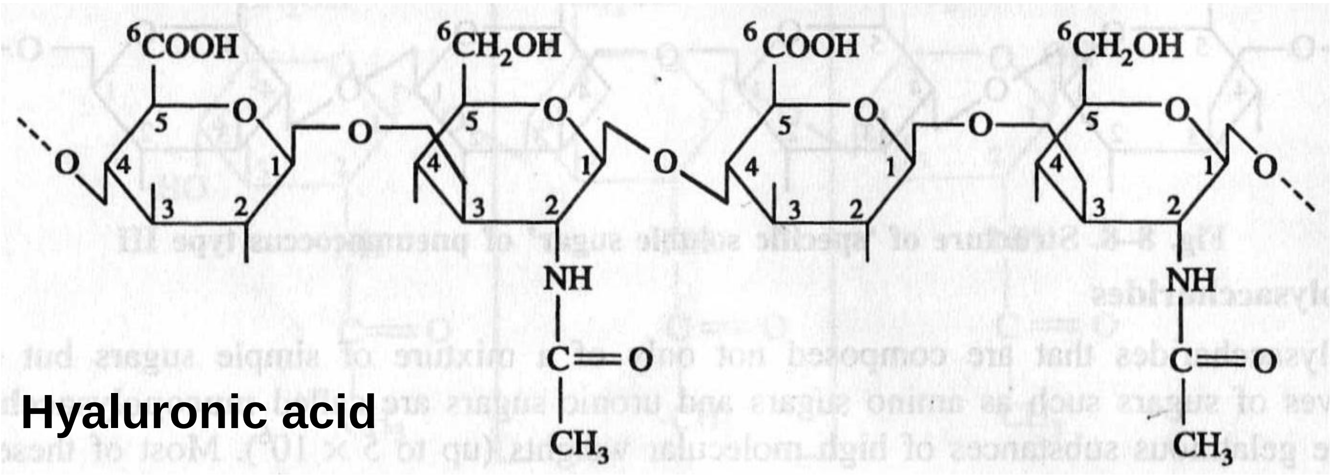
- Most abundant extra cellular polysaccharides
- A linear molecule of β D-glucose which are joined through β (1-4) linkages
- Contains about 1250 – 12500 glucose residues per molecule of cellulose



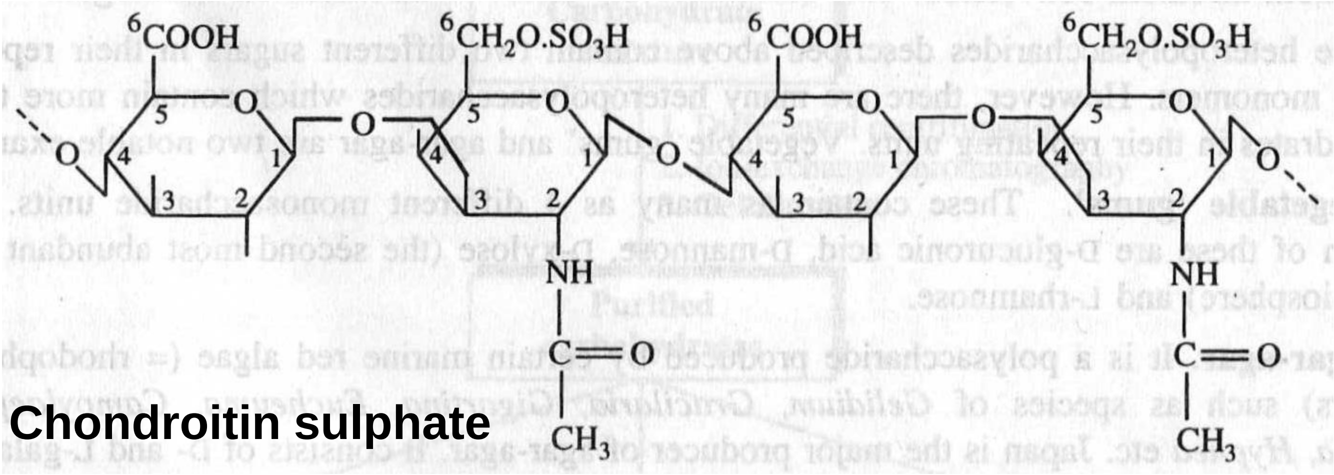
- Cellulose can not be hydrolysed by α – amylase and β – amylase, hence can not be hydrolysed by mammals.
- Ruminants e.g. cows can utilise cellulose for energy generation because the bacteria in their rumen posses cellulase which hydrolyses cellulose to glucose

Heteropolysaccharides

Heteropolysaccharide	**Constituents**	**Linkage between 2 monosaccharide of disaccharide units**	**Linkage between repeating unit**
Hyaluronic acid	D-glucuronic acid and N-Acetyl-D-glucosamine	β (1-3)	β (1-4)
Chondroitin	D-glucuronic acid and N-Acetyl-D-galactosamine	β (1-3)	β (1-4)

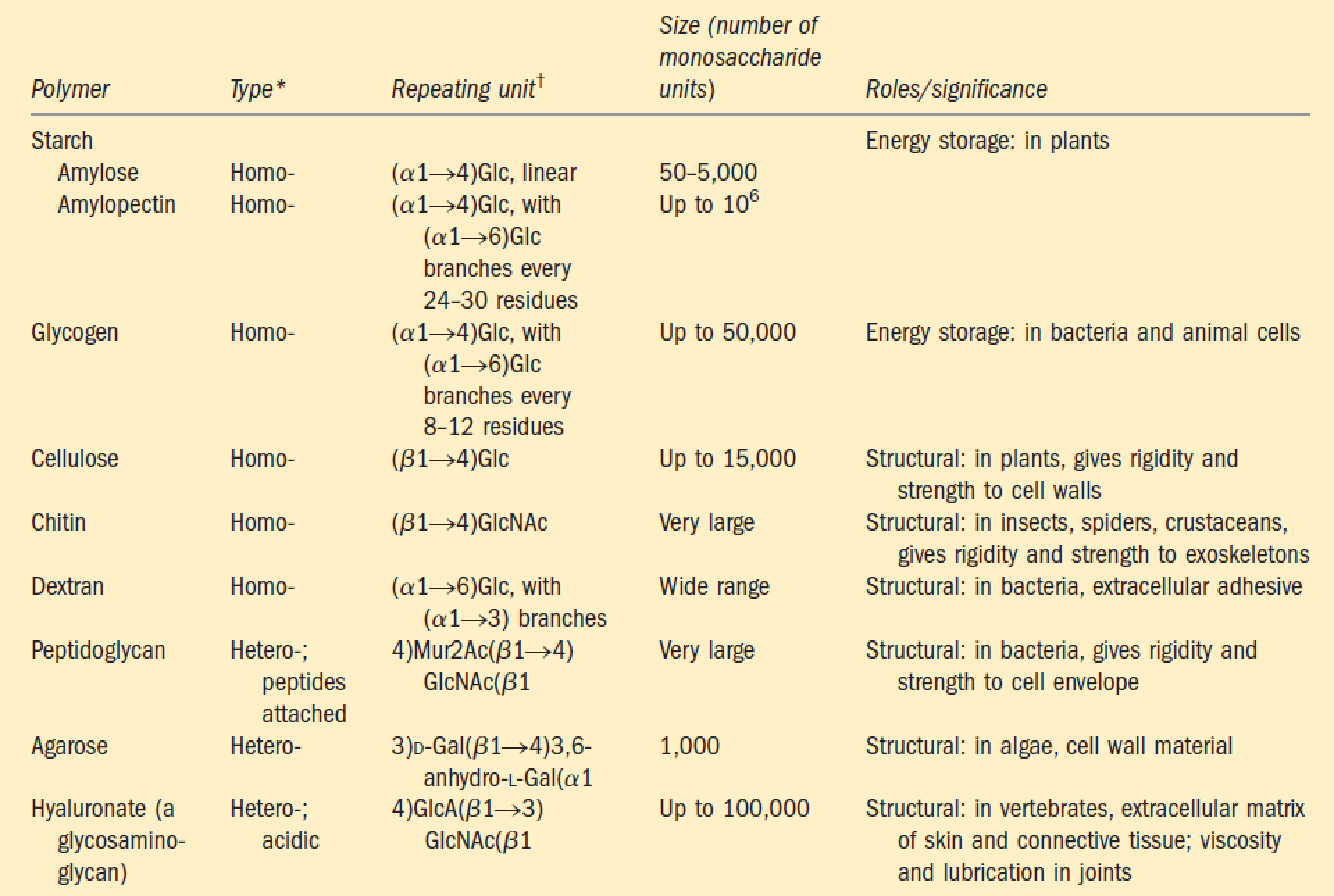


Hyaluronic acid



Chondroitin sulphate

Structures and Roles of Some Polysaccharides



Polymer	*Type**	*Repeating unit†*	*Size (number of monosaccharide units)*	*Roles/significance*
Starch				Energy storage: in plants
Amylose	Homo-	(α1→4)Glc, linear	50–5,000	
Amylopectin	Homo-	(α1→4)Glc, with (α1→6)Glc branches every 24–30 residues	Up to 10^6	
Glycogen	Homo-	(α1→4)Glc, with (α1→6)Glc branches every 8–12 residues	Up to 50,000	Energy storage: in bacteria and animal cells
Cellulose	Homo-	(β1→4)Glc	Up to 15,000	Structural: in plants, gives rigidity and strength to cell walls
Chitin	Homo-	(β1→4)GlcNAc	Very large	Structural: in insects, spiders, crustaceans, gives rigidity and strength to exoskeletons
Dextran	Homo-	(α1→6)Glc, with (α1→3) branches	Wide range	Structural: in bacteria, extracellular adhesive
Peptidoglycan	Hetero-; peptides attached	4)Mur2Ac(β1→4) GlcNAc(β1	Very large	Structural: in bacteria, gives rigidity and strength to cell envelope
Agarose	Hetero-	3)D-Gal(β1→4)3,6-anhydro-L-Gal(α1	1,000	Structural: in algae, cell wall material
Hyaluronate (a glycosaminoglycan)	Hetero-; acidic	4)GlcA(β1→3) GlcNAc(β1	Up to 100,000	Structural: in vertebrates, extracellular matrix of skin and connective tissue; viscosity and lubrication in joints