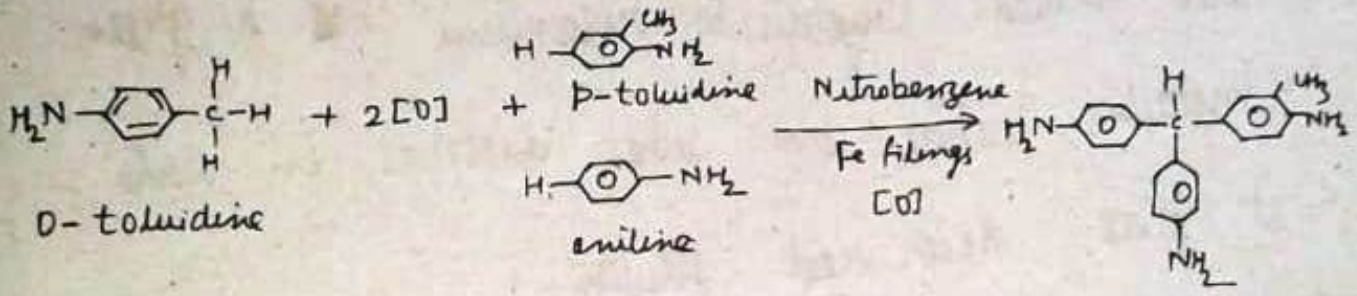
Q Write a note on Rosaniline dye

Ans → Rosaniline dye comes under the catagory of Triphenylmethane dyes and Subgroup is called Fuchsine sub group.

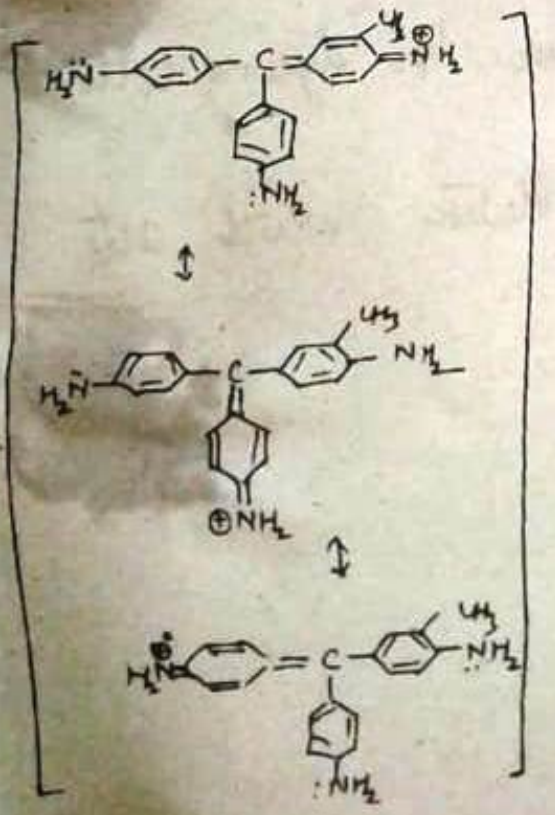
This is prepared by oxidising a mixture of one molecule of p-toluidine, one molecule of o-toluidine and one molecule of aniline as their hydrochloride, with nitrobenzene in presence of iron filing.




o-toluidine

Leucobase

[O]



Excess of HCl

Colour base of rosaniline

Rosaniline hydrochloride

Here a small amount of pararosaniline is also formed. Crystals of rosaniline has a green metallic lustre but when dissolves in water it gives deep red solution.

Rosaniline is used to dye wool and silk directly giving red violet colour. For dyeing cotton it is first soaked in tannic solution which acts as mordant.

Q write a note phenolphthalein dye.

Ans → This is also a type of Phthalein group dye

Phthalein group is subdivided into subgroups

a) Eosine group

& b) Rhodamine group.

Eosine group of T.P.M. dyes are those which are prepared by condensing phthalic anhydride with Phenol.

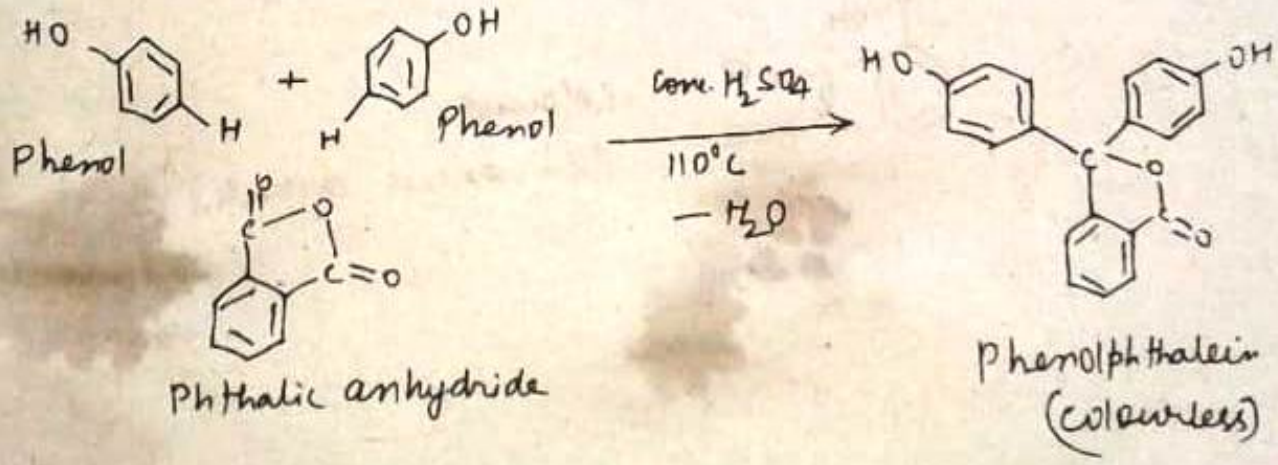
Important members are

i) Phenolphthalein

ii) Fluorescein

iii) Eosin.

Phenolphthalein is prepared by condensing one molecule of phthalic anhydride with two molecules of Phenol in presence of conc $H_2SO_4$ at 110°C.



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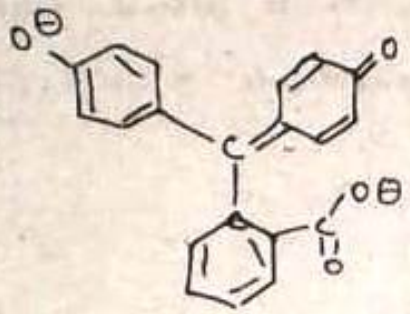
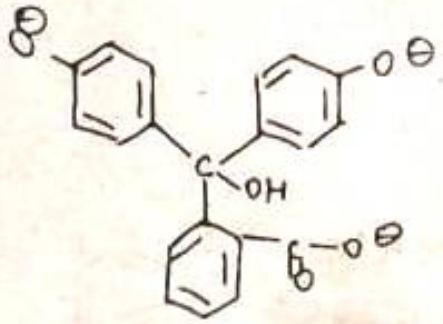
This is a white crystalline powder insoluble in water but soluble in alcohol.

In alkaline medium, it give quinonoide form which is deep red in colour



deep red.

In presence of excess alkali, it loses its quinonoid form and again becomes colourless



Colourless
(In excess alkali)

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Q How can you establish the open chain formula of Fructose.

Ans → Open chain formula of Fructose can be established on the basis of following facts and reactions:

1. Analysis and molecular mass determination show that molecular formula of Fructose is $C_6H_{12}O_6$.

2. Fructose when reduced with sodium-amalgam and water it gives one molecule of sorbitol and one molecule of mannitol (both are hexahydric alcohols).

These hexahydric alcohols when further reduced by Red P and conc. HI acid, it gives 2-iodohexane and n-Hexane.

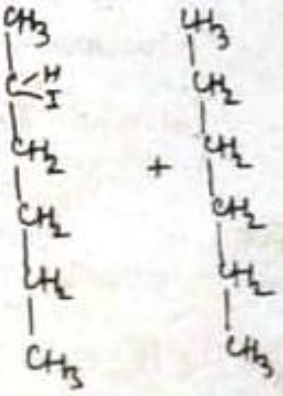
Formation of these products, indicate that Fructose molecule has a straight chain of six carbon atoms

$$C_6H_{12}O_6 + 2[H] \xrightarrow[\text{water}]{Na\text{-}Hg} C_6H_{14}O_6 \xrightarrow[[H]]{\text{Red P/Conc. HI}}$$

Fructose

Hexa hydric alcohol

[Sorbitol one molecule + Mannitol one molecule]



2-Iodohexane + n-Hexane

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3. Fructose reacts with acetic anhydride in presence of pyridine to form Fructose penta acetate

$$C_6H_{12}O_6 \xrightarrow[(CH_3CO)_2O/\text{Pyridine}]{\text{Acetylation}} C_6H_7O.(O.CO.CH_3)_5$$

or. $C_6H_7O.(OH)_5$
Fructose

Fructose penta acetate

This reaction indicates the presence of 5 —OH groups in Fructose molecule.

4. Fructose reacts with one molecule of hydrogen cyanide to form cyanohydrin and with hydroxyl amine to form oxime.

$$C_6H_{12}O_6 + H-CN \xrightarrow{\text{Addition reaction}} C_6H_{12}O_5(OH)(CN)$$

$(C_6H_{12}O_5.O)$
Fructose

Fructose cyanohydrine

[Similar to reaction $-\underset{|}{C}=O + H-CN \rightarrow -\underset{|}{\overset{CN}{C}}-OH$ ]

Also, $C_6H_{12}O_6 + \begin{matrix} H \\ H \end{matrix}\!\!>\!N-OH \xrightarrow[\text{reaction}]{\text{Substitution}} C_6H_{12}O_5(=N-OH)$

$(C_6H_{12}O_5.O)$

Fructose oxime

[Similar to reaction $-\underset{|}{C}=O + \begin{matrix} H \\ H \end{matrix}\!\!>\!N-OH \rightarrow -\underset{|}{C}=N-OH + H_2O$

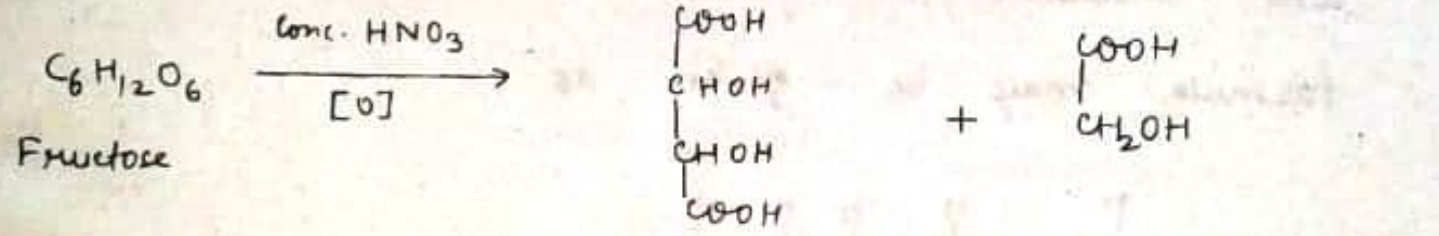
oxime ]

These reactions indicate the presence of a carbonyl group ($-\overset{O}{\overset{\|}{C}}-$) in fructose molecule.

Now we have to decide whether this carbonyl group is in the form of ketone or in the form of an aldehyde.

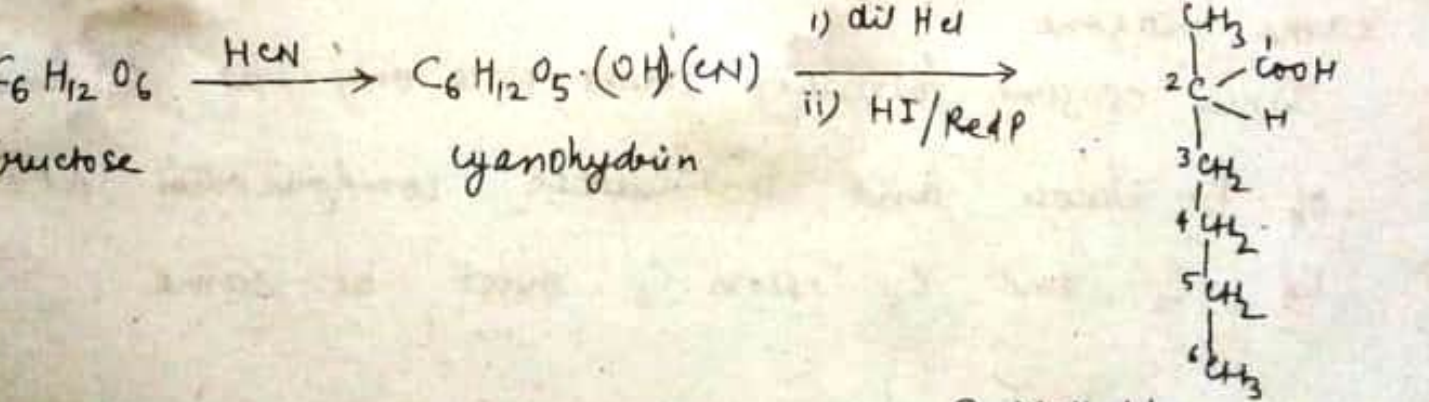
5. Fructose on oxidation with conc$^{n}$ nitric acid, gives tartaric acid and Glycollic acid.

Formation of two carboxylic acids with lesser number of carbon atoms, indicate the presence of a Keto group instead of presence of an aldehyde group.




Tartaric acid  Glycollic acid.

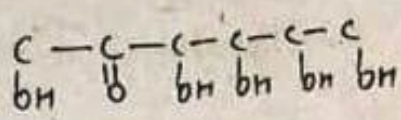
6. Cyanohydrin formed in the above reaction ④, when hydrolysed by dil HCl and then reduced by Red Phosphorus and Conc$^{n}$ hydroiodic acid, gives 2-Methyl hexanoic acid.



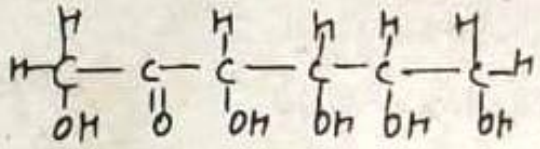

2-Methyl hexanoic acid

Formation of the product 2-Methyl hexanoic acid indicates that Keto group is at $C_2$ position of Fructose molecule.

7. Since fructose molecule is stable molecule hence, all the five $-OH$ groups must be present at five different C-atoms, the skeleton can be written as



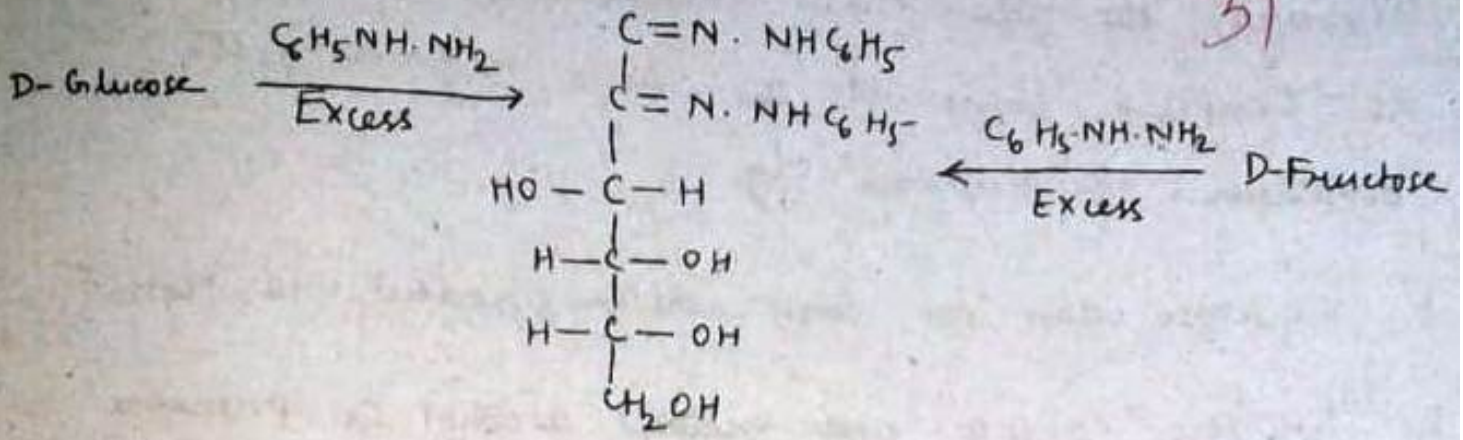
Now, keeping in mind the tetravalency of Carbon and molecular formula of fructose the open chain formula may be given as



Configuration of Fructose molecule →

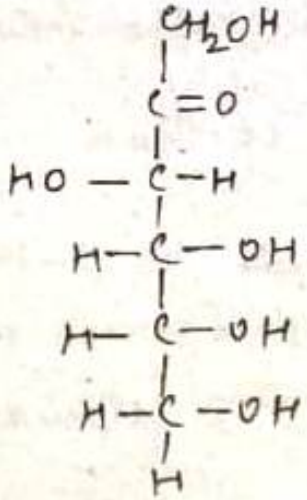
D-Glucose and D-Fructose when treated with excess of Phenyl hydrazine then osazone formation takes place. Here we find that both D-Glucose and D-Fructose give same osazone.

Since osazone formation takes place only at $C_1$ and $C_2$ of D-Glucose and D-Fructose, configuration at $C_3$, $C_4$ and $C_5$ and $C_6$ must be same.




Same osazone of Glucose and Fructose
M.P. 208°C

Since keto group in fructose molecule is at $C_2$ position and there are 5 –OH groups and all the 6 Carbon atoms are in straight line. Hence the configuration may be written as

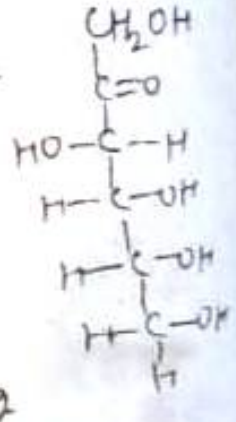



open chain formula of glucose.

However, the open chain formula of Fructose does not explain some of the facts regarding the behaviour of Fructose eg

1. Fructose does not form addition product with $NaHSO_3$
2. Fructose reacts with methyl alcohol in presence of dil HCl to give a mixture of two stereoisomeric methyl fructoside corresponding to α- and β-Fructoses
3. Phenomenon of mutarotation exhibited by fructose can not be explained by open chain formula of D-Fructose
4. Fructose does not react with Grignard's reagent
5. Fructose does not show appreciable carbonyl absorption in its IR spectrum.

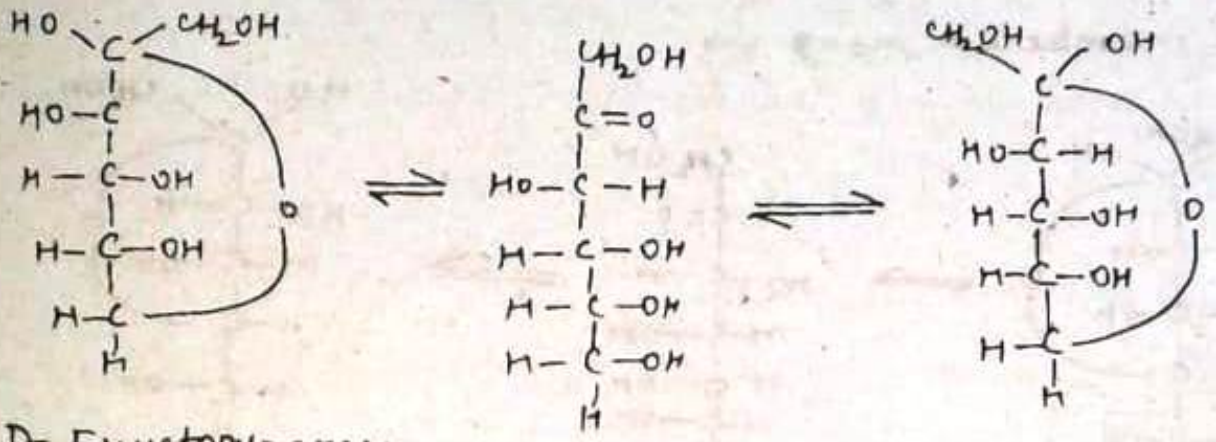
Since the open chain formula of D-Fructose does not explain all the properties of D-Fructose, hence a ring structure was suggested.



It has been found that naturally occurring Fructose has 6-membered ring. Ring formation takes place at $C_2$ and $C_6$.

However, in combined state eg in sucrose, in inulin, it has 5-membered ring. Ring formation takes place at $C_2$ and $C_5$.

6-membered ring →



β-D-Fructopyranose

$[\alpha]_D = -133°$

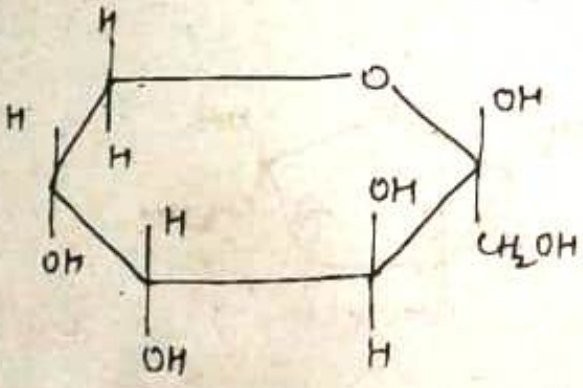
D-Fructose

$[\alpha]_D = -92°$

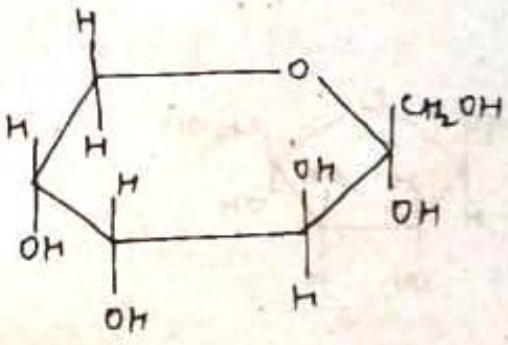
α-D-Fructopyranose

(not isolated)

Haworth Projection formula

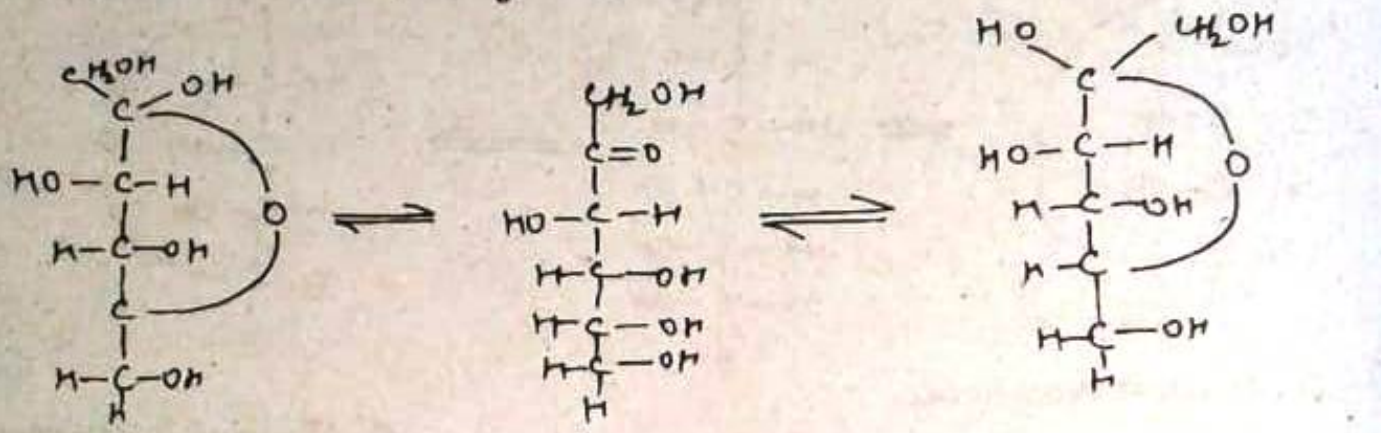


β-D-Fructopyranose



α-D-Fructopyranose

5- membered ring →



α-D-Fructofuranose

β-D-Fructofuranose

Haworth Projection Formula →