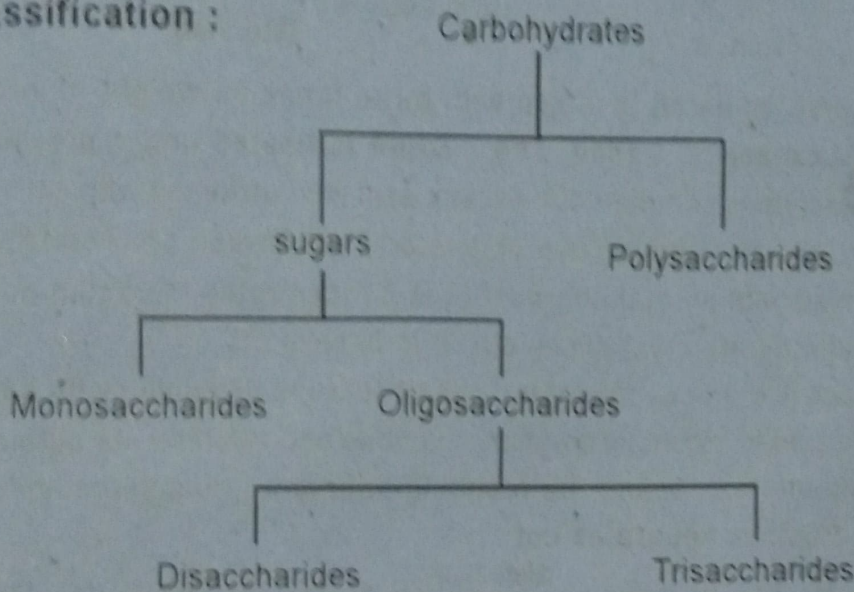


UNIT - II

CARBOHYDRATES

What are they? All optically active polyhydroxyaldehydes, all polyhydroxy ketones and all compounds which give the above said two classes of compounds on hydrolysis are called carbohydrates. E.g., Glucose, fructose, maltose, cellobiose, starch, cellulose etc.

Classification :



Carbohydrates are divided into main classes, viz., sugars and polysaccharides. Sugars are crystalline substances. They have sweet taste. They are soluble in water. Polysaccharides are complex in nature. They have high molecular weights. Most of them are non-crystalline. They are not sweet. They are insoluble in water or less soluble in water than sugars.

Sugars are further subdivided into two groups namely monosaccharides and oligosaccharides. Sugars which can not be further hydrolysed into smaller molecules are called monosaccharides. E.g., Glucose and fructose. Sugars which yield 2 to 9 monosaccharide molecules on hydrolysis are called oligosaccharides. If sugar yields two monosaccharides on hydrolysis it is called a disaccharide. E.g., Sucrose, maltose, etc. If it yields three monosaccharides on hydrolysis it is known as a trisaccharide and so on.

Polysaccharides are carbohydrates which yield a large number of monosaccharide molecules on hydrolysis. E.g., Starch Cellulose, etc

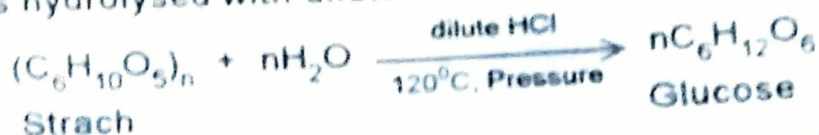
Glucose

Glucose is found along with fructose in sweet fruits like grapes, banana and also in honey, beetroots also contain glucose

Preparation :

1. From starch (Manufacture):

Starch is hydrolysed with dilute mineral acid. We get pure glucose



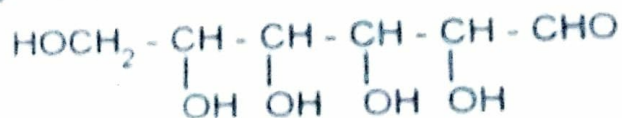
The starchy material is mixed with three times its weight of water. Dilute sulphuric acid is added. The mixture is heated under pressure. When the reaction is complete the excess acid is neutralised with calcium carbonate. Calcium sulphate is precipitated. It is filtered off. The filtrate is decolourised with animal charcoal. It is concentrated in vacuum pans. Glucose monohydrate crystallises out. It is filtered off.

2. Glucose is made by the hydrolysis of sucrose by boiling with dilute hydrochloric acid in alcoholic solution. Glucose and fructose are obtained in equal amounts. On cooling the resulting solution, glucose being less stable than fructose separates out.



Properties :

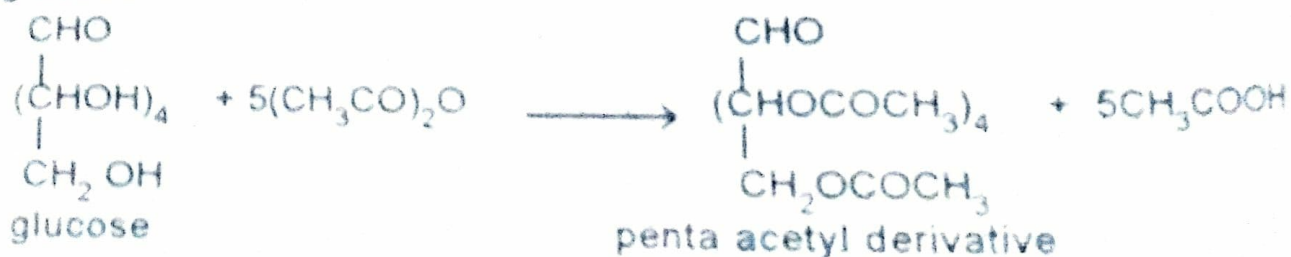
It is a white crystalline solid. It is sweet. It is optically active. It is dextro rotatory. Therefore it is also called dextrose.



The structural formula of glucose is $\text{CHO}(\text{CHOH})_4\text{CH}_2\text{OH}$. Therefore it behaves as an aldehyde, a primary alcohol and a secondary alcohol.

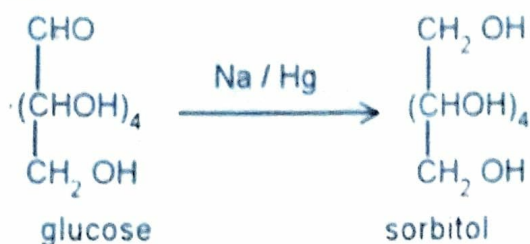
1. Acetylation (as an alcohol) :

It reacts with acetic anhydride giving a penta acetyl derivative of glucose.



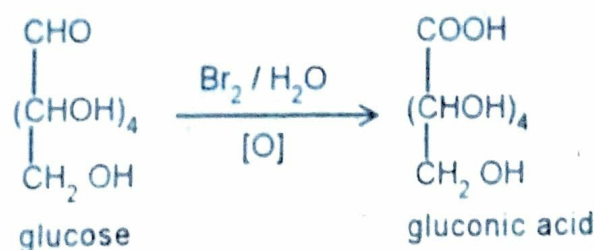
2. Reduction (as an aldehyde):

When glucose is reduced with sodium amalgam in aqueous solution, we get sorbitol.

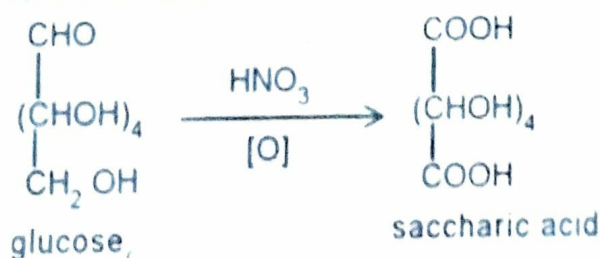


3. Oxidation :

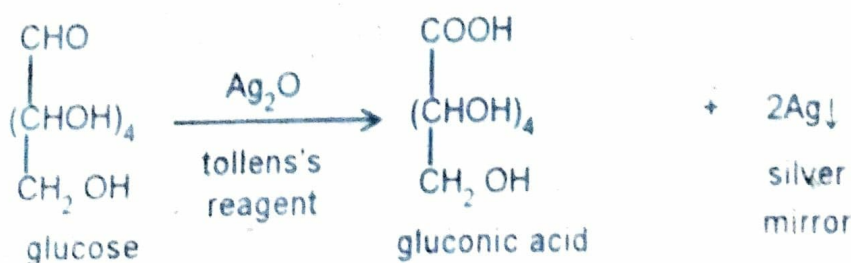
Glucose on treatment with bromine water (mild oxidising agent) is oxidised to gluconic acid. The bromine water is decolourised



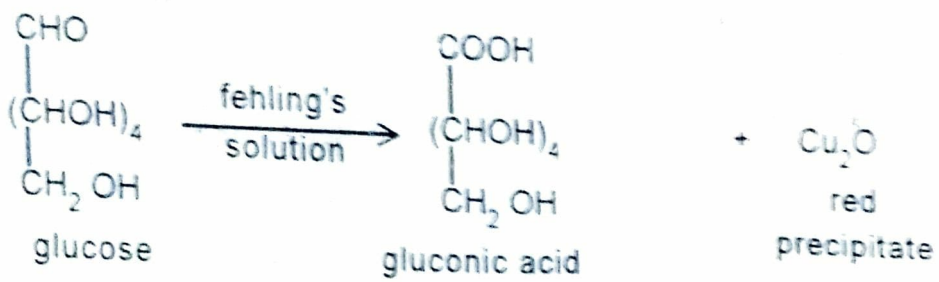
4. Glucose on treatment with nitric acid (strong oxidising agent) is oxidised to saccharic acid.



5. a) It reduces Tollens's reagent (ammoniacal silver nitrate solution) giving silver mirror. It is oxidised to gluconic acid

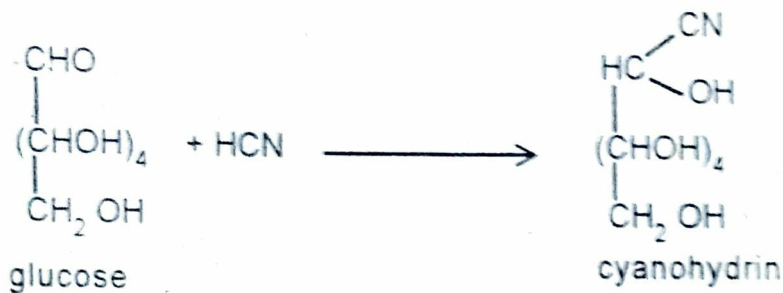


b) It reduces Fehling's solution giving a red precipitate. It is oxidised to gluconic acid.



6. Addition reactions :

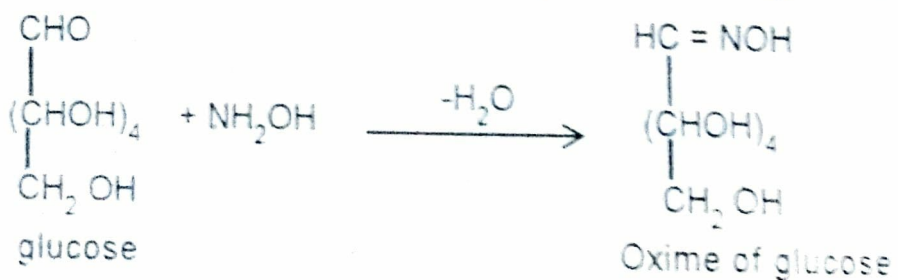
It adds HCN giving the cyanohydrin of the glucose.



It does not add sodium bisulphite and ammonia. This is because glucose possesses a ring structure. HCN is able to open the ring and react with the aldehydic group whereas sodium bisulphite or ammonia could not open the ring structure and react with the aldehydic group.

7. Condensation reactions :

It condenses with hydroxylamine giving the oxime of glucose.



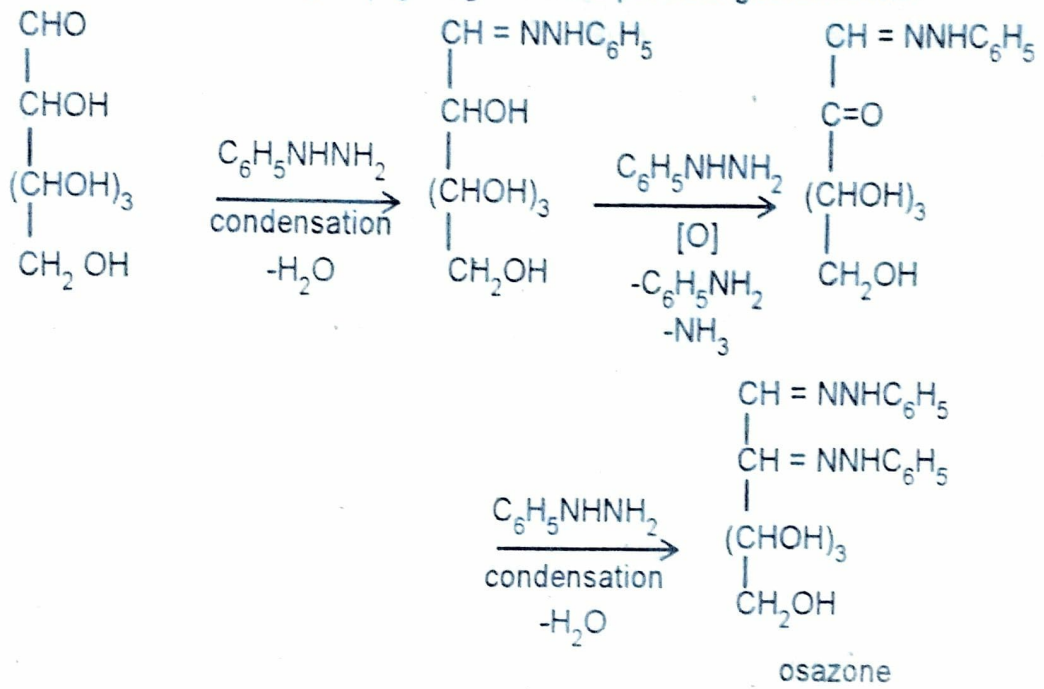
8. Action with phenyl hydrazine :

When treated with excess phenyl hydrazine, glucose gives osazone

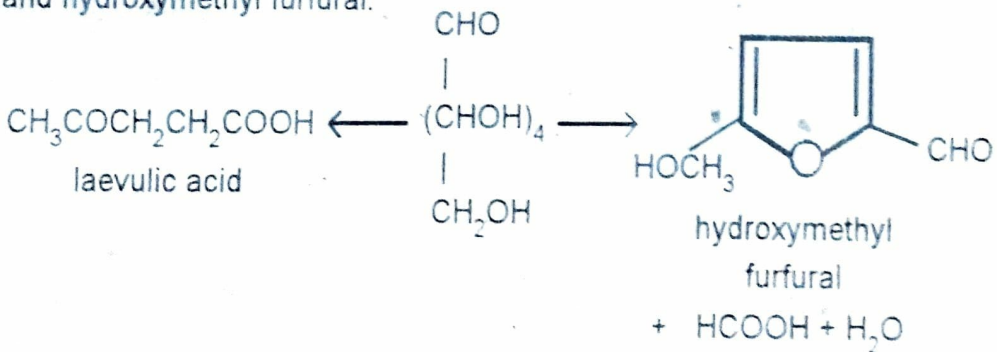
Mechanism : (Fischer)

- One molecule of phenyl hydrazine condenses with the aldehydic group of glucose and forms the corresponding phenyl hydrazone:

- ii. When glucose is warmed with excess phenyl hydrazine, a second molecule of the phenyl hydrazine oxidises the secondary alcoholic group on the carbon atom next to the aldehyde group. The corresponding ketone is formed.
- iii. Now a third molecule of phenyl hydrazine condenses with this newly produced keto group giving the final product glucosazone.



9. When heated with concentrated hydrochloric acid, it gives laevulic acid and hydroxymethyl furfural.

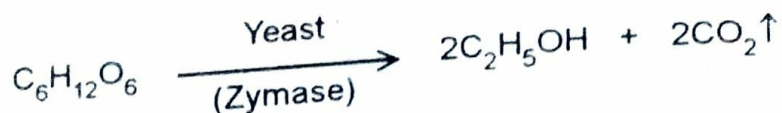


10. Glucose react with calcium hydroxide to give calcium glucosate



11. Fermentation :

When a solution of glucose is treated with yeast we get ethanol. The enzyme zymase present in yeast converts glucose into ethanol and carbon dioxide.

**Tests :**

1. On heating in a nickel spatula it melts and then turns brown (chars) giving a smell of burnt sugar.
2. On treating with conc. H_2SO_4 it chars. CO_2 and SO_2 are formed.
3. With NaOH solution it turns yellow and then brown and finally gives a resinous mass.
4. It gives a yellow precipitate of osazone with excess phenyl hydrazine.

Muta Rotation

When a monosaccharide is dissolved in water, the specific rotation of the solution gradually changes and reaches a constant value. This change in the value of specific rotation is known as mutarotation. All reducing sugars except some ketoses undergo mutarotation. E.g., A solution of glucose has a specific rotation of $+111^\circ$ when it is freshly prepared. On standing the specific rotation decreases slowly and reaches the constant value of $+52.5^\circ$.

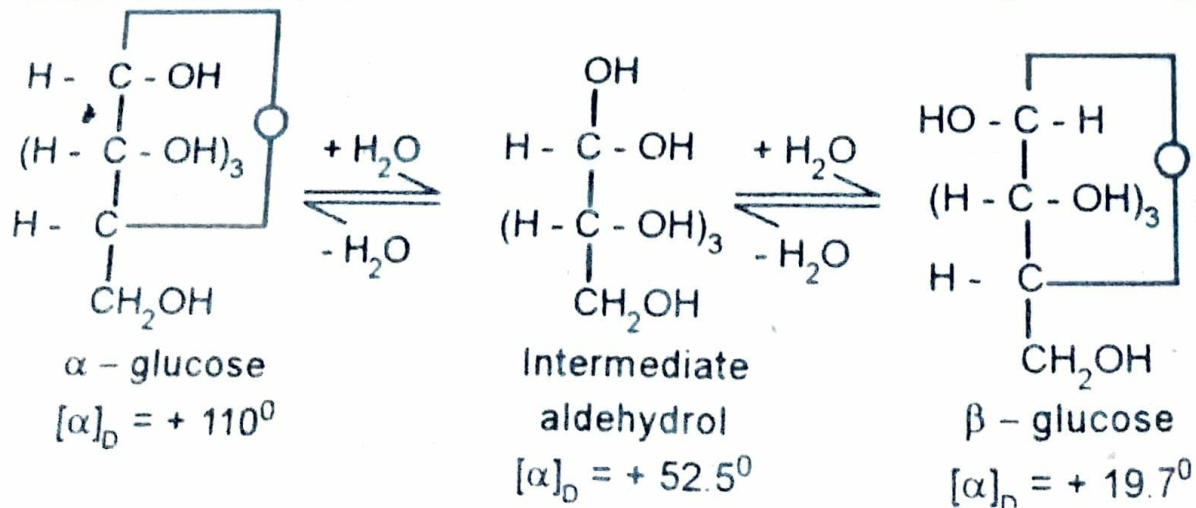
Reason :

Glucose exists in two stereoisomeric forms viz. α and β glucose. Because of this it shows mutarotation.

The specific rotation of α - glucose is $+110^\circ$ and that of β - glucose is $+19.7^\circ$ in aqueous solution, the specific rotation of α - glucose decreases slowly from $+110^\circ$ to $+52.5^\circ$ but the specific rotation of β - glucose increases from $+19.7^\circ$ to $+52.5^\circ$. This shows that the following equilibrium is existing in solutions.

Mechanism (Lowry) :

Mutarotation takes place only in the presence of a solvent like water which behaves both as an acid and a base. According to Lowry, in



presence of water, the ring structure of glucose opens. Then it recloses either in the original position or in the inverted position via an intermediate product aldehydrol.

Significance :

The fact that glucose shows mutarotation has helped to prove that glucose has cyclic structure and not an open chain structure.

Uses :

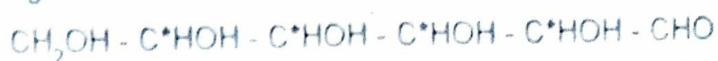
1. It is used as a sweetening agent in confectionery.
2. It is used in the preparation of vinegar.
3. It is used in silvering of mirrors.
4. It is used to reduce Indigo blue to Indigo white.
5. It is used as a food for infants and invalids.
6. It is used for the preparation of vitamin - B, Vitamin - C and ethyl alcohol.

Elucidation of Structure of Glucose

A. Open chain structure for glucose :

1. Molecular formula $C_6H_{12}O_6$.
2. a. On treatment with acetic anhydride it gives a penta acetyl derivative. Therefore it contains five 'OH' groups.
b. It is not easily dehydrated. Therefore each hydroxy group must be linked to different carbon atoms.
3. It forms a cyanohydrin with HCN and an oxime with hydroxyl amine. This shows the presence of a carbonyl group in glucose.
4. Glucose decolorises bromine water. It is oxidised to gluconic acid. Glucose and gluconic acid have the same number of carbon atoms. Therefore the carbonyl group present is an aldehydic group. Aldehyde group is monovalent. Therefore it must be present at one end of the molecule.
5. When glucose is reduced with concentrated hydriodic acid and red phosphorus at $100^\circ C$ we get a mixture of 2-iodohexane and hexane. Thus all the six carbon atoms in glucose are in a straight chain.

From the above evidences Baeyer suggested an open chain structural formula for glucose.



There are four asymmetric carbon atoms. Hence it must have $2^4 = 16$ optically active forms. All of them are known.

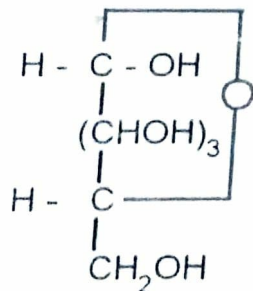
Need structural elucidation of Fructose

B. Cyclic structure for glucose:

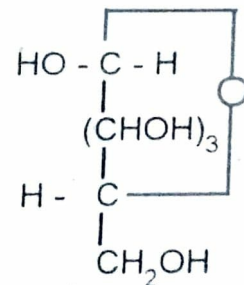
The open chain structure of glucose does not explain the following reactions of glucose.

- i. It does not add sodium bisulphite and NH_3 . This raises a doubt whether the aldehyde group is actually present or not.
- ii. When glucose is crystallised from an alcoholic solution or from acetic acid solution we get a glucose with specific rotation $+110^\circ$. But when glucose is crystallised from pyridine solution we get a glucose with specific rotation $+19.7^\circ$. This shows that glucose exists in two stereoisomeric forms.
- iii. When an aqueous solution of glucose is allowed to stand, its specific rotation slowly decreases from 110° to $+52.5^\circ$. This is called mutarotation.
- iv. When glucose is treated with methyl alcohol and dry HCl gas, we get two stereoisomeric methyl glucosides.

To account for the above observations the following ring structures have been assigned to glucose.

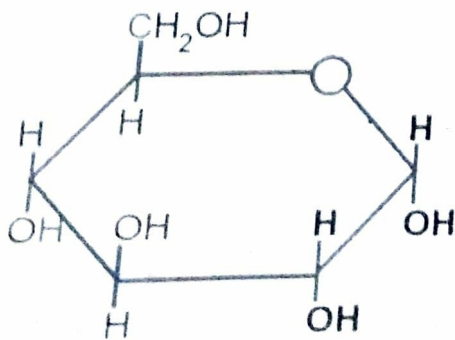


α - glucose
(α - D gluco pyranose)

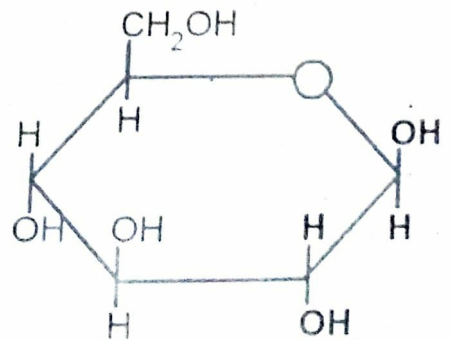


β - glucose
(β - D gluco pyranose)

Hawarth structure :



cis structure



trans structure

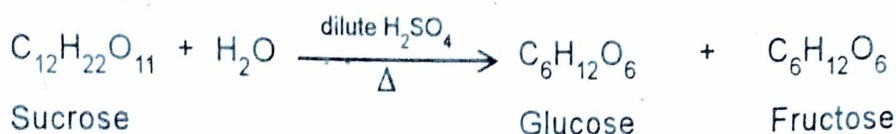
Fructose

Fructose occurs in the free state along with glucose in most of the sweet fruits and honey. It is also found in inulin.

Preparation :

i. From cane sugar :

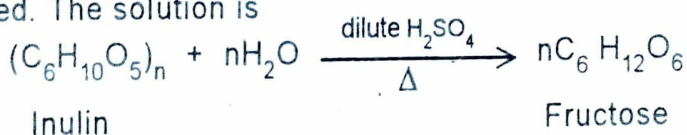
A concentrated solution of cane sugar is hydrolysed with dilute hydrochloric acid. When the hydrolysis is over,



the solution is treated with lime. Calcium fructosate $\text{C}_2\text{H}_{12}\text{O}_6\text{CaO}$, is precipitated. Calcium glucosate remains in solution. The precipitate is removed. It is suspended in water. Carbon dioxide is passed through the solution. Calcium carbonate is precipitated. It is removed. The solution is concentrated. Fructose crystallises out.

ii. From Inulin :

(Manufacture) When inulin, a polysaccharide, is hydrolysed with dilute sulphuric acid fructose is got. When the hydrolysis is over, the solution is treated with barium carbonate. Barium sulphate is precipitated. It is removed. The solution is

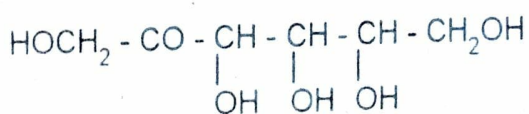


concentrated. Fructose crystallises out.

Properties :

1. It is a white crystalline solid.
2. It is sweeter than cane sugar. It is optically active.
3. It is laevo-rotatory. Therefore it is called leavulose.

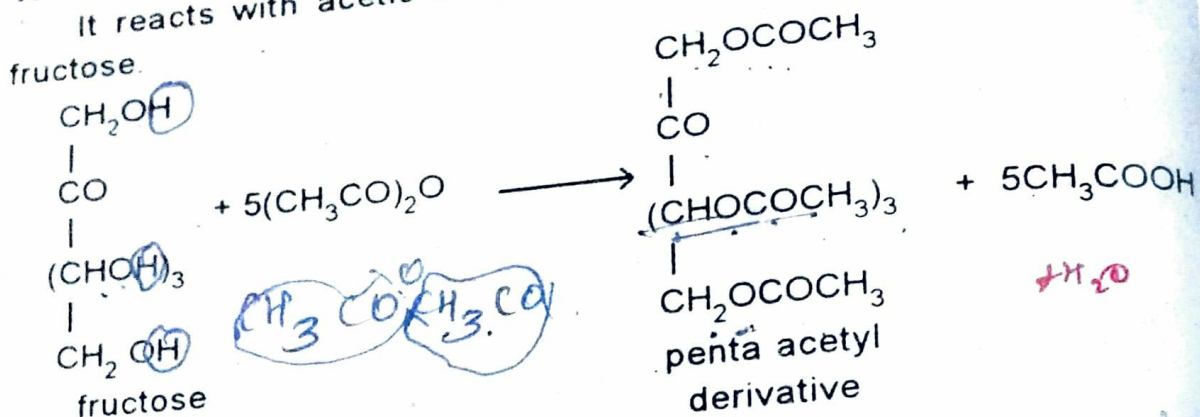
The structural formula of fructose is



Therefore it behaves as ketone, primary alcohol and secondary alcohol.

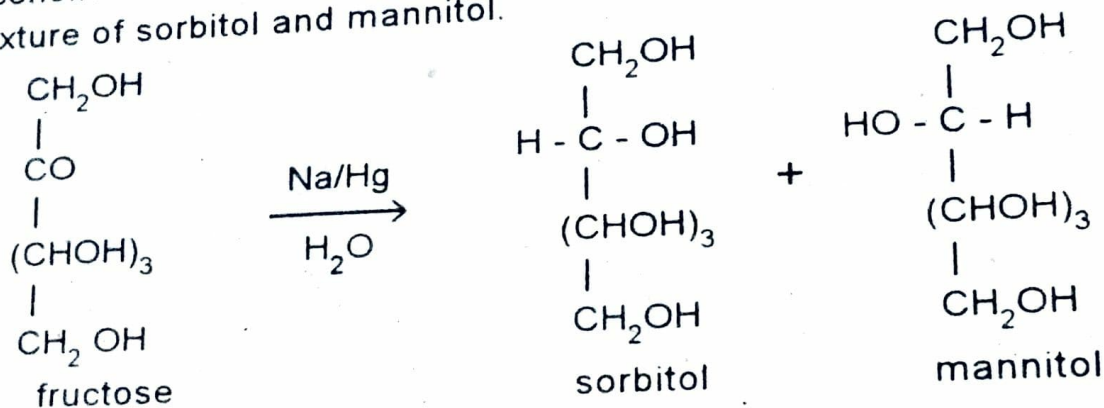
1. Acetylation (as on alcohol):

It reacts with acetic anhydride giving penta acetyl derivative of fructose.

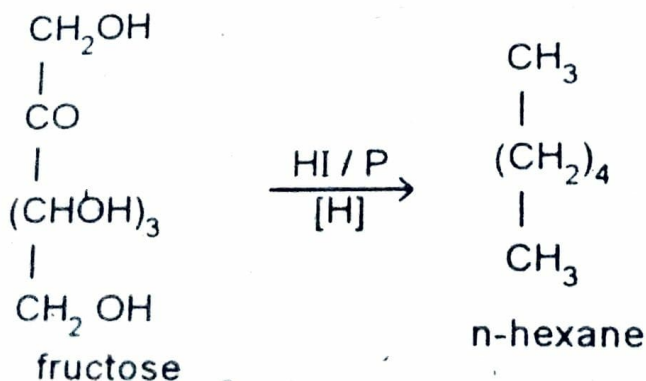


2. Reduction (as a ketone):

When fructose is reduced with sodium amalgam in aqueous or alcoholic solution or using catalysts or even electrolytically we get a mixture of sorbitol and mannitol.

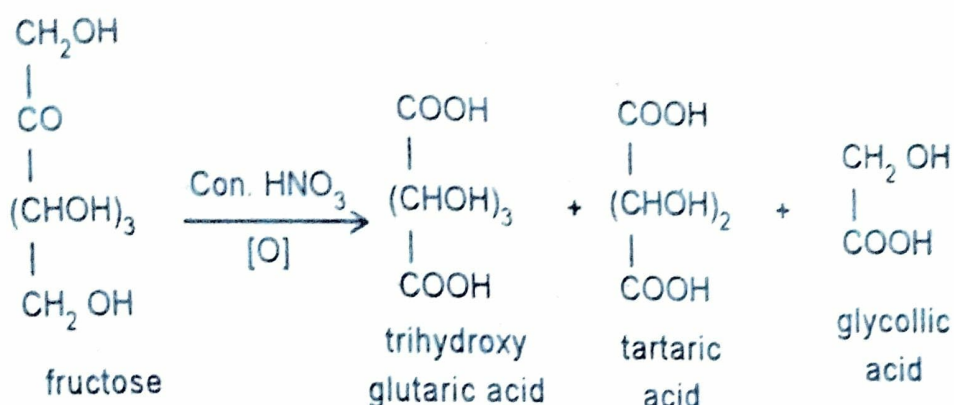


3. On complete reduction with HI and red phosphorus, it forms n-hexane.

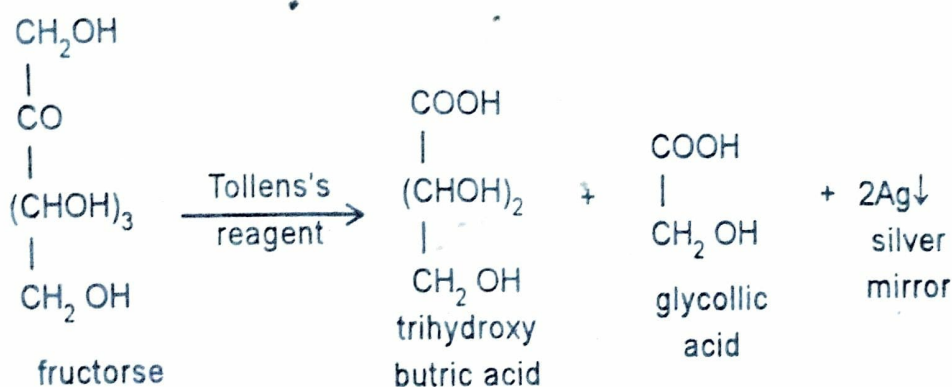


4. Oxidation :

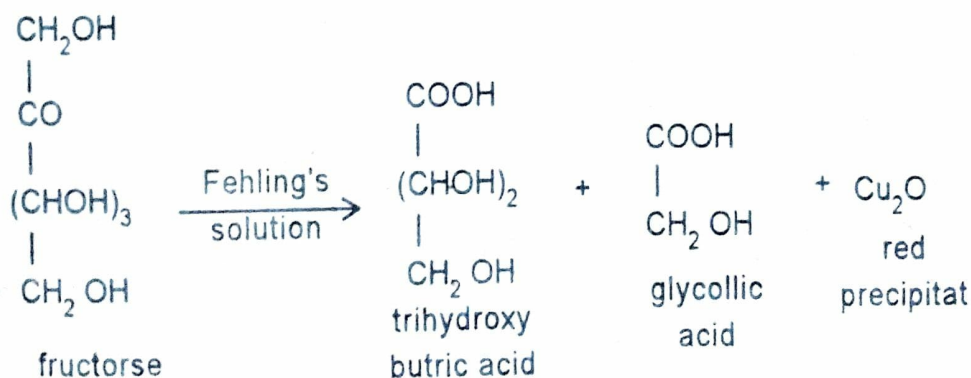
It resists oxidation. On strong oxidation with nitric acid fructose gives a mixture of trihydroxy glutaric acid, tartaric acid and glycollic acid.



5. It reduces Tollens's reagent (ammoniacal silver nitrate solution) giving silver mirror. It is oxidised to glycollic acid

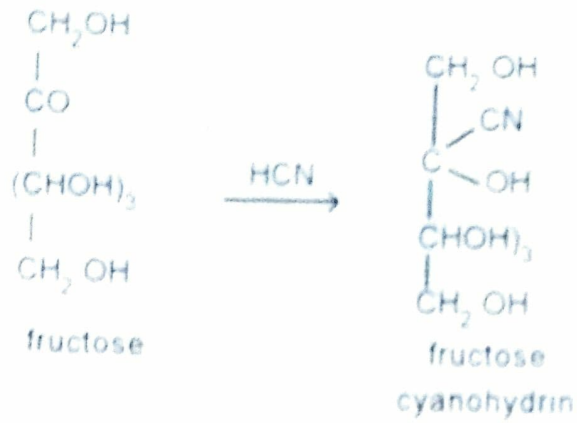


6. It reduces Fehling's solution giving a red precipitate.



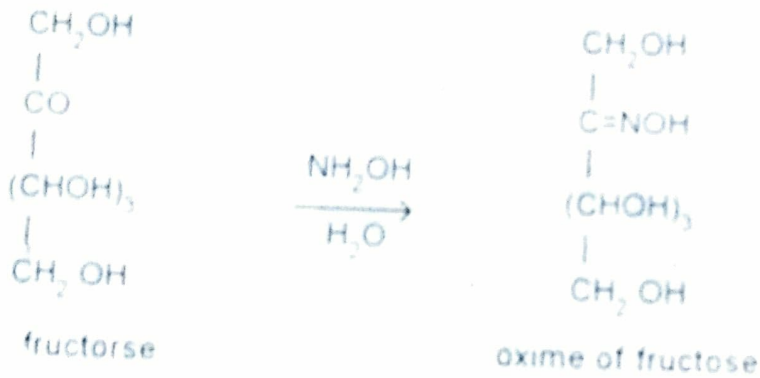
7. Addition reactions :

It adds HCN giving the cyanohydrin of the fructose.



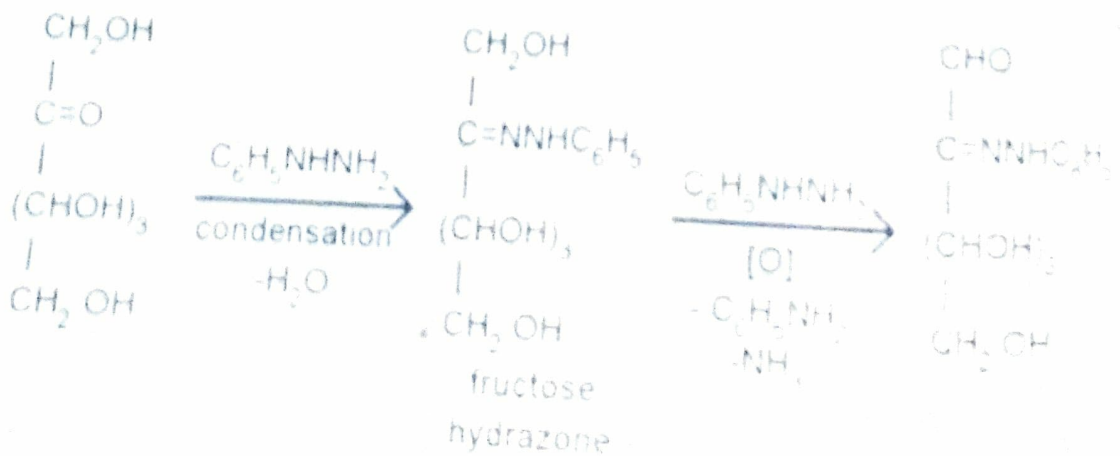
8. Condensation reaction :

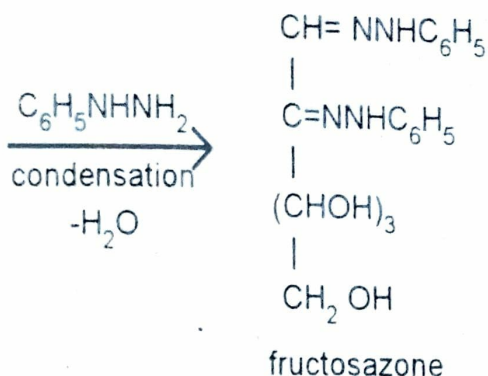
It condenses with hydroxylamine giving the oxime of fructose.



9. Action with phenyl hydrazine :

When treated with phenyl hydrazine, fructose gives an osazone. The osazone obtained in this reaction is the same as the one obtained from glucose.





Mechanism (Fischer):

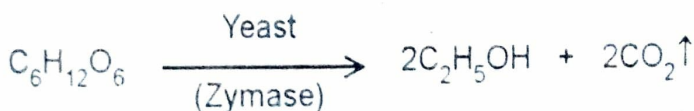
- i. One molecule of phenyl hydrazine condenses with the keto group of fructose and forms the corresponding phenyl hydrazine.
- ii. When fructose is warmed with excess phenyl hydrazine, a second molecule of the phenyl hydrazine oxidises the adjacent primary alcoholic group into an aldehyde group.
- iii. Now a third molecule of phenyl hydrazine condenses with this newly produced aldehyde group giving the final product osazone (same as glucosazone).

Thus both fructose and glucose give the same osazone because

1. In both reactions condensation with phenylhydrazine is followed by oxidation and then another condensation.
2. In both reactions only the first two carbons are involved.
3. The configuration of $\text{C}_3, \text{C}_4, \text{C}_5$ and C_6 of both glucose and fructose are the same.

10. Fermentation :

When a solution of fructose is treated with yeast we get ethanol. The enzyme zymase present in yeast converts fructose into ethanol and carbon dioxide.



Comparison between glucose and fructose

Similarities :

- i) With phenyl hydrazine both give the same osazone.
- ii) Both reduce Tollen's reagent and Fehling's solution.
- iii) On fermentation with yeast both give ethanol.
- iv) Both are acetylated to give pentacetyl derivatives.
- v) Both exhibit mutarotation.

Distinctions :

Reaction	Glucose	Fructose
i) Optical activity	Dextro-rotatory	Leavo-rotatory
ii) With concentrated alkali	Resin is formed	No resin is formed
iii) With lime	Forms glucosate soluble in water	Forms fructosate insoluble in water
iv) Oxidation with bromine (mild oxidising agent)	Oxidised. Gluconic acid is got. Bromine water is decolourised	No reaction

Sucrose

Manufacture from Cane Sugar

The sugarcane is cleaned. It is cut into bits. They are crushed in crushers. The juice is extracted. It is subjected to clarification by sulphitation and by carbonation. Clarification is done to avoid fermentation of sucrose into glucose and fructose and for removing unwanted matter. In sulphitation, the juice is treated with lime and then with sulphur dioxide. In carbonation, the juice is treated with lime and then with carbon dioxide. Precipitates are removed. The clear juice is concentrated in a 'multiple' effect evaporator. The acidity of the solution is carefully maintained at a desired level in order to avoid loss of sucrose by inversion and destruction. The clear syrupy juice thus got is boiled in a vacuum pan. Sugar crystals begin to form. They are centrifuged out. They are dried and bagged.

Properties :

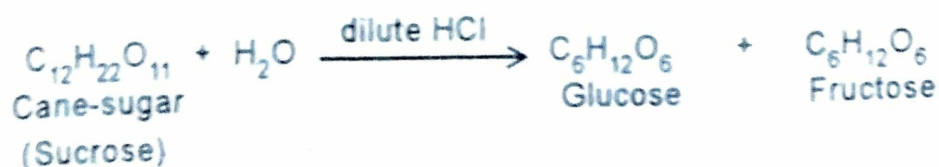
It is a colourless crystalline substance. It is sweet. It is dextrorotatory. It does not show mutarotation

1. Action of heat:

- i. When heated with a small quantity of water, it melts and on cooling gives an amorphous glassy mass called barley sugar.
- ii. When heated to about 200°C it loses water and gives a brown mass called caramel. Caramel is used in confectionery and colouring wine.
- iii. When heated to very high temperatures it carbonises to give sugar charcoal.

2. Hydrolysis (Inversion of cane-sugar):

When warmed with dilute mineral acids it is hydrolysed to glucose and fructose



Cane-sugar has a specific rotation of $+66.5^{\circ}$. On hydrolysis it is converted to glucose and fructose. Glucose has a specific rotation of $+52.5^{\circ}$ and fructose has a specific rotation of -92° . Thus during hydrolysis the specific rotation changes from a +ve value to a -ve value. This change of dextro-rotatory sucrose into levorotatory mixture of glucose and fructose is called inversion of cane-sugar.

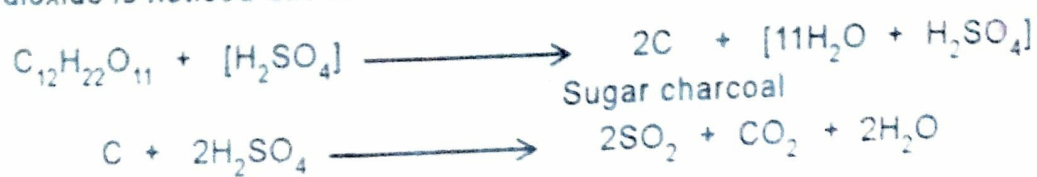
3. Oxidation:

When treated with concentrated nitric acid it is oxidised to oxalic acid.



4. Dehydration:

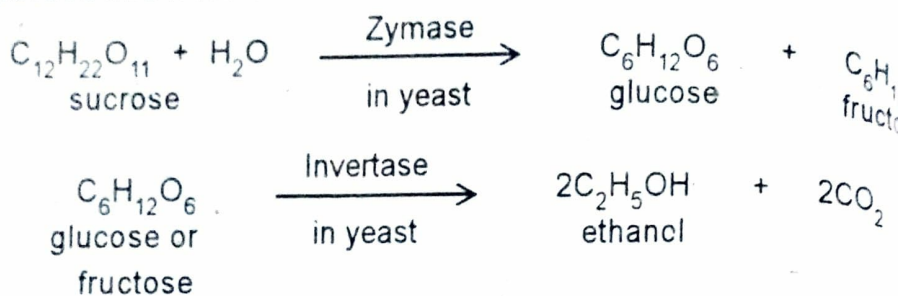
When treated with concentrated sulphuric acid, it is dehydrated giving sugar charcoal. This is called charring of sugar. A smell of sulphur dioxide is noticed due to reduction of sulphuric acid.



5. Fermentation:

When a solution of sucrose is fermented with yeast we get ethanol.

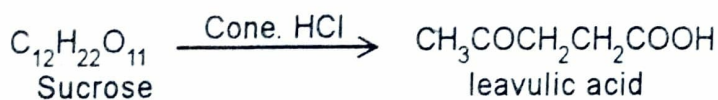
The enzyme invertase is the yeast converts sucrose into a mixture of glucose and fructose. The enzyme zymase present in yeast converts glucose and fructose into ethanol and carbon dioxide.



6. Acetylation:

It reacts with acetic anhydride giving an octa acetyl derivative.

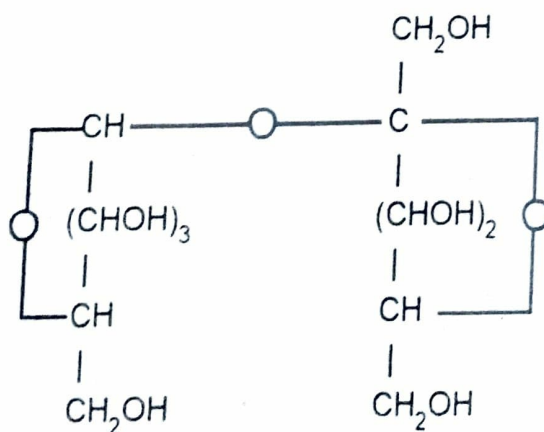
7. Sucrose reacts with cone. HCl to form levulic acid.



8. It does not give resin with sodium hydroxide. It does not give osazone with phenyl hydrazine. It does not exhibit mutarotation.

9. It does not reduce, i.e., give a red precipitate with Fehling's solution. It does not reduce i.e., give a silver mirror with Tollen's reagent. So it is a non reducing sugar.

Ring structure



sucrose

STARCH

What is it? It is a polysaccharide. It consists of a large number of molecules of glucose. It occurs in green plants. Maize, wheat, barley, rice, potato are some of the sources of starch.

Starch is a polysaccharide the molecular formula is $(C_6H_{10}O_5)_n$. It occurs in rice, potatoes, wheat, maing barlly etc. Starch consists of two components namely amylose and amylopectin.

Amylose :

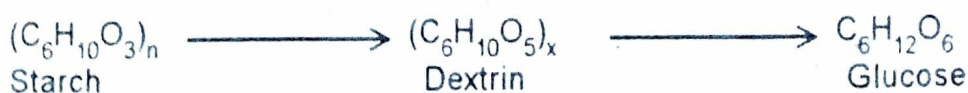
Starch consists of about 10 - 20 % of amylose. It is soluble in water. It gives blue colour with iodine. It consists of several glucose units in the form of linear chains. The glucose units are joined together with each other by α - glucosidic linkage between C_1 of one glucose unit and C_4 of the next glucose unit. The molecular weight of amylose ranges from 10,000 to 5,00,000 a single chain of amylose may contain about 60 to 300 D - glucose units. There is no cross link between the amylose chains.

Amylopectin :

Starch consists of about 80 - 90% amylopectin. Its molecular weight is very high. It is sparingly soluble in water. It consists of several glucose units linked together by α - glucoside linkage in the form of chains. There is cross link between the chains and has branched structure. Each chain consists of about 300 to 600 D - glucose units and the molecular weight ranges from 50,000 to 1,000,000.

Properties :

1. It is a white amorphous powder.
2. On boiling with water the starch granules swell and burst. We get a paste like colloid.
3. **Action of heat:**
When heated to 470-530K starch is converted into dextrin. Charring occurs at still higher temperatures.
4. **Hydrolysis:**
When it is boiled with dilute mineral acids, it is converted to dextrine and finally to glucose ($n > x$).



5. Action of iodine:

It gives a blue colour with iodine. The colour disappears on heating and reappears on cooling. This is a sensitive test for starch.

Uses :

- It is one of the most valuable constituents of food as rice, bread, cornflour, potato etc.
- It is used in the manufacture of glucose, alcohol, dextrin and adhesives.
- It is used in laundry as a stiffening agent.
- It is used in calico printing.
- In textile industry it is used as sizing and stiffening agent.
- In paper industry is used for coating and sizing paper so as to improve the quality of paper.
- In volumetric analysis it is used as an indicator in iodimetry and iodometry.

Cellulose**Occurrence:**

It occurs in the cell walls of plants and in certain animal tissues. It is the main structural material of trees and plants. Its main source is cotton and wood. Other sources are straw, corncobs, and similar agricultural wastes.

Properties :

It is an amorphous white solid insoluble in water. It is soluble in Schwitzers' reagent (ammoniacal copper hydroxide solution). When acids, alcohols or salts are added to the solution it is precipitated. This property is made use of in the manufacture of rayon (artificial silk).

Cellulose on treatment with concentrated sodium hydroxide, becomes a gelatinous translucent mass. Cotton goods treated in this way get a silky lustre. Such cotton is known as mercerized cotton. The process is called mercerizing.

Reactions:**1. Action of concentrated sulphuric acid:**

Cellulose dissolves in cold concentrated sulphuric acid. On dilution it precipitates as amyloid. For example, when an ordinary paper is dipped in concentrated sulphuric acid for a few seconds and then washed with water, amyloid is precipitated on the surface of the paper and the surface of the paper becomes rough. Such a paper is called parchment paper.

2. Hydrolysis:

When it is boiled with dilute acids it is hydrolysed to glucose.

3. Acetylation:

On treatment with acetic anhydride it forms triacetate.

4. Nitration:

On treatment with acetic anhydride it forms triacetate.

5. Formation of esters:

On treatment with acids like acetic acid, nitric acid etc., it gives esters. These esters are commercially important.

Uses :

- Cellulose forms the raw material for the textiles and paper industries.
- Cellulose nitrate is called gun cotton. Gun cotton is used in the manufacture of explosives like blasting gelatin and cordite.
- Lower cellulose nitrates are called pyroxylin. Pyroxylin is used in the manufacture of collodion which is used in photography. It is also used to manufacture celluloid which is used for making toys, photographic films etc.
- Cellulose is used for the preparation of artificial silk like viscose rayon. This is used in weaving cloth.
- Cellophane is made from viscose and this is used as a picture film.
- Cellulose nitrate when dissolved in proper solvents produces lacquer.

Comparison of starch and cellulose**Similarities:**

- Both are white amorphous powders insoluble in water.
- Both on hydrolysis give glucose.
- Their nitro derivatives are explosives.

Reaction	Starch	Cellulose
1. with I_2	Gives a blue colour	No colour
2. With Schwitzer's Reagent (ammoniacal copper hydroxide)	No reaction	Soluble
3. with conc. H_2SO_4	Chars	Dissolves in conc. H_2SO_4 and gives a red colour

3. Acetylation:

On treatment with acetic anhydride it forms triacetate

4. Nitration:

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5. Formation of esters:

On treatment with acids like acetic acid, nitric acid etc, it gives esters. These esters are commercially important.

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2. With Schewitzer's Reagent (ammoniacal copper hydroxide)	No reaction	Soluble
3. with conc H_2SO_4	Chars	Dissolves On dilution reprecipitated

Cellulose as a cattle Food :

Grazing animals like cattle, goats have in their digestive system, an enzyme called **cellulase**, which digests cellulose by hydrolysing it into glucose. So they can take grass, straw etc., directly as their food. But man and similar mammals do not have this cellulase in their digestive system. So they can not take directly grass and straw as their food. They have only the enzyme amylase, diastase and maltase in their digestive system. Diastase hydrolyses starch into maltose, which is then hydrolyse into glucose with the help of maltase.

University Questions :

1. What are carbohydrates? - Nov 81, Ap 93
2. How are carbohydrates classified? Give example for each - Several times
3. What is (a) disaccharide? Give one example - Sep 85, 86
4. What are polysaccharides? Give two examples. - Ap 86, 88
5. Classify the following carbohydrates. Glucose, starch cane sugar (sucrose), cellulose. - Nov 93
6. How is glucose prepared? / Explain the method of preparation of glucose. - Mar, Oct 88
7. Explain the chemical properties of glucose. - Oct 88
8. How does glucose react with acetic anhydride? - Several times
9. How does glucose react with sodium amalgam / What happens when glucose is reduced? / How will you prepare sorbitol from glucose? - Several times
10. What happens when glucose is oxidised by mild oxidising agents? / How does glucose react with bromine water? - Several times
11. Explain the reaction of glucose / How does glucose react with (excess of) phenyl hydrazine / How will you prepare osazone from glucose? - Several times
12. Explain fermentation / How will you prepare ethyl alcohol from glucose? - Sep, Nov 90
13. What is / Explain (with example) / Write notes on mutarotation.
14. Give Two tests for aldehydes.