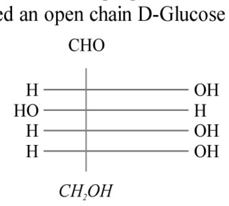
The alcoholic group bonded to?

BIOMOLECULES

Continued from 26th February

- **Epimers are a pair of diasteriomers that differ only in the configuration about a single carbon atom.**
  Ex : Glucose and Mannose are C_2 epimers
  D- Iodose and D- Talose → c-3 Epimers
  D-Allose and D-gulose → c-4 Epimers
  D- Altrose andD-Iode → c-4 epimers
- Based on the above properties Glucose has been assigned an open chain D-Glucose by Baeyer.



D-GLUCOSE

Glucose is (2R, 3S, 4R, 5R) – 2, 3, 4, 5, 6 – pentahydroxyhexanal.

Cyclic structure of Glucose: The open chain structure of Glucose proposed by Baeyer explained most of its properties. But it could not explain the following.

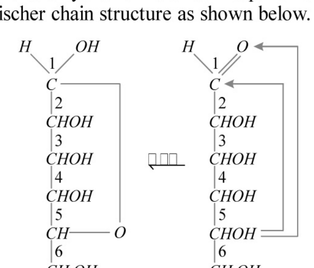
- Glucose does not give schiff's test and does not react with $NaHSO_3$ and NH_3, inspite of presence of -CHO group
- Pentacetate of glucose does not react with $-NH_2OH$ group indicating absence of - CHO group.
  The aqueous solution of glucose shows mutarotation.

Mutarotation of glucose: When glucose was crystallised from a concentrated solution at 30^0 C, it gives α - form with melting point $146^0 c$ and $[\alpha]_D = +111^0$.

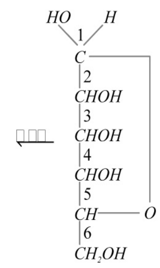
- When glucose crystallised from a hot saturated aqueous solution at a temperature greater than $98^0 C$, gives β-form with a melting point $150^0 C$ and $[\alpha]_D = +19.2^0$.
- These two forms of glucose differ in the stereochemistry at C-1. These two α and β forms, when separately dissolved in water and allowed to stand, their specific rotation gradually change and reach to a specific constant value 52.5^0.
- **This spontaneous change in specific rotations of an optically active compound is called mutarotation..**

α - D(+)Glucose ⇌ eq.mix ⇌ β - D(+)glucose
$[\alpha]_D = +111^0$ $+52.5^0$ $+19.2^0$

- Equilibrium mixture consists of 36% α-D(+)Glucose and 64% β-D(+)Glucose.
- Above anomalies can be explained by cyclic structure of glucose. Glucose forms a stable cyclic hemiacetal.
- Generally alcoholic groups undergo rapid and reversible addition to aldehyde group to form hemiacetals.
- The alcoholic group bonded to $C-5$ of glucose reacts intramolecularly with $-CHO$ forming a 6-membered hemiacetal ring.
- The asymmetric carbon now at $C-1$ gives two optical isomers. They are not mirror images of each other and hence they are **diastereomers**. They differ in the configuration only at $C-1$ and are called **anomers**.
- The two cyclic forms exist in equilibrium with Fischer chain structure as shown below.

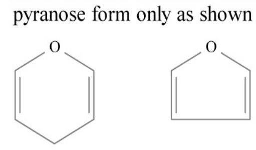


α-D-(+)-glucose

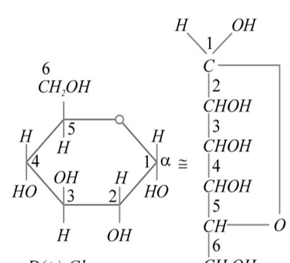


β-D-(+)-glucose

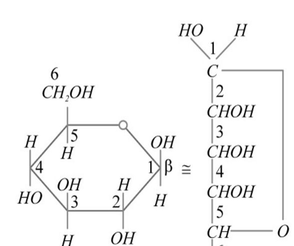
- The α and β forms are confirmed by the reaction of glucose, with methanol in the presence of dry HCl to give methyl α - *D-Glucoside* and methyl β - *D- Glucoside.*
- Glucose forms a six membered ring pyranose containing 5 carbon atoms and one oxygen atom like pyran. The five membered ring formed like furan is called furanose. Glucose is present in pyranose form only as shown in figure.



- The Haworth horizontal structure of glucopyranose is identical to the Fischer vertical projection structure.
- The groups present on the right side in Fischer formula are written below the plane of the ring and those on the left side are written above the plane.
- The cyclic structure of glucose explains the presence of α – and β – forms, mutarotation.
  It explains the inability of glucose to form aldehyde ammonia and bisulphite compound. In the presence of other carbonyl reagents, the ring is opened and free aldehyde group is produced,



α-D(+)-Glucopyranose



α-D(+)- Glucopyranose

Fructose ($C_6H_{12}O_6$)

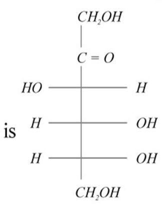
- Fructose is a ketohexose. It is also called **Laevulose and fruit sugar**.
- It is laevorotatory compound and belongs to D-series. D-(-) Fructose.
- It is found in ripe fruits and honey.

Preparation

- $C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$
  Sucrose   Glucose   Fructose
- Like glucose, fructose also shows mutarotation.
- It is reducing sugar.

Structure of Fructose: Fructose contains five hydroxyl groups, out of which two are primary and three are secondary.

- Fructose contains a carbonyl group and it was found to be ketonic from its oxidation products with a strong oxidising agent.
- Fructose was found to contain ketonic functional group at second carbon atom and all the six carbon atoms are in unbranched chain as in the case of glucose.
- Since fructose and glucose form identical osazones when heated with excess of phenyl hydrazine, it was found that both glucose and fructose have the same configuration at $C-3$; $C-4$ and $C-5$.
  Though fructose does not contain an aldehydic group, it behaves as reducing sugar due to Lobry de Bruyn van Ekenstein rearrangement.
- Its structure is



- Fructose exists two cyclic forms which are obtained by the addition of -OH at C_5 to the carbonyl group .It is a 5-membered ring and named as furanose ring
  To explain all of fructose properties it is suggested with two cyclic structres i.e. $\alpha-D-(-)$ – fructofuranose and $\beta-D-(-)$ – fructofuranose.
  α – and β – forms of fructose are anomers at $C-2$.
  Anomers: Anomers are steroisomers of a cyclic monsaccharide that differ in the position of the OH group at the hemiacetal carbon
  Anomers can also be defined as " two sugars that differ in configuration only at the carbon that was the carbonyl carbon in the chain form"

Ex- 1) $\alpha-D$ glucose and $\beta-D$ glucose are anomers
2) $\alpha-D$ fructose and $\beta-D$ -fructose are anomers

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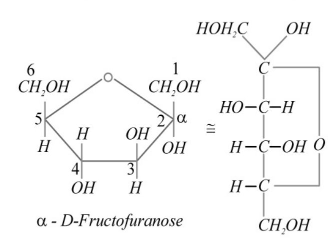
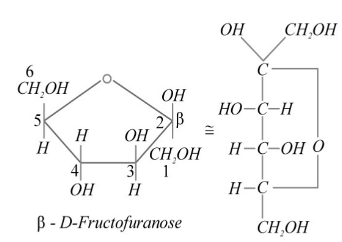
Cyclic structure of Two anomers of fructose(Haworth structures)



α - D-Fructofuranose



β - D-Fructofuranose

Oligo Saccharides: The disaccharides are composed of 2 molecules of monosaccharides.

- These on hydrolysis with dil acids(or) enzymes yield two molecules of either the same (or) different monosaccharides.

$C_{12}H_{22}O_{11} \xrightarrow{H_3O^+} C_6H_{12}O_6 + C_6H_{12}O_6$
Sucrose   Glucose   Fructose

$C_{12}H_{22}O_{11} \xrightarrow{H_3O^+} C_6H_{12}O_6 + C_6H_{12}O_6$
Lactose   Glucose   Galactose

$C_{12}H_{22}O_{11} \xrightarrow{H_3O^+} C_6H_{12}O_6 + C_6H_{12}O_6$
Maltose   Glucose   Glucose

- In disaccharides, the two mono- saccharides are joined together by glycosidic linkage (-O-)
- A glycoside bond is formed when hydroxy group of the hemiacetal carbon of one monosaccharide condenses with a hydroxy group of another monosachharide, to give -O-bond, by loss of H_2O.

Sucrose (Cane Sugar) $C_{12}H_{22}O_{11}$

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For Feedback...
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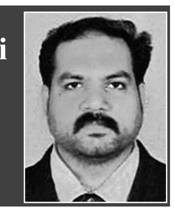

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- It is the most common disaccharide present in plants.
- It is obtained mainly from sugarcane (or) beetroot.
- Naturally available sucrose is a dextrorotatory substance $[\alpha]_D = +66.5^0$.
- It is non reducing sugar.
- It does not show mutarotation.
- It is a colorless and odourless crystaline substance, which is highly soluble in water.
- Even though sucrose is a dextro rotatory, on hydrolysis with dil.acids(or)enzyme invertase, it gives equimolar mixture of dextro rotatory glucose and laevo rotatory fructose.

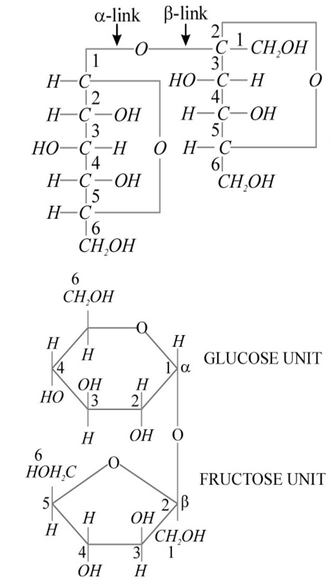
$\text{D-Sucrose} \xrightarrow{H_2O} \text{D-Glucose} + \text{D-Fructose}$
$[\alpha]_D = +66.5^0$ $[\alpha]_D = +52.5^0$ $[\alpha]_D = -92.4^0$

The net specific rotation of equimolar mixture of D-Glucose and D-frctose is

$\frac{+52.5 - 92.4}{2} = -20^0$.

- As the laevo rotation of fructose (-92.4^0) is more than dextrorotation of glucose $(+52.5^0)$, the mixture is laevorotatory.
- In the hydrolysis of sucrose there is a change in the sign of rotation from 'd' to 'l'. This change is known as **inversion** and the mixture is called **invert sugar**.
  1. $\alpha-D$ Glucose and $\beta-D$ fructose units are linked through α, β - glycosidic linkage between C-1 of $\alpha-D$- Glucose and C - 2 of $\beta-D$- fructose.
  2. Glucose unit is in pyranose and fructose unit is in furanose form.
- The reducing groups of glucose and fructose are involved in glycosidic linkage So sucrose is a **non- reducing sugar**

Cyclic structure of sucrose



SUCROSE