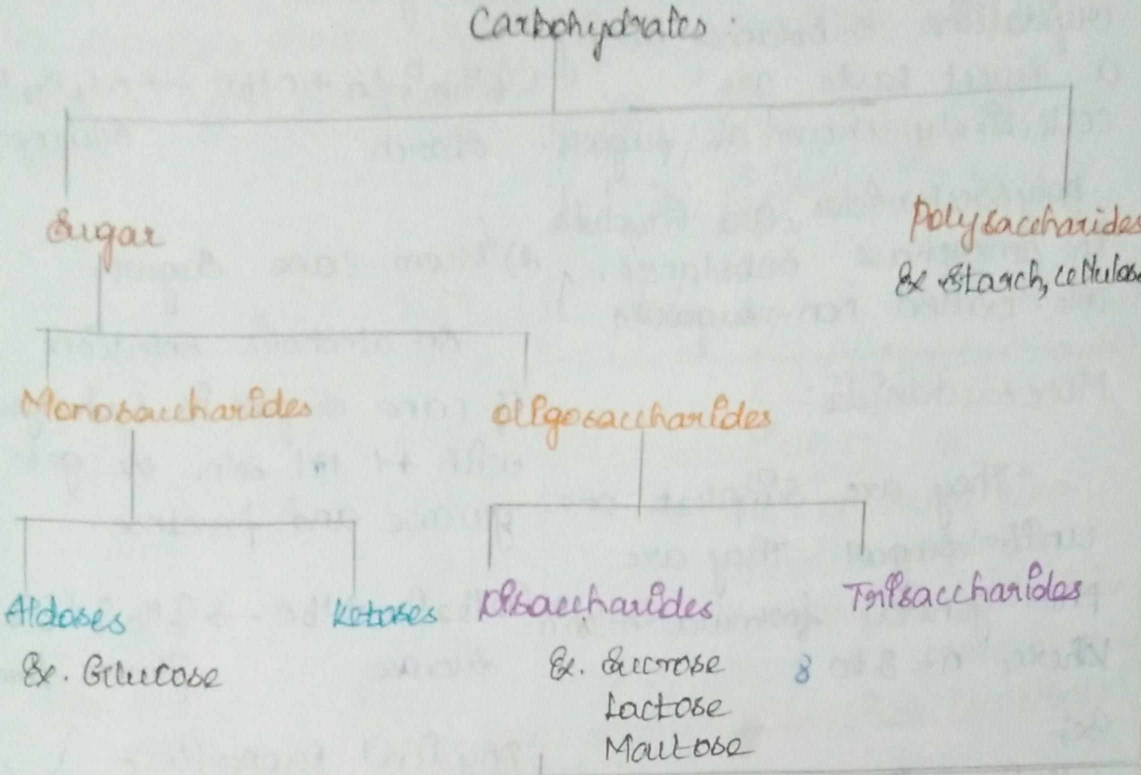
Organic chemistry.

UNIT-1:-

Chemistry of Carbohydrates



Carbohydrates:-

All optically active polyhydroxyaldehydes all polyhydroxyketones and all these compound obtained by hydrolysis of poly -saccharides.

Carbohydrates are divided into main classes, sugars and polysaccharides. Sugars are crystallie substances divided sweet taste and soluble in water.

Polysaccharides are complex in nature amorphous, not sweet. They are insoluble in water as or less soluble in water.

Sugar are further sub-divided into groups namely monosaccharides oligo saccharides.

Sugar which cannot be further hydrolysed into smaller molecules are called monosacchorides. Sugars which yield 2 to 9 monosaccharides molecules on hydrolysis are called oligosaccharides.

Polysaccharides are carbohydrates which yield large no. of monosacchorides molecules on hydrolysis.

Sugars and Non-sugars:-

The monosaccharides and oligosaccharides are soluble crystalline substances having a sweet taste are collectively known as sugars.

polysaccharides are insoluble in amorphous substances are called non-sugars.

Monosaccharides:-

They are simplest one unit sugar. They are the general formula $C_nH_{2n}O_n$. where $n = 3$ to 8.

Ex:-

$C_3H_6O_3$ Trioses $C_6H_{12}O_6$ Hexoses

$C_4H_8O_4$ Tetroses $C_7H_{14}O_7$ Heptoses

$C_5H_{10}O_5$ Pentoses

The most important naturally occurring monosaccharide or pentose or hexose.

Glucose: (Dextrose) $C_6H_{12}O_6$:-

It is known as Dextrose because it occurs in nature as the optically active dextro rotatory isomers. Glucose found in most sweet fruits, Grapes and honey. It is essential constituent of human blood (65-110mg per 100 ml)

Preparation:

1) Starch on hydrolysis gives glucose.

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} + nH_2O \rightarrow \underset{\text{Glucose}}{nC_6H_{12}O_6}$$

2) From cane sugar:-

An alcoholic solution of cane sugar is hydrolysed with 1% HCl soln, we get glucose and fructose.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructo}}{C_6H_{12}O_6}$$

Physical properties:-

→ It is a white crystalline solid,

→ m.p 146°C

→ When crystallised from cold water, it forms glucose monohydrate ($C_6H_{12}O_6 \cdot H_2O$) m.p 86°C.

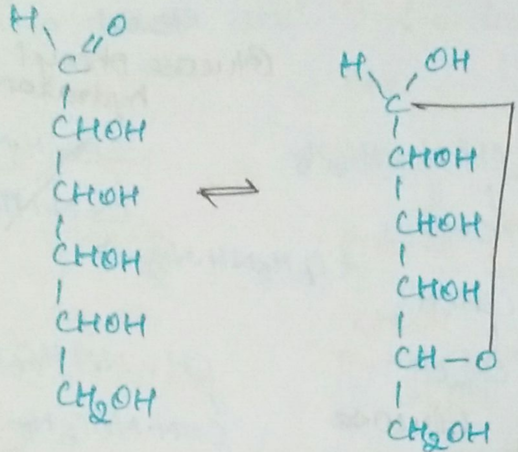
→ It is extremely soluble in water, only sparingly so in ethanol, and insoluble in ether.

→ It is about three-fourth as sweet as cane sugar (sucrose).

→ It is optically active and the ordinary naturally occurring form is (+)-glucose.

Properties:-

The D-glucose is an equilibrium mixture of a straight chain form and a cyclic hemiacetal form.

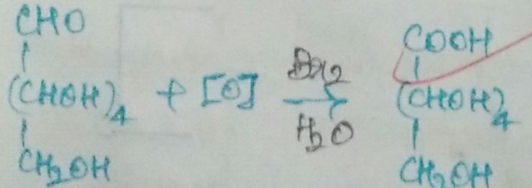


Open-chain form (0.01%) cyclic hemiacetal (99.99%)

1) Oxidation:-

a) With weak oxidizing Agents:-

On treatment with a weak oxidizing agent such as bromine water, CHO is oxidised to COOH and Gluconic acid results.

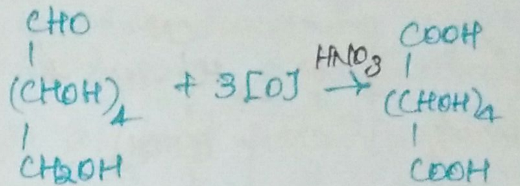


$$CHO-(CHOH)_4-CH_2OH + [O] \xrightarrow[H_2O]{Br_2} COOH-(CHOH)_4-CH_2OH$$

D-Glucose Gluconic acid

b) With strong oxidizing Agents:-

A strong oxidizing agent like nitric acid and oxidizes both the CHO and CH_2OH groups of glucose, yielding glucaric acid (saccharic acid)

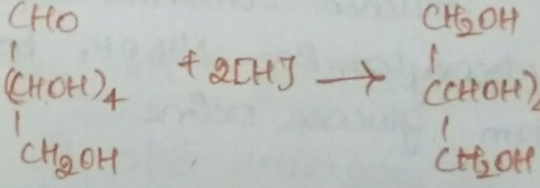


$$CHO-(CHOH)_4-CH_2OH + 3[O] \xrightarrow{HNO_3} COOH-(CHOH)_4-COOH$$

D-Glucose Glucaric acid (saccharic acid)

2) Reduction:-

Glucose on reduction with sodium borohydride, $NaBH_4$, or catalytic reduction (H_2/Pd) gives the corresponding alcohol D-Glucitol (sorbitol)

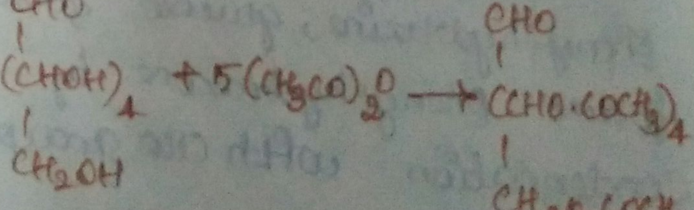


$$CHO-(CHOH)_4-CH_2OH + 2[H] \longrightarrow CH_2OH-(CHOH)_4-CH_2OH$$

D-Glucose D-Glucitol

3) Acetylation:-

Glucose reacts with acetic anhydride in the presence of anhydrous zinc chloride to form Pentaacetyl glucose.



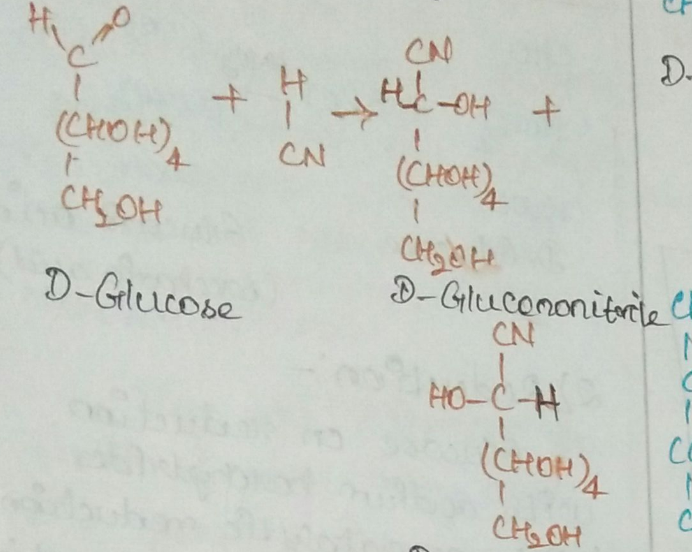
$$CHO-(CHOH)_4-CH_2OH + 5(CH_3CO)_2O \longrightarrow CHO-(CHO.COCH_3)_4-CH_2O.COCH_3$$

D-Glucose Pentaacetyl gluco

$+ 5CH_3COOH$

HCN:-

Like other aldehydes, HCN reacts by addition at the aldehyde carbonyl group.



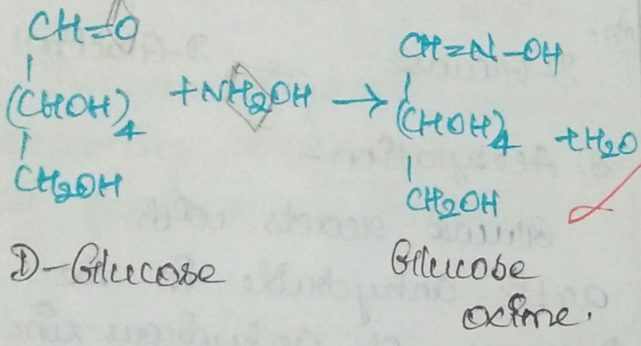
$$CHO\text{-}(CHOH)_4\text{-}CH_2OH + HCN \rightarrow H\text{-}C(CN)(OH)\text{-}(CHOH)_4\text{-}CH_2OH + CN\text{-}C(H)(OH)\text{-}(CHOH)_4\text{-}CH_2OH$$

D-Glucose D-Gluconononitrile

D-Mannononitrile

5) Rxn with Hydroxylamine:-

Glucose condenses with hydroxylamine, NH_2OH, to form glucose oxime.



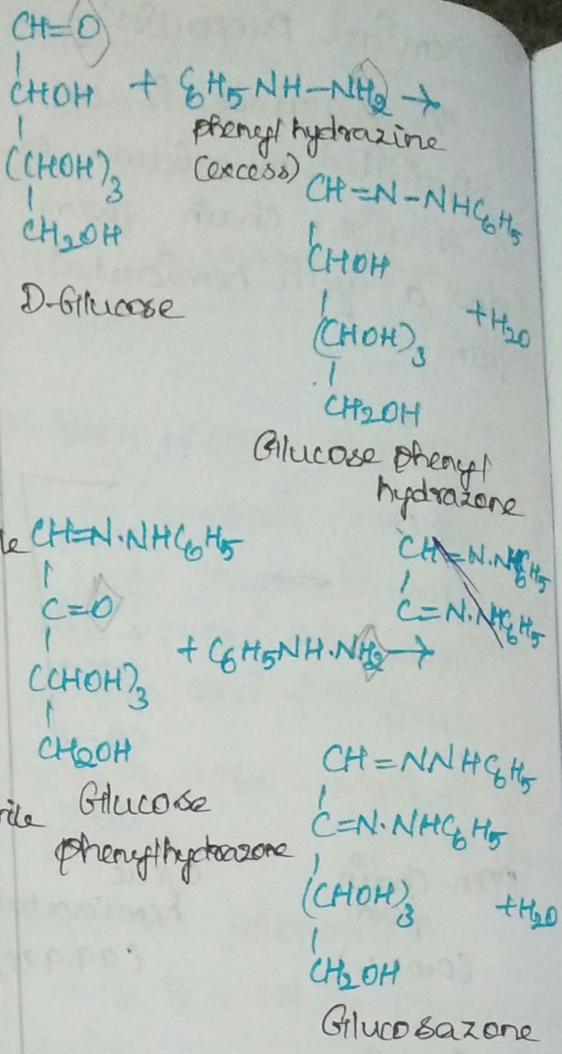
$$CH{=}O\text{-}(CHOH)_4\text{-}CH_2OH + NH_2OH \rightarrow CH{=}N\text{-}OH\text{-}(CHOH)_4\text{-}CH_2OH + H_2O$$

D-Glucose Glucose oxime.

6) Rxn with Phenylhydrazine:-

When warmed with excess phenylhydrazine, glucose first forms phenyl hydrazone by condensation with CHO group.

The resulting carbonyl group reacts yielding product to form glucosazone.



$$CH{=}O\text{-}CHOH\text{-}(CHOH)_3\text{-}CH_2OH + C_6H_5NH\text{-}NH_2 \rightarrow CH{=}N\text{-}NHC_6H_5\text{-}CHOH\text{-}(CHOH)_3\text{-}CH_2OH + H_2O$$

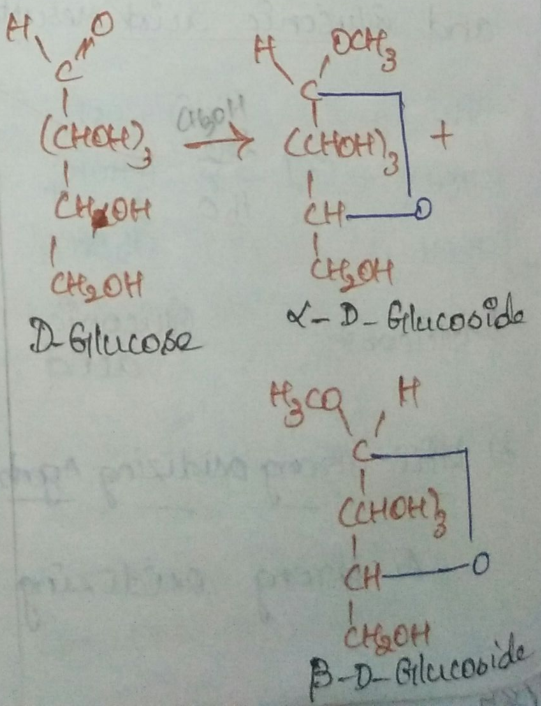
D-Glucose phenyl hydrazine (excess) Glucose phenyl hydrazone

$$CH{=}N{\cdot}NHC_6H_5\text{-}C{=}O\text{-}(CHOH)_3\text{-}CH_2OH + C_6H_5NH{\cdot}NH_2 \rightarrow CH{=}NNHC_6H_5\text{-}C{=}N{\cdot}NHC_6H_5\text{-}(CHOH)_3\text{-}CH_2OH + H_2O$$

Glucose phenylhydrazone Glucosazone

7) Rxn with Alcohols:-

Glucose is treated with methanol in the presence of dry HCl, it corresponds to give glucosides

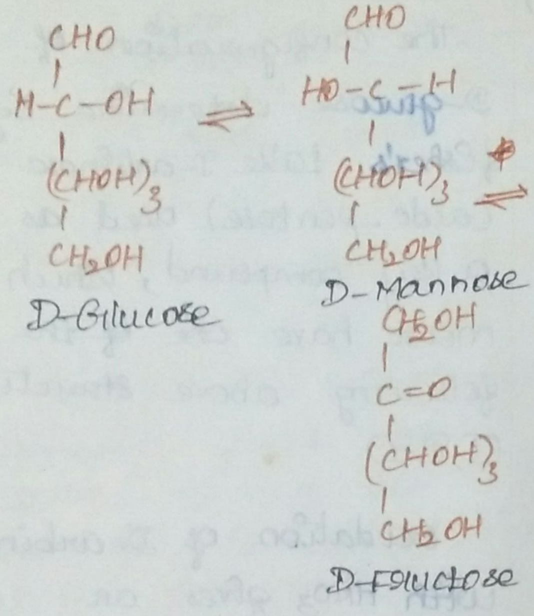


$$CHO\text{-}(CHOH)_3\text{-}CHOH\text{-}CH_2OH \xrightarrow{CH_3OH} H\text{-}C(OCH_3)\text{-}(CHOH)_3\text{-}CH(O)\text{-}CH_2OH + H_3CO\text{-}C(H)\text{-}(CHOH)_3\text{-}CH(O)\text{-}CH_2OH$$

D-Glucose α-D-Glucoside β-D-Glucoside

8) **Action with Alkalies:-**

When warmed with strong sodium hydroxide solution, glucose forms a brown resinous product. D-glucose rearrange to give a mixture of D-glucose, D-mannose and D-fructose



9) **Fermentation:-**

A soln. of D-glucose is readily fermented by the enzyme zymase present in yeast, in the absence of air to form ethanol and CO_2.

$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2\uparrow$
glucose ethanol

10) **Dehydration:-**

When heated strongly or when heated with warm conc. sulfuric acid, glucose is dehydrated to give a black mass of sugar carbon.

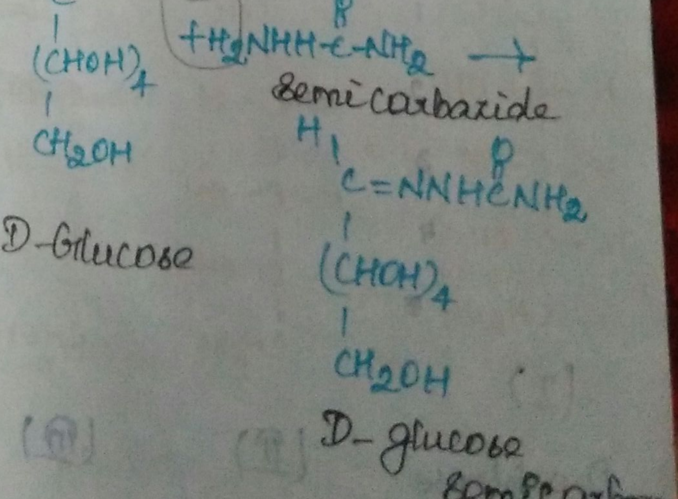
Uses:-

Glucose is used:-
1) as a sweetening agent in syrups & confectionery.
2) as food for infants.
3) as a reducing agent in silvering of mirrors and to convert indigo blue to indigo white in vat dyeing. preparation of candy, flavouring syrups, gelly
4) as a raw material for wine and alcohol manufacture

Chemical properties:-

11) **Rxn with semicarbazide:-**

It also undergoes condensation reaction with semicarbazide to form semicarbazone called D-glucose semicarbazone.

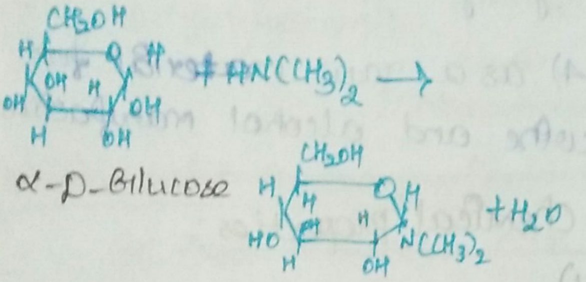


D-glucose semicarbazo
(semicarbazone)

12) Rxn with amines:-

(N-glucoside formation)

Instead of giving schiff's bases, amines (dimethyl amine) condense with glucose to form N-glucosides. (N,N-dimethyl, α, D-glucoside) which are similar to the ordinary glucosides from alcohols, which are isomeric N-glucosides.



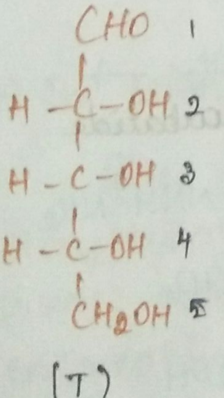
α-D-Glucose

N,N-Dimethyl-α-D-Glucoside

Structure of D-glucose:-

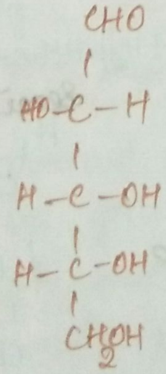
Configuration of D-glucose:-

(Fisher's proof)

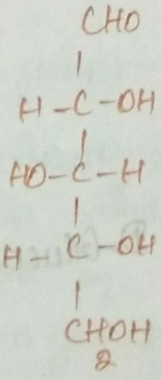


(I)

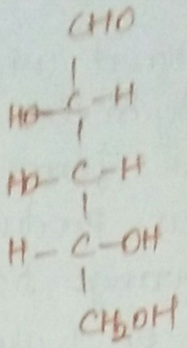
D-arbinose



(II)



(III)



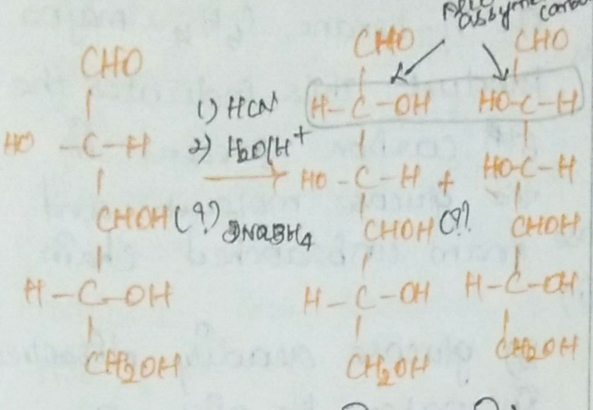
(IV)

The configuration of D-glucose determine by fisher's take D-arbinose (aldo-pentose) used as a key compound, which must have one of the following above structure (I, II, IV)

Oxidation of D-arbinose with HNO_3 gives an optically active dicarboxylic acid. Under these conditions, the structure (I) and (III) could have optically inactive meso diacids Due to presence of internal plane of symmetry. D-arbinose is therefore either two or four and represented in configuration in doubt at C_3.

When D-arbinose is subjected to Killani-Fisher synthesis

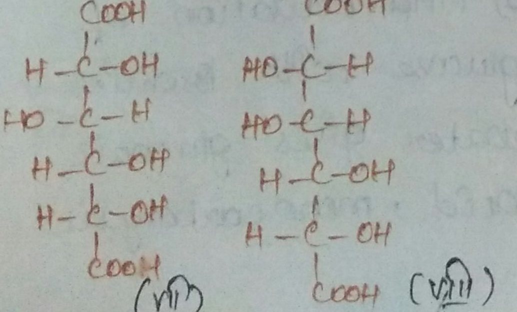
It gives two sugars namely glucose and mannose, which are different only in configuration at C-2, is the new assymetric center created in the chain extention.

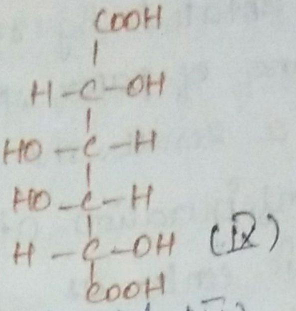


(V) (VI)

Structures (V) and (VI) must represent glucose and mannose, the next step is to determine the configuration at C-4 and then decide which is glucose and which is mannose.

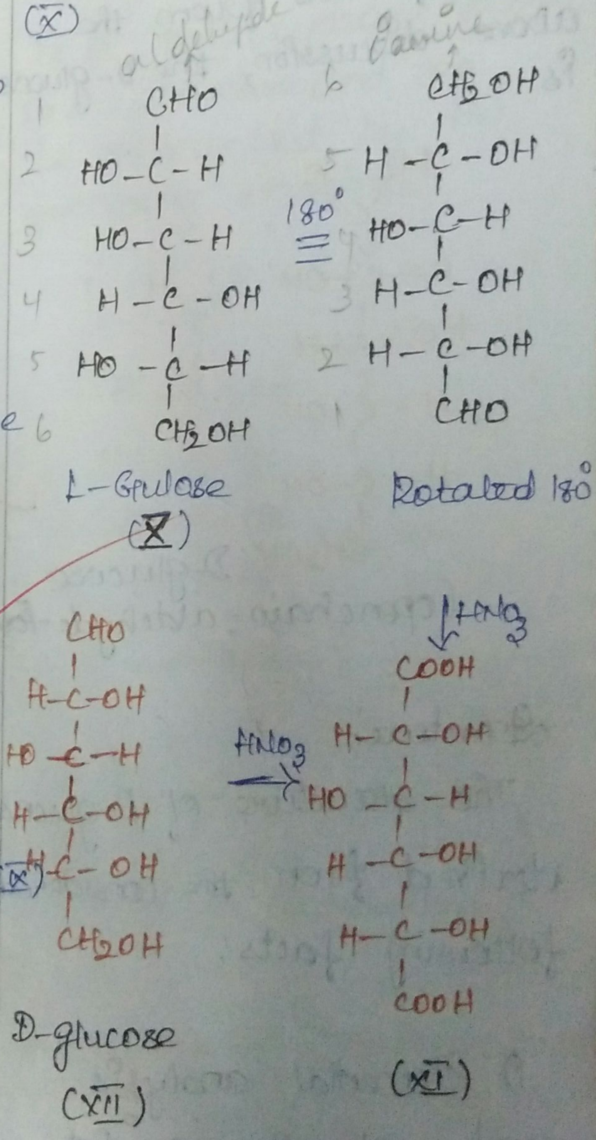
Both glucose and mannose on oxidation with HNO_3 give diacids which are optically active. this means that the hydroxyl group C-4 is of the right side VII & VIII. If ~~it~~ is OH group present on the left side, (VII) would have yielded in optically inactive Mesodiacid (IX)





Mesodiacid, (IX).

Structure (VII) and (VIII) represent D-glucose and D-mannose. But, it decided to either ~~so~~ (VII) is glucose and (VIII) is mannose. which is determine by we may use of another Aldoses, hexose, L-~~Glucolose~~ Gulose (X)



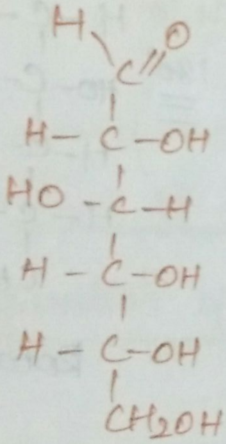
L-Gulose (X)

D-glucose (XII)

(XI)

by 180°
in the plane of paper, upside down as a result. the same configuration at the assymetric center as D-glucose, expect the aldehyde and primary alcohol groups interchanged. Such a result is not possible with structure (vii). Hence D-glucose is represented by structure (vii) and D-mannose by structure (viii).

It follows from the above discussion, the D-glucose is



D-glucose
(open chain-aldehyde-form)

Structure:

The structure of D-glucose derived from the consideration following facts:

1) Elemental analysis and molecular weight determination show the mol. formula of glucose

2) complete reduction of glucose with conc. HI (Hydro Iodidi) in the presence of red phosphorous produced as n-hexane, C_6H_{14} major product. This indicates the 6th carbon present in the glucose molecule and form unbranched chain.

3) glucose readily dissolve in water to give a neutral solution. This indicates, the glucose molecule does not contain a carboxylate group $(-\overset{O}{C}-O)$

4) Glucose reacts with hydroxylamine to form a monooxime, or adds one mole of HCN to give a cyanohydrin. these reactions indicate a presence of either aldehyde or ketone but not both.

5) Mild oxidation of glucose with Bromine water gives gluconic acid, monocarboxylic

acid with mol· formula of $C_6H_{12}O_7$· This indicates the presence of an aldehyde group. Must ocupy one end of this chain

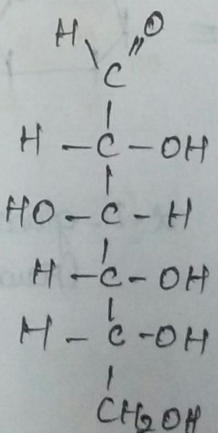
b) Further oxidation of gluconic acid with HNO_3 gives glucaric acid, dicarboxylic acid with mol formula $C_6H_{10}O_8$: This indicates the presence of the primary alcohol group which involved oxidation with loss of 2 hydrogen and gain of 1 oxygen atom.

7) glucose reduces an ammonical solution of (AgO_2) [Tollen's reagent] two metallic silver as mirror, similarly, a basic solution of cupric ion [Fehling's soln.] to form red cuporous oxide [Cu_2O]. These reactions further conformed the presence of a terminal CHO group.

8) glucose reacts with acetic anhydride in the presence of pyridine to form a pentaacetate. This indicates the presence of 5 hydroxyl group in the glucose.

9) Organic compounds with 2 hydroxyl groups attached to a single C-atom or rare and involved loss of water to produce a carbonyl group. This suggest each hydroxyl group attached to a different carbon atom.

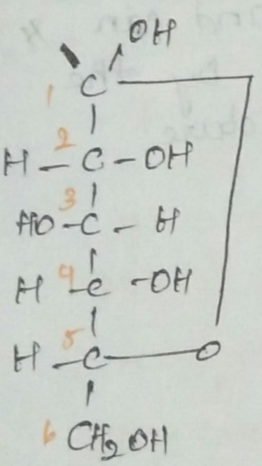
From the above evidence we conclude that glucose is a pentahydroxyl hexanol and aldose and can be represented by the following structure.



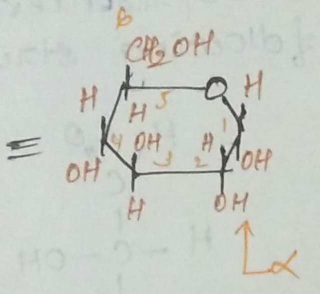
D-glucose
(openchain-aldehyde form)
(or)
2,3,4,5,6- Pentahydroxyl hexanol

Haworth Representation:-

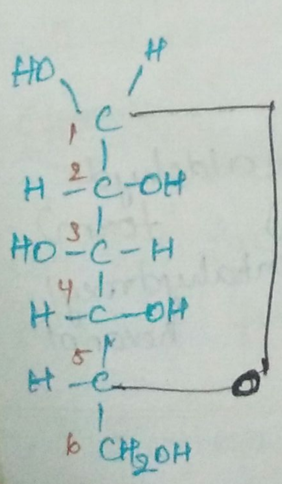
Fischer projection formulas for representing the cyclic forms of D-glucose Haworth thought that these structures were awkward. He introduced the hexagonal representation resembling the heterocycle pyran which contains five carbons and one oxygen in the ring. Thus he claimed the names α-D-glucopyranose and β-D-glucopyranose for the hexagonal structures of α-D-glucose and β-D-glucose

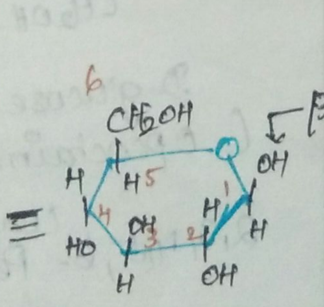


α D-Glucose (Fischer)



α-D-glucopyranose (Haworth)





β-D-glucopyranose (Haworth)

β-D-Glucose

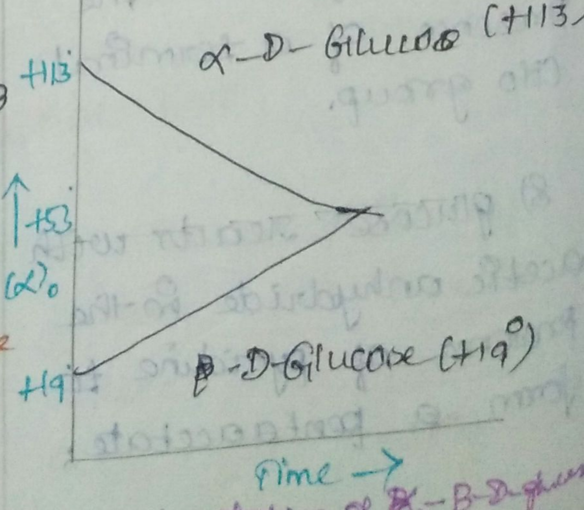
It may be noted that in Haworth formula, all the OH groups on the right in Fischer formula are directed below the plane of the ring, while those on the left go above the plane. The terminal CH_2OH projects above the plane of the ring.

Muta Rotation:-

Two crystalline forms of D-glucose have been isolated

1) α-D-Glucose which crystallises from a conc. aqu. soln at 30°c. It has mp 146°c and specific rotation +112°

2) β-D-Glucose which crystallises from a hot, glacial acetic acid soln. It melts at 148-150°c and has specific rotation +19°

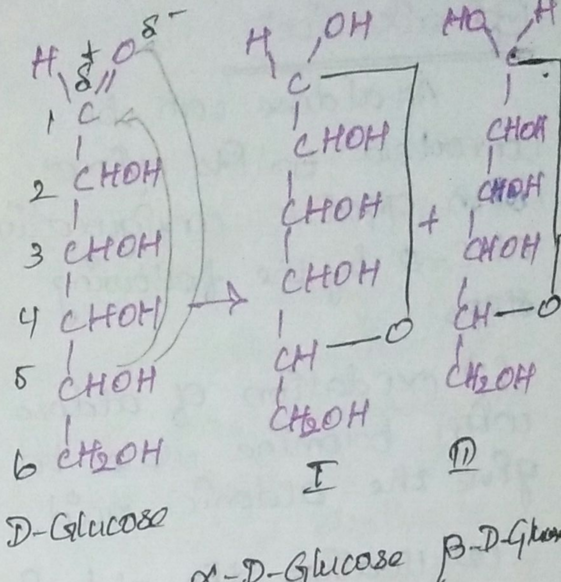


When either of these forms of D-glucose is diss. in water and allowed to stand, a gradual change in specific rotation occurs. The specific rotation of the α-form falls and that of the β-form rises until a constant value of +53° is reached. This change in the optical rotation of a solution of either form of glucose until a constant value is obtained, is called Mutarotation (Latin, muto = to change)

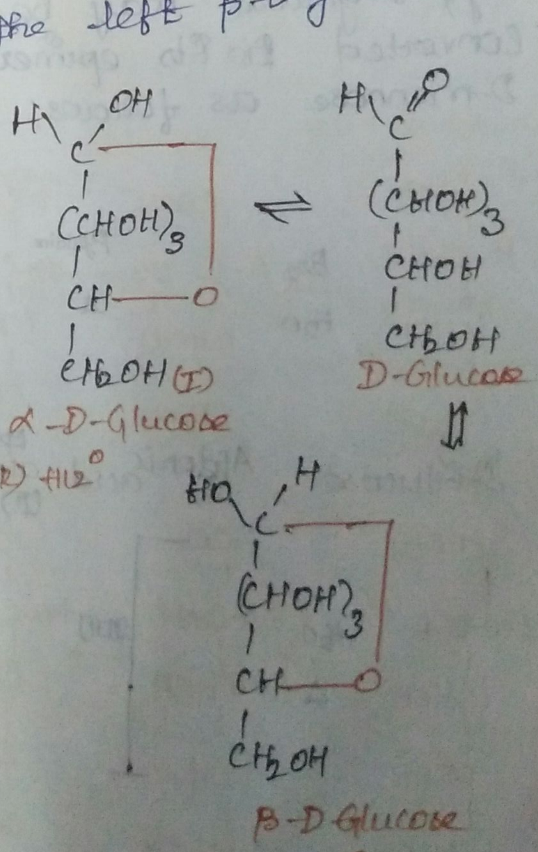
Many sugars, other than glucose also exist in an α and β form and undergo mutarotation. For eg, α-D-fructose has specific rotation, -31°, β-D-fructose -133° and the constant value -92°.

Explanation:-

Glucose forms a stable cyclic hemiacetal b/w the CHO group and the OH group on the fifth carbon. In this process, the first carbon becomes assymmetric, giving two isomers (I and II)



These are called Anomers and the new asymmetric carbon is referred to as Anomeric carbon. The anomer I with OH to the right is designated as the α-D-glucose and with OH to the other the left β-D-glucose.



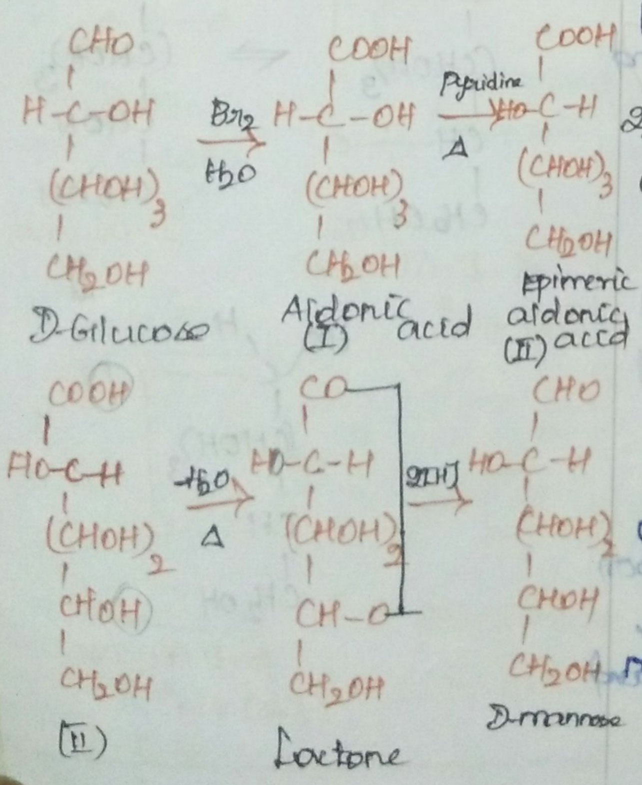
Epimerization:-

An aldose can be converted to its epimer with opposite configuration at C-2 by the following steps:

(1) oxidation of aldose with bromine water to give the aldonic acid.

(2) Heating the aldonic acid with pyridine, C_5H_5N, to give an equ. mixture of original and its epimeric acid.

(3) Separation of the epimeric acid and red. of its lactone to yield the epimer aldose. For eg, D-glucose may be converted to its epimer D-mannose as follows:



It may be noted that the configuration at C-2 has been changed, and the remaining part is identical in the two sugars. The change in configuration of one asymmetric carbon (C-2) in a compound containing two or more asymmetric carbon atoms is known as Epimerization.

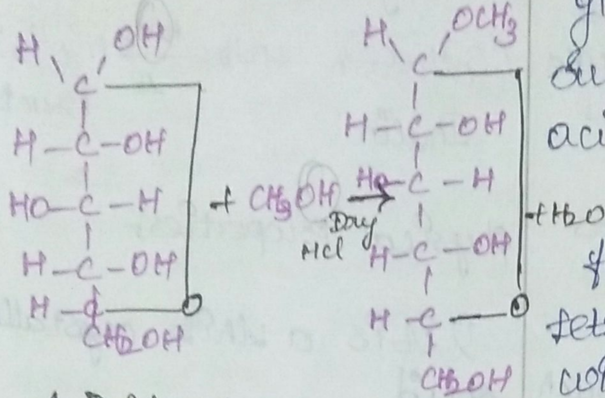
Cyclic Structure:-

1) Open-chain structure not wholly true:

Fischer realized that the open-chain pentahydroxy aldehyde structure of glucose did not wholly explain its chemical behaviour.

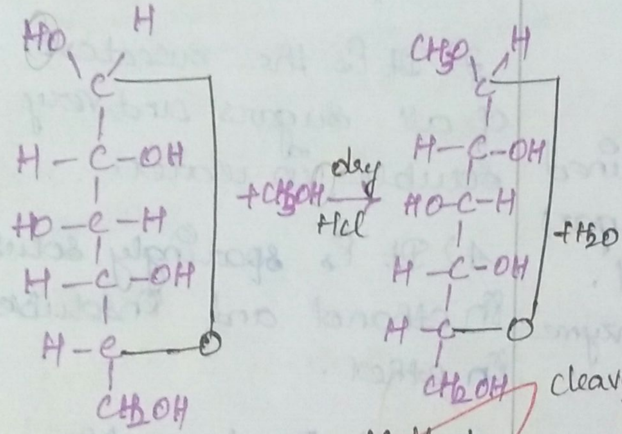
2) Glycoside formation confirms cyclic structure:

Glucose when treated with methanol in the presence of dry HCl, gives two isomeric acetals or glycosides. these crystalline glycosides, methyl-α-D-glucoside and methyl-β-D-glucoside have been actually isolated. They are optically active but do not give any of the reactions of free CHO group.



α-D-Glucose

Ethyl-α-D-glycoside



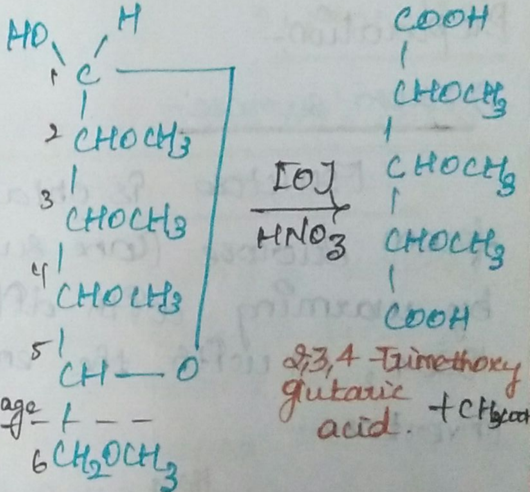
β-D-Glucose

Methyl β-D-glycoside

3) Determination of ring size:-

D-glucose though contain a ring of six members, five carbons and one oxygen. this has been proved to be correct and a five-membered ring has been ruled out.

Hearst (1926) prepared tetra-O-methyl-D-glucose by treating methyl-D-glucoside with dimethyl sulfate and subsequent acid hydrolysis of the pentamethyl derivate formed. the oxidation of tetra-O-methyl-D-glucose with HNO3 yielded trimethoxy glutaric acid.



cleavage

Tetra-O-Methyl-D-glucose

FRUCTOSE, Levulose, $C_6H_{12}O_6$

This important ketohexose is also called levulose because the naturally occurring form of fructose is levorotatory. Fructose is found along with the glucose in the juices of ripe fruits and in honey. In the combined state, it occurs in sucrose and in the polysaccharide Inulin obtained from plants such as dahlia and dandelion.

Preparation:-

1) From sucrose:-

Fructose is obtained from sucrose (cane sugar) by warming with dil. H_2SO_4, or with the enzyme invertase.

$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H_2SO_4} C_6H_{12}O_6 + C_6H_{12}O_6$
sucrose
Fructose glucose

Fructose is separated from the invert sugar by crystallization from alcohol. Glucose being insoluble in alcohol is left behind in solution.

2) From Inulin:-

Fructose is prepared commercially by the hydrolysis of inulin by heating with dil. H_2SO_4

$(C_6H_{10}O_5)_n + nH_2O \xrightarrow[\Delta]{H_2SO_4} nC_6H_{12}O_6$
Inulin
Fructose

Physical properties:-

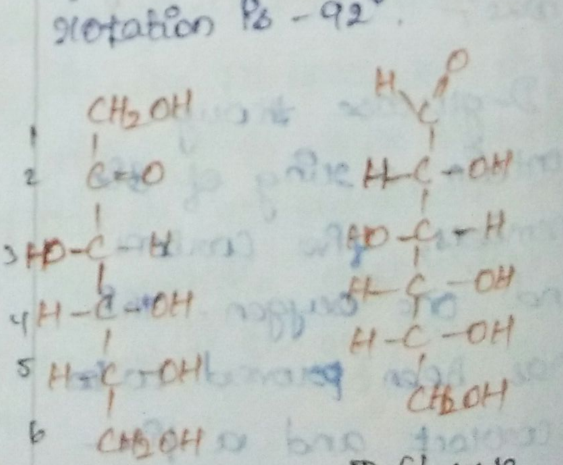
1) It is a white crystalline solid

2) M.P 103-105°C with decomposition.

3) It is the sweetest of all sugars and very soluble in water.

4) It is sparingly soluble in ethanol and insoluble in ether.

5) D(-)-Fructose, the natural sugar, exhibits mutarotation and the final value of specific rotation is -92°.



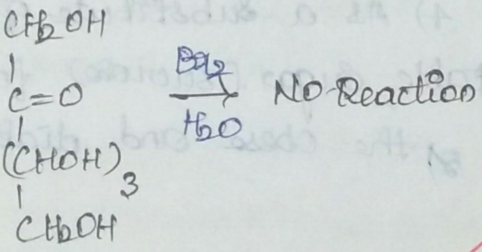
D-Fructose
D-Glucose

Chemical properties:-

In the two sugars, the configuration of the three asymmetric carbons in the box is identical. thus fructose gives reactions similar to ~~for~~ glucose, any difference being due to fact that the former contains a ketonic group $-CO-$, while the latter an aldehyde group $-CHO$. Some of the few reactions are,

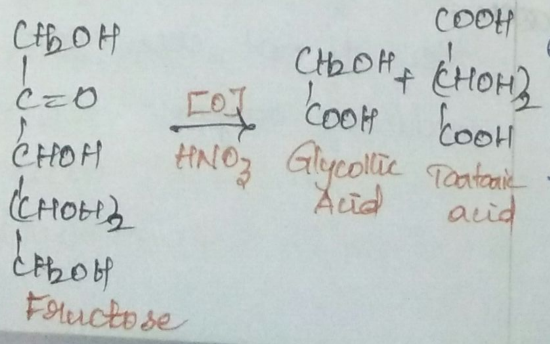
a) Oxidation:-

Bromine water oxidizes glucose to gluconic acid, but does not react with fructose.



$$\begin{matrix} CH_2OH \\ | \\ C=O \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{matrix} \xrightarrow[H_2O]{Br_2} \text{No Reaction}$$

Oxidation of fructose with HNO_3 occurs with the breaking of the carbon chain and formation of glycollic acid and tartaric acid.



$$\begin{matrix} CH_2OH \\ | \\ C=O \\ | \\ CHOH \\ | \\ (CHOH)_2 \\ | \\ CH_2OH \end{matrix} \xrightarrow[HNO_3]{[O]} \begin{matrix} CH_2OH \\ | \\ COOH \end{matrix} + \begin{matrix} COOH \\ | \\ (CHOH)_2 \\ | \\ COOH \end{matrix}$$

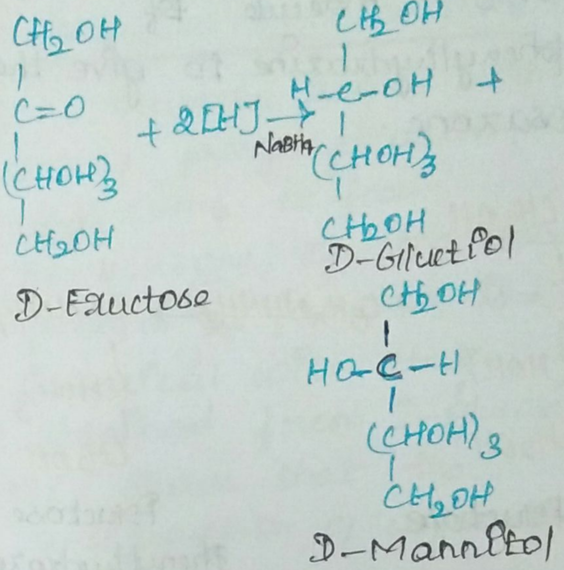
Fructose

Glycollic Acid

Tartaric acid

2) Reduction:

Reduction of fructose gives two epimeric hexahydric alcohols as C-2 now becomes asymmetric.



$$\begin{matrix} CH_2OH \\ | \\ C=O \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{matrix} + 2[H] \xrightarrow{NaBH_4} \begin{matrix} CH_2OH \\ | \\ H-C-OH \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{matrix} + \begin{matrix} CH_2OH \\ | \\ HO-C-H \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{matrix}$$

D-Fructose

D-Glucitol

D-Mannitol

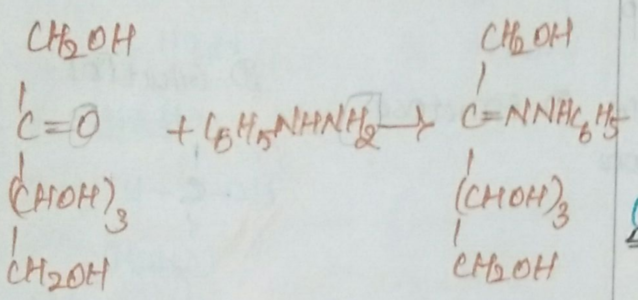
3) Action with Fehling's soln & Tollen's Reagent:

Unlike a simple ketone, fructose reduces Fehling soln and Tollen's reagent. This is because the alkaline reagents fructose to give D-glucose and D-mannose which are strong reducing agents.

4) Action with phenylhydrazine

When treated with excess phenyl hydrazine, $C_6H_5NHNH_2$, fructose 1st forms phenylhydrazone.

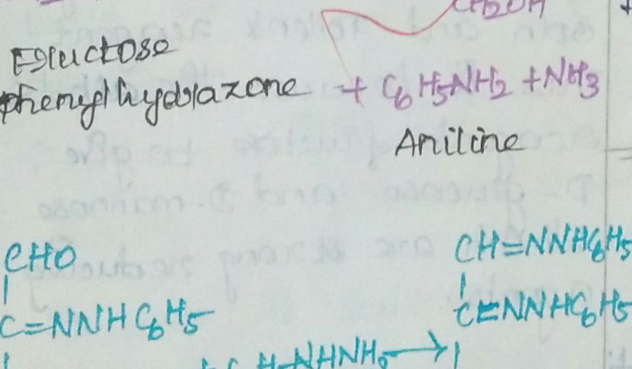
Then CH_2OH involving C-1 is oxidized to -CHO by a second molecule of phenylhydrazine. the -CHO g. finally reacts with a 3rd molecule of phenylhydrazine to give the osazone.



$$\begin{array}{l}CH_2OH\\ |\\ C=O\\ |\\ (CHOH)_3\\ |\\ CH_2OH\end{array} + C_6H_5NHNH_2 \rightarrow \begin{array}{l}CH_2OH\\ |\\ C=NNHC_6H_5\\ |\\ (CHOH)_3\\ |\\ CH_2OH\end{array}$$

Fructose

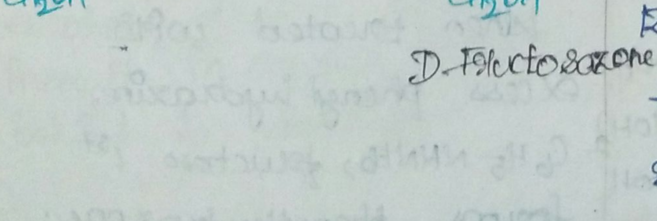
Fructose phenylhydrazone



$$\begin{array}{l}CH_2OH\\ |\\ C=NNHC_6H_5\\ |\\ (CHOH)_3\\ |\\ CH_2OH\end{array} + C_6H_5NHNH_2 \rightarrow \begin{array}{l}CHO\\ |\\ C=NNHC_6H_5\\ |\\ (CHOH)_3\\ |\\ CH_2OH\end{array} + C_6H_5NH_2 + NH_3$$

Fructose phenylhydrazone

Aniline



$$\begin{array}{l}CHO\\ |\\ C=NNHC_6H_5\\ |\\ (CHOH)_3\\ |\\ CH_2OH\end{array} + C_6H_5NHNH_2 \rightarrow \begin{array}{l}CH=NNHC_6H_5\\ |\\ C=NNHC_6H_5\\ |\\ (CHOH)_3\\ |\\ CH_2OH\end{array}$$

D-Fructosazone

5) Fermentation:-

Like glucose, a soln. of D-fructose is readily fermented by the enzyme zymase present in yeast to form mainly ethanol and CO_2.

$$C_6H_{12}O_6 \xrightarrow{zymase} 2C_2H_5OH + 2CO_2$$

Fructose

Uses:-

1) As a sweetening agent in confectionery

2) In medical syrups,

3) To prevent sandiness in ice-cream.

4) As a substitute of table sugar (sucrose) for the obese and diabetic

Reducing sugar:-

Those saccharides which obey Felling soln. and Tollen's reagent are called Reducing sugar, while they do not are non-reducing sugar.

Structure of Fructose.

A) Open-chain formula:-

1) Mol. formula, As established by elemental analysis and mol. weight determination the mol. formula of fructose is $C_6H_{12}O_6$.

2) presence of 6-C chain.

Fructose on complete reduction with HI and red P forms n-Hexane. therefore, it contains an unbranched 6-carbon chain.

3) presence of 5 OH groups.

Fructose reacts with acetic anhydride to give pentaacetyl derivate. It indicates the presence of five hydroxy groups, each attached to a separate carbon.

4) presence of C=O:-

It forms an oxime with hydroxylamine and hence contains a carbonyl group, $>C=O$

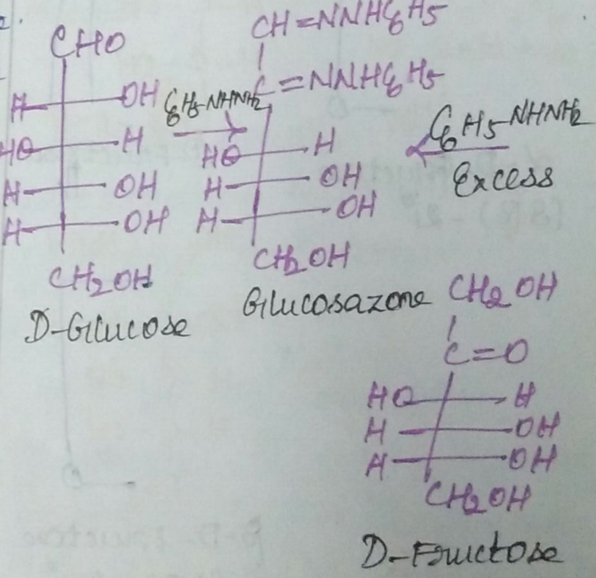
5) C=O is ketonic.

On oxidation with HNO_3, fructose yields a mixture of tartaric acid (4C) and glycollic acid (2C) both containing fewer carbon atoms than six. therefore, fructose behaves like a simple ketone and the C=O is ketonic.

B) Configuration:-

Formation of Glucosazone.

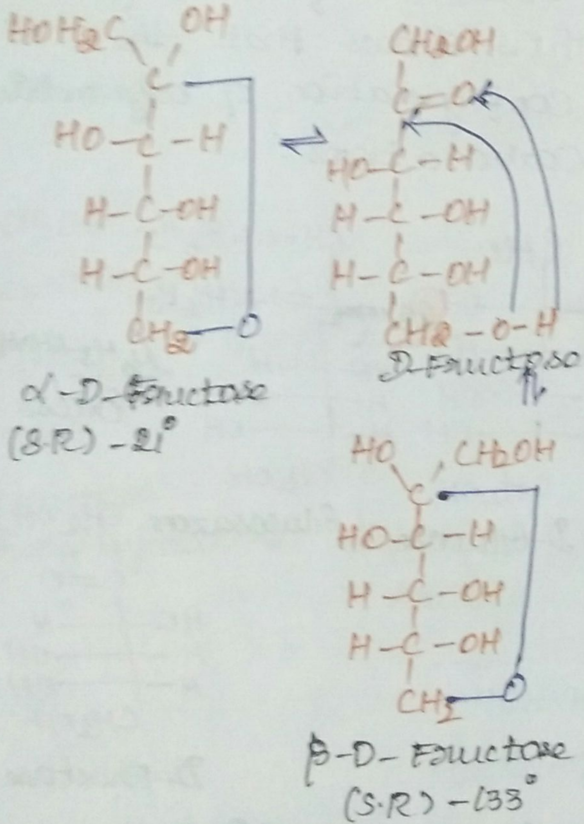
Fructose reacts with excess phenyl hydrazine, $C_6H_5-NHNH_2$ to form glucosazone, or the ozazone formed by fructose is identical with that obtained from D-glucose this shows that the configuration of asymmetric carbon atoms.



Hence the configuration of D-fructose is proved

C) Cyclic Structure of D-Fructose:-

By analogy to D-glucose and to explain its dual behaviour, a six-membered hemiketal ring structure was proposed for D-fructose. Since D-fructose also exhibits mutarotation, the α and β forms in equilibrium via the open-chain form may be represented as,



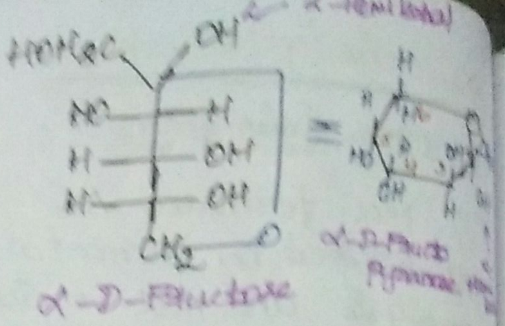
α-D-Fructose (S.R) -21°

D-Fructose

β-D-Fructose (S.R) -133°

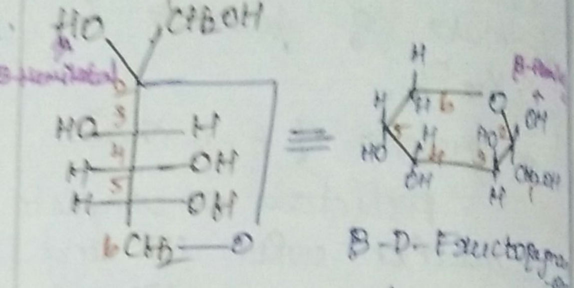
D) The Haworth Representation:-

The Fischer projection formulas α-D-Fructose and β-D-Fructose have been represented by Haworth as follows.



α-D-Fructose

α-D-Fructopyranose (Haworth)



β-D-Fructose

β-D-Fructopyranose (Haworth)

DISACCHARIDES.

Disaccharides ($C_{12}H_{22}O_{11}$) are carbohydrates that produce two monosaccharides on acid-hydrolysis.

Sucrose $\xrightarrow{H_2O/H^+}$ Glucose + Fructo

Maltose $\xrightarrow{H_2O/H^+}$ 2 Glucose unit

Lactose $\xrightarrow{H_2O/H^+}$ Glucose + Galacto

In a disaccharide, the two monosaccharides are joined together by acetal or glucoside formation. The hemiacetal OH of one monosaccharide and an OH of the second monosaccharide dehydrate to establish the bond b/w the two monosaccharides.

Sucrose :- (Cane sugar)

Sucrose is ordinary table sugar. It is obtained from cane sugar. Sucrose is composed of α-D-glucose unit and β-D-glucose. These units are joined by α, β-glucosidic linkage b/w C-1 of the glucose unit and C-2 of the fructose unit. It occurs chiefly in sugar cane and sugar beets. In smaller amounts it is present in maple sap, honey and several fruits.

Properties:-

Sucrose is a colourless, odorless, crystalline substance,

M.P → 185-186°C

It is very soluble in water, slightly soluble in alcohol and insoluble in ether. An aqu. soln of sucrose is dextorotatory its specific rotation being 66.5°.

Chemical:-

Sucrose molecule is made up of one D-glucose and one D-fructose unit joined by a glucosidic bond.

It gives all the reactions of glucose and fructose, thus it fails to reduce Fehling's solution and does not react with HCN or phenylhydrazine.

Hydrolysis or Inversion of sucrose:-

The hydrolysis of sucrose by boiling with a mineral acid, or by the enzyme invertase, produces a mixture of equal molecules of D-fructose & D-glucose.

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{Invertase}]{H^+} \underset{\text{D-Glucose}}{C_6H_{12}O_6} + \underset{\text{D-Fructose}}{C_6H_{12}O_6}$$

Sucrose solution is dextrorotatory but during hydrolysis it becomes levorotatory.

The specific rotation of sucrose is +66°5, D-glucose has S.R +52° and D-fructose -92°, Therefore, the net specific rotation of an equimolar mixture of D-fructose and D-glucose is,

$$\frac{+52° - 92°}{2} = -20°$$

In the process of hydrolysis, the S.R changes from +66.5° to -20°. The sign of specific rotation changes from (+) to (-) or is said to 'invert'. Hence the hydrolysis of sucrose to D-glucose and D-fructose is termed Inversion and the hydrolysis mixture is called Invert sugar.

$$\text{Sucrose} \xrightarrow{\text{Inversion}} \underbrace{\text{D-glucose} + \text{D-Fructose}}_{\text{Invert sugar}}$$

S.R
+66.5'

S.R -20°

The enzyme that brings about inversion is named as Invertase.

Structure:-

1) Elemental analysis and mol. weight determination show that the mol. formula of sucrose is $C_{12}H_{22}O_{11}$.

2) Sucrose reacts with acetic anhydride in the presence of sod. acetate to form sucrose octaacetate. This reaction indicates the presence of eight hydroxyl groups in a sucrose mol. since sucrose is a stable compound.

3) Hydrolysis of sucrose with dil. acids yields an equimolecular mixture of D-glucose and D-fructose. This indicates the sucrose molecule is made up one unit of these monosaccharides.

~~4) sucrose does not reacts with~~

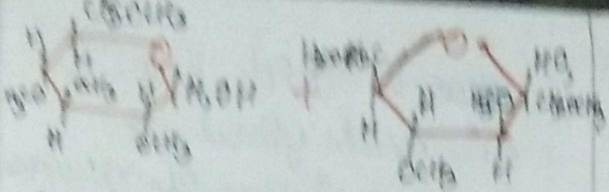
4) Sucrose does not reduce Tollen's reagent or Fehling's soln; does not form an osazone, when glucosazone is formed, does not form methyl glucosides; and does not undergo mutarotation.

5) Sucrose reacts with dimethyl sulfate in an alkaline solution to form octamethyl sucrose, which on hydrolysis yields a mixture of 2,3,4,6-tetra methyl-D-glucopyranose and 1,3,4,6-Tetramethyl-D-fructofuranose.

$$C_{12}H_{14}O_{3}(OH)_8 + (CH_3)_2SO_4 \xrightarrow{NaOH}$$

$$C_{12}H_{14}O_3(OCH_3)_8 \xrightarrow[H^+]{H_2O}$$

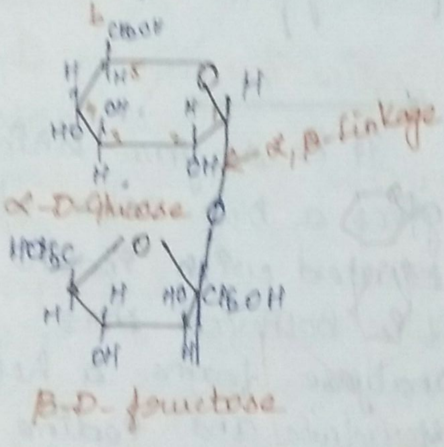
Octamethyl
sucrose



2,3,4,6-Tetra methyl-D-glucopyranose

1,3,4,6-Tetra methyl-D-fructofuranose

(b) Sucrose is hydrolysed by maltase, an enzyme that hydrolyses only α-glycosides. It is also hydrolysed by invertase, an enzyme that hydrolyses β- but not α-fructofuranosides.



POLYSACCHARIDES

Polysaccharides are made of many (10 or more) monosaccharide units joined together by glycosidic linkages. By far the most important naturally occurring polysaccharides are starch and cellulose.

Starch: $(C_6H_{10}O_5)_n$

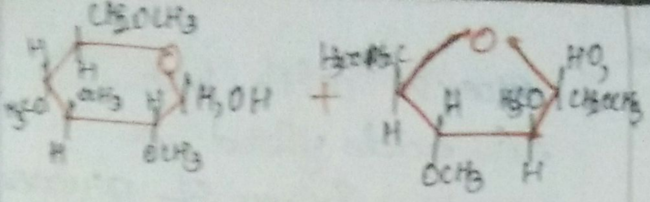
Starch is the main constituent of carbohydrates in our diet. It exists exclusively in plants, stored in the seeds, roots and fibres as food reserve. The chief sources of starch such are cereals, potatoes, corn and rice.

Manufacture:

Starch occurs naturally as small granules enclosed in cellular tissue. These are soaked in water and crushed. The pulp thus obtained is carried by a stream of water on to a sieve. The starch is separated from the liquid passing through the sieve by decantation and dried.

Structure:

Starch is actually a mixture of two structurally different polysaccharides. Amylose (20%) and Amylopectin (80%). When starch is heated with hot water, it can be separated



2,3,4,6-Tetra methyl-D-glucopyranose

1,3,4,6-Tetra methyl-D-fructofuranose

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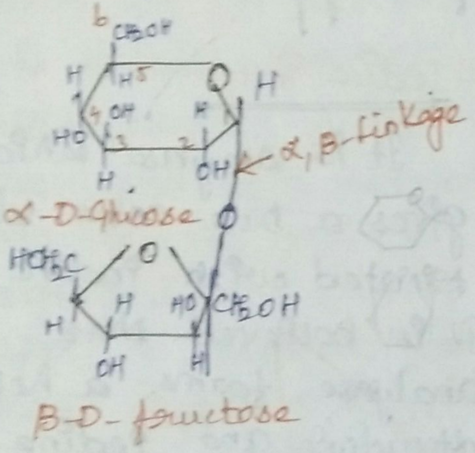

POLYSACCHARIDES

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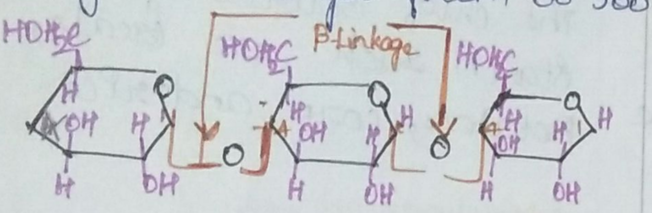
Starch is the main contributor of carbohydrates in our diet. It exists exclusively in plants, stored in the seeds, roots and fibres as food reserve. The chief sources of starch such are cereals, potatoes, corn and rice.

Manufacture:-

Starch occurs naturally as small granules enclosed in cellular tissue. these are soaked in water and crushed. The pulp thus obtained is carried by a stream of water on to a sieve. The starch is separated from the liquid passing through the sieve by decantation and dried.

Structure:-

Starch is actually a mixture of two structurally different polysaccharides. Amylose (20%) and Amylopectin (80%) When starch is heated with hot water, it can be separated into those components. The part that is soluble in water is amylose and remaining fraction is amylopectin. Both amylose and amylopectin are composed of D-glucose units. The no. of D-glucose units in amylose ranges from 60-300.



Amylose

Amylopectin has a branched chain structure. It is composed of chains of 25 to 30 D-glucose units joined by α-glycosidic linkages b/w C-1 of one glucose unit and C-4 of the next glucose unit. The no. of D-glucose units in amylopectin ranges from 300 to 6000.

Properties:-

It is a colourless amorphous, powder having no definite m.p. It gives colloidal soln. in water.

1) Hydrolysis:-

The hydrolysis of starch with hot dil. acids yield a syrupy mixture of glucose, maltose and high-molecular weight saccharides. The mixture is called Dextrin and marketed as Corn syrup. The digestive enzymes in human convert starch ultimately to glucose which is the source of energy.

2) Iodine Test:-

It is amylose which gives a blue color when treated with iodine. It is believed that analyse forms a helical structure and iodine is lodged in it.

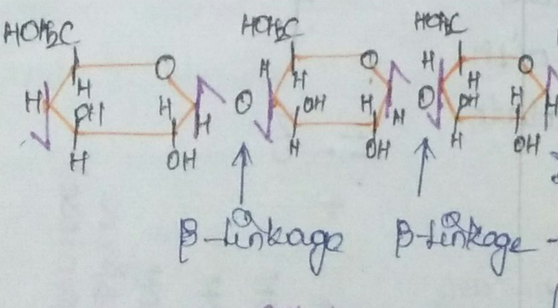
Starch does not reduce Tollen's reagent and Fehling's soln. It does not form an osazone with phenylhydrazine.

Cellulose, $(C_6H_{10}O_5)_n$

Cellulose is the main structural material of trees and other plants. Wood is 50% cellulose, while cotton wool is almost pure cellulose. Other sources of cellulose are straw, corncobs, bagasse and similar agricultural wastes.

Manufacture:

Cotton wool is about 97 per cent cellulose. It is ready for use after washing away the waxes and fats associated with it. The cellulose required for making paper is obtained from wood. Lignin and resinous substances present along with cellulose are removed by digesting the wood chips under pressure with a soln of cal. hydrogen sulfite $Ca(HSO_3)_2$.



Cellulose

Structure:-

Cellulose is a straight chain polysaccharide composed of D-glucose units. These units are joined by β-glycosidic linkages b/w C-1 of one glucose unit and C-4 of the next glucose unit. The no. of D-glucose units in cellulose ranges from 200-2500.

Properties:-

Cellulose is a colorless amorphous solid having no m.p. It decomposes on strong heating. It is insoluble in water and most organic solvents. However, it dissolves in Schweitzer's reagent which is ammoniacal soln. of cupric hydroxide.

Hydrolysis:-

Cellulose when hydrolysed by heating with dil. HCl, gives D-glucose. Cellobiose is formed in case of incomplete hydrolysis.

The cattle, goats and other ruminants have digestive enzymes (cellulases) capable of hydrolysing cellulose into glucose.

Important Derivatives of cellulose:-

Each glucose unit in cellulose molecule has three -OH groups. thus cellulose gives industrially important derivatives involving one or more of these three -OH groups.

1) Nitrated cellulose:-

Cellulose reacts with HNO_3 in the presence of H_2SO_4 to form an ester, cellulose nitrate called Gun cotton or cordite.

$$\underset{\text{cellulose}}{Cell-OH} + HNO_3 \xrightarrow{H_2SO_4} \underset{\text{cellulose nitrate}}{Cell-ONO_2}$$

2) cellulose Acetate:-

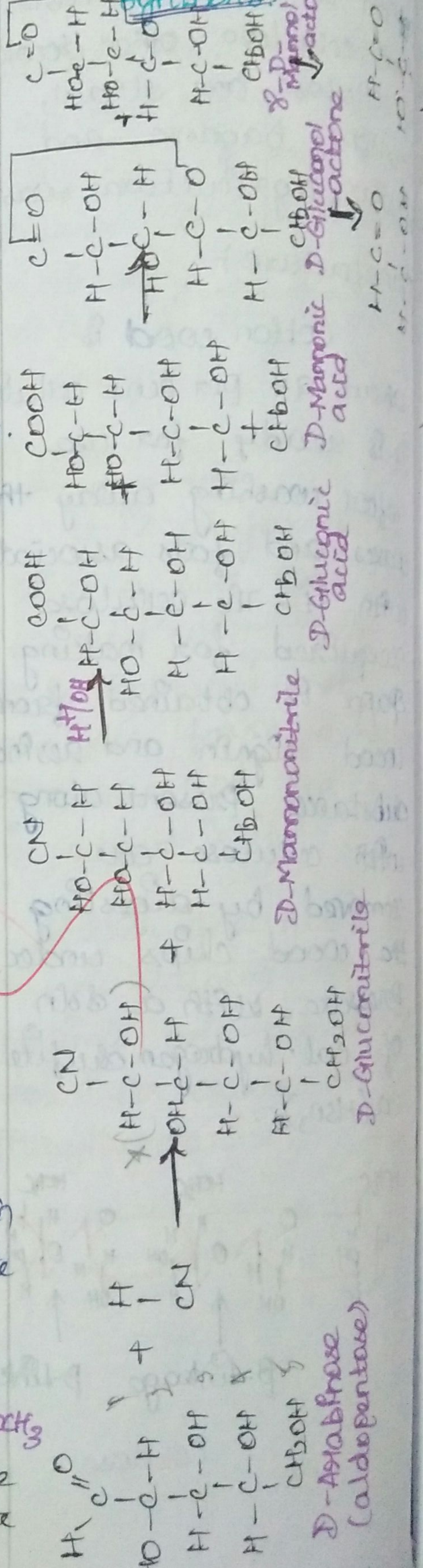
Cellulose when acetylated with acetic anhydride with H_2SO_4, forms cellulose acetate or triacetate

$$\underset{\text{Cellulose}}{Cell-OH} + \underset{\text{Acetic anhydride}}{(CH_3CO)_2O} \rightarrow \underset{\text{Cellulose acetate}}{Cell-O-COCH_3}$$

Ascending series:-

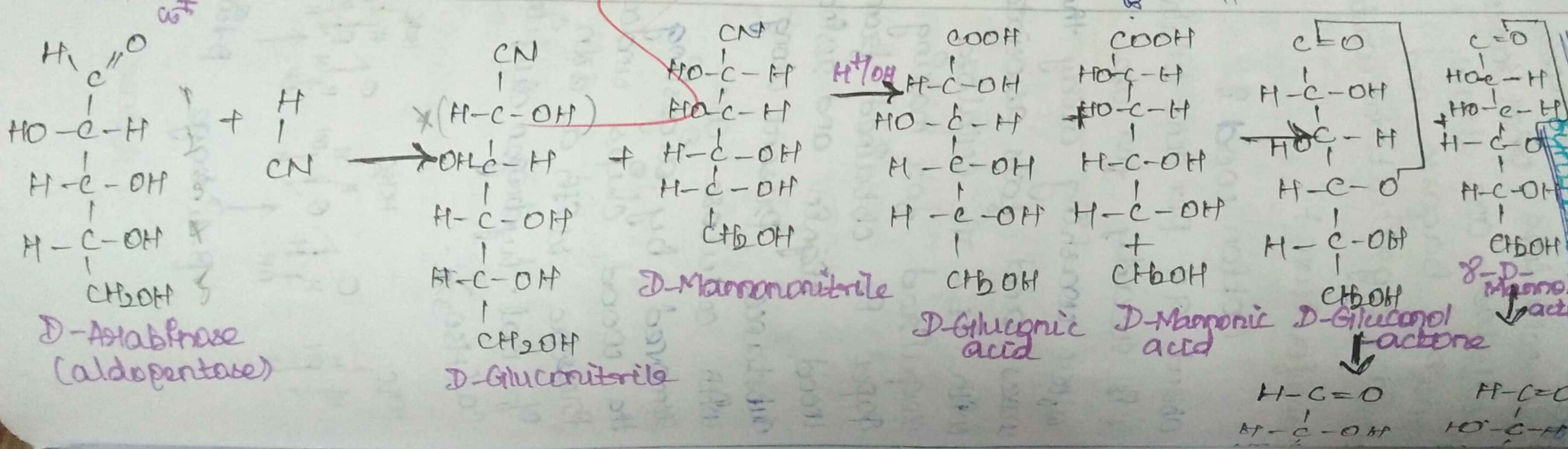
Conversion of an Aldo into the next higher

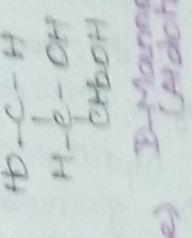
1) Kiliani-Fischer cyanohydrin synthesis:-



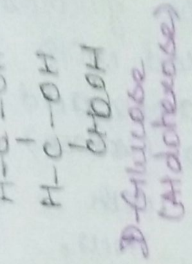
Conversion of an Aldose into the next higher al

(i) Killiani-Fischer cyanohydrin synthesis:-





D-Mannose (Aldohexose)



D-Glucose (Aldohexose)

D-Arabinose is first allowed to react with HCN. As a result, a new assymetric centre formed in the formation in two cyanohydrin (Aldonitriles). These two compounds are different only in configuration about C-2 and are called epimers. these cyanohydrins then hydrolysed with dil. acids to give D-Gluconic acid, D-Mannonic acid. Then heating it to close the molecule of water to form γ-Lactones. these are solids separated by fractional crystallisation. the individual lactones then reduced with $LiAlH_4$ or with Na-Hg in weak acidic soln. to form one more carbon atoms contain the higher aldose namely D-glucose and D-Mannose

Maltose (Malt sugar), $C_{12}H_{22}O_{11}$

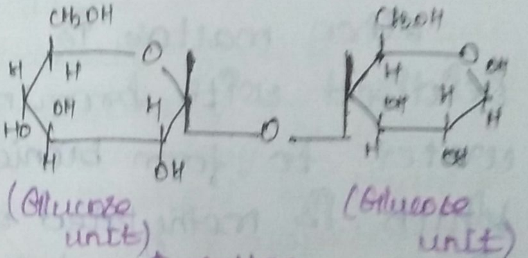
Intro:

Maltose does not occur in the free state in nature but as combined state it is present in barely and other cereal grains.

Preparation:

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} + H_2O \xrightarrow[\text{enzyme}]{\text{Diastase}} \underset{\text{Maltose}}{C_{12}H_{22}O_{11}}$$

The starch is hydrolysed with enzyme present in yeast and form maltose. It is also obtained by partial hydrolysis with dil. acid.



β-Maltose

It undergoes mutarotation in aq. soln. So it exist in α and β-forms. It reacts with excess phenyl hydrazine form malt osazone. this shows carbonyl group present in maltose.

It is hydrolysed to give α-molecule of D-glucose. this indicates α-glucose molecules are linked through an oxygen atom.

It's oxidised by bromine water to form maltobionic acid. Which has a same no. of carbon atoms, so it contains carbonyl group as aldehyde form.

It is a reducing sugar, because it reduce Felhing's soln. and Tollen's reagent. This indicate that atleast one aldehyde group of 2-molecules of glucose present in maltose.

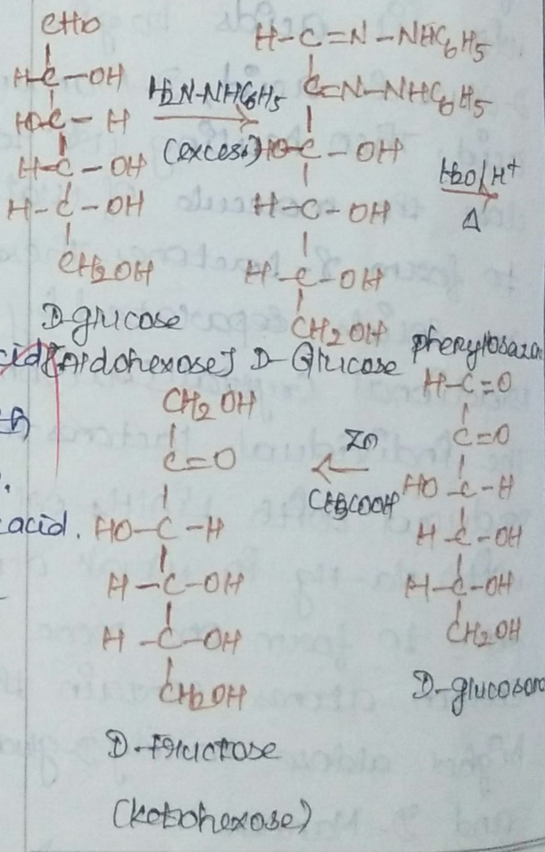
When maltose is oxidised with bromine water to form bionic acid which is methylated with dimethyl sulphate and NaOH. forms, O-methyl meta-maltobionic acid.

This on hydrolysis give 2,3,5,6- Tetra-O-methyl gluconic acid.

Interconversion:-

Conversion of D-Glucose into the corresponding D-Fr

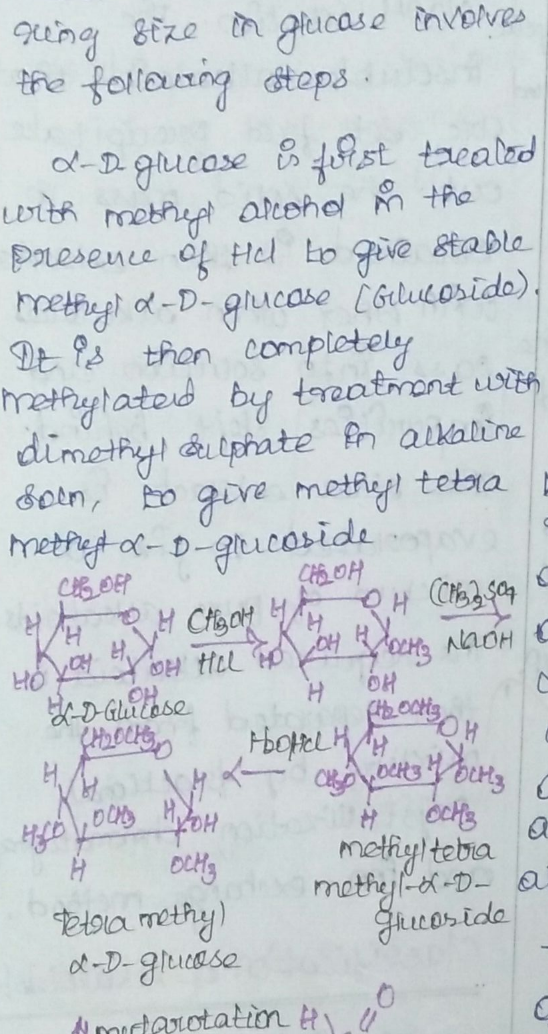
The aldose is first allowed to react with excess phenylhydrazine to give ozazone the ozozone is next hydrolysed with dil. HCl to give glucozone this is then reduced with zinc and glacial acetic acid to give D-Fructose (ketose) which is isomeric with original D-Glucose. thus, D-glucose may be converted into D-Fructose as follows.

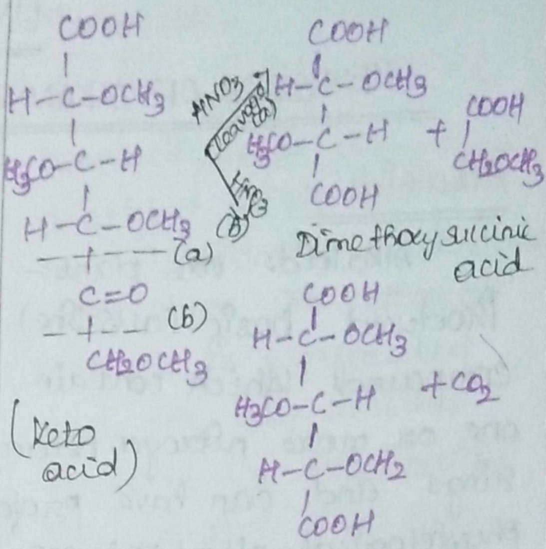


Determination of the ring size

We assumed that both α- and β- D-glucose have 6-membered rings structures. Alternatively the hydroxyl groups at C-2, C-3, C-4 or C-6 involved in the ring closure, which makes possible, the formation of 3, 4, 5 or 7 membered rings. this problem was solved by Haworth and the method used to determine the exact ring size in glucose involves the following steps.

α-D glucose is first treated with methyl alcohol in the presence of HCl to give stable methyl α-D-glucose (Glucoside). It is then completely methylated by treatment with dimethyl sulphate in alkaline soln, to give methyl tetra methyl α-D-glucoside.





Trimethoxy glutaric acid

Then, the hydrolysis with dil. HCl selectively removes the methoxy group at C-1 to give tetramethyl-α-D-glucose which is undergoes mutarotation to give open chain aldehyde form which is then oxidised with conc. HNO3 ultimately give a mixture of Dimethoxy succinic acid and trimethoxy glutaric acid obtained by cleavage at a and b respectively.

The isolation and identification of these diacids clearly shows that ketone group must formed at C-5, and that α-D glucose has six-membered ring structure which is also confirmed by x-ray analysis.

the carbohydrate containing six membered ring is otherwise called pyranose (pyran + ose) similarly, five membered ring structures are also common in sugar, which are called furanose (furan