Which are called reducing sugars?

విజేత

For Feedback...
vijetha.nt@gmail.com

Dr. Krupakar Pendli
Centre Head
Urbane junior colleges
7893774888

JEE MAIN Special

SYNOPSIS

Carbohydrates: Initially carbohydrates were considered as hydrates of carbon as most of them have general formulae $C_n(H_2O)_m$

Eg: **Glucose :** $C_6H_{12}O_6$ or $C_6(H_2O)_6$,

Sucrose : $C_{12}H_{22}O_{11}$ or $C_{12}(H_2O)_{11}$.

But all the compounds with formula $C_n(H_2O)_m$ are not necessarily carbohydrates.

eg: Formaldehyde : $HCHO$ or $C(H_2O)$; Acetic acid : CH_3COOH or $C_2(H_2O)_2$.

A few carbohydrates may not have the formula $C_n(H_2O)_m$. eg : Rhamnose, $C_6H_{12}O_5$.

- They can be better described as optically active polyhydroxy aldehydes (or) ketones (or) the compounds which yield them on hydrolysis.
- Most of them are similar to sugar in taste, and hence they are also known as Saccharides. (Latin word for sugar is saccharum)

Classification of carbohydrates: The carbohydrates are divided into 3 major classes based on hydrolysis.

Monosaccharides(Simple Sugars): These cannot be further hydrolysed to simpler molecules.

Ex: Erythrose, Threose, Glucose, fructose, ribose etc..

- There are about 20 monosaccharides occur in nature.
- Their general formula is $(CH_2O)_n$ where $n = 3-7$.
- Depending upon the total number of carbon atoms in monosacharides and on nature of functional groups present (aldehyde or ketone), the terms for their classification are as follows:

NO.OF CARBON ATOMS	GENERAL TERM	ALDOSE	KETOSE
3	Triose	Aldotriose	Keto triose
4	Tetrose	Aldotetrose	Keto tetrose
5	Pentose	Aldopentose	Keto pentose
6	Hexose	Aldohexose	Keto hexose
7	Heptose	Aldoheptose	Keto heptose
8	Octose	Aldooctose	Keto octose

Oligosaccharides: These undergo hydrolysis and yield 2 to 10 monosaccharide units.

Disaccharide: A disaccharide on hydrolysis gives 2 monosaccharide units of same or different kind.

Ex:- Sucrose, Maltose and Lactose

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

- A trisaccharide on hydrolysis gives 3 monosaccharide units.
  Example: Raffinose on hydrolysis gives Glucose, Fructose and Galactose.

Polysaccharides: These undergo hydrolysis and give more than 10 monosaccharide units.

Example: Starch, cellulose, glycogen, dextrin, Gums. General fomula $(C_6H_{10}O_5)_n$

$$(C_6H_{10}O_5)_n + nH_2O \xrightarrow[393k]{H^+/2\text{-}3\ atm} n\,C_6H_{12}O_6$$

Sugars and Non Sugars: Both monosaccharides and oligosaccharide are crystalline solids, soluble in water and sweet in taste. These are colletively known as **sugars**.

- Polysaccharides are amorphous, sparingly soluble in water and taste less and are known as **non-sugars**.
- The Carbohydrates are also classified as either reducing or non-reducing sugars.

Reducing and Non Reducing Sugars: The saccharides, that reduce Fehling's reagent, Tollen's reagent, are called as **reducing sugars**.

- They form silver mirror with Tollens' reagent and give red precipitate with Fehling's solution.
- All monosaccharides, whether aldose(or) ketose, are reducing sugars.
- **All reducing sugars exhibit mutarotation.**
  ex:- Glucose , fructose, triose, tetroses, pentoses & Hexoses
  All Disaccharides are Redcing sugars except sucrose
  ex :- maltose, lactose
- The Saccharides, which do not reduce Fehling's reagent and Tollen's reagent, are called **non-reducing sugars**.
- All polysaccharides are non redcing sugars
  ex:- starch ,celluose , glycogen ,dextrin

Class	Molecular	Structural formula	n No.of Chiral Carbons	2^n No.of Optional Isomers	Examples Aldose
Aldotrioses	$C_3H_6O_3$	$CH_2OH.CHOH.CHO$	1	2	Glyceraldehyde
Aldotetroses	$C_4H_8O_4$	$CH_2OH.(CHOH)_2.CHO$	2	4	Erythose, threose
Aldopentoses	$C_5H_{10}O_5$	$CH_2OH.(CHOH)_3.CHO$	3	8	Arabinose, ribose, xylose, lyxose
Aldohexoses	$C_6H_{12}O_6$	$CH_2OH.(CHOH)_4.CHO$	4	16	Glucose, mannose, galactose, glucose, talose, idose, allose, altrose
Ketoses					
Ketotrioses	$C_3H_6O_3$	$CH_2OH.CO.CH_2OH$	-	-	Dihydroxyacetone
Ketotetroses	$C_4H_8O_4$	$CH_2OH.CO.CHOH.CH_2OH$	1	2	Erytrulose
Ketopentoses	$C_5H_{10}O_5$	$CH_2OH.CO.(CHOH)_2.CH_2OH$	2	4	Ribulose, xylulose
Ketohexoses	$C_6H_{12}O_6$	$CH_2OH.CO.(CHOH)_3.CH_2OH$	3	8	Fractiose, sorbose, tagatose etc.

- Non reducing sugars do not exhibit mutarotation and does not form osazone.
- In disaccharides depending upon the position of linkages between monosaccharide units, the resulting disaccharide may be reducing (or) non reducing.
  The stereo chemistry of all sugars is determined with respect to D- or L- Glyceraldehyde.
  Sugars can be classified into D- and L- forms basing on their configuration.
- The enantiomer whcih rotates the monochromatic light to right is written as (+) or 'd' and the other which rotates the monochromatic light to the left is written as (–) or '*l*'
- The direction of the rotation of monochromatic light can be denoted by (+) or (–), but cannot indicate the arrangement of –OH and –H around chiral carbon atom.
- Rosanoff proposed a system to designate the stereo chemistry of carbohydrates by considering the simplest sugar, glyceraldehyde as standard.
- The sugars having the same configuration as D–glyceraldehyde at the least prioarity chiral carbon adjacent to primary alcoholic group $(-CH_2OH)$ are called D–sugars and having the configuration as L–glyceraldehyde are called L–sugars.
- Practically D–sugars may be D–(+) or D–(–) and L–sugars may be L–(+) L–(–). The symbol (+) or 'd' is used for dextro and (–) or '*l*' is used for laevo rotatory compound.
- It is observed that natural glucose, ribose and fructorse are D–form.

Monosaccharides

Glucose: Glucose is an aldo hexose and is alsoknown as dextrose because it occurs in nature as the optically active dextro rotatory isomer.

- It is also called grape sugar as it is found in fruits especially grapes contains 20% of Glucose.
- The human blood normally contains 65 to 110mg.of glucose per 100ml.
- In combined form, it occurs in cane sugar and also in polysaccharides such as starch and cellulose.

Preparation: Glucose is prepared in the laboratory by acid hydrolysis of cane sugar in alcoholic solution.

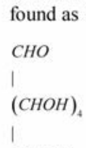
$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

- It is obtained in large scale by the hydrolysis of starch with dil. H_2SO_4 (or) HCl at 2-3 atm pressure & 393 k temp.

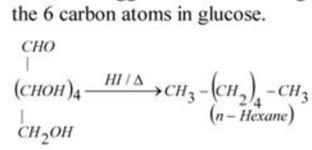
$$(C_6H_{10}O_5)_n + nH_2O \xrightarrow{H^+} nC_6H_{12}O_6$$

Properties and Sturcutral elucidation

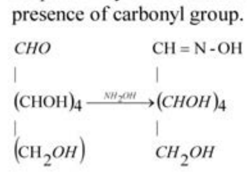
- Molecular formula of glucose is experimentally found as $C_6H_{12}O_6$

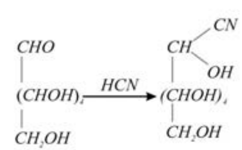


- Glucose on prolonged heating with HI gives n-hexane. It suggests the linear arrangement of all the 6 carbon atoms in glucose.

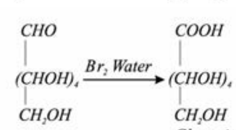


- Glucose reacts with NH_2OH and one molecule of HCN and forms monoxime and cyanohydrin respectively. These reactions suggest the presence of carbonyl group.

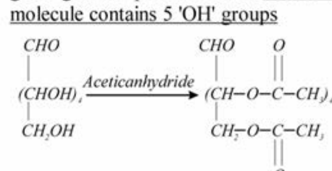




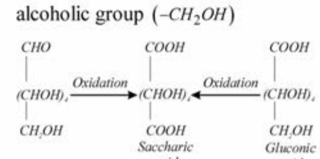
- On reaction with a mild oxidising agent like bromine water, glucose converts to gluconic acid. This indicates that the carbonyl group is present as an aldehydic group



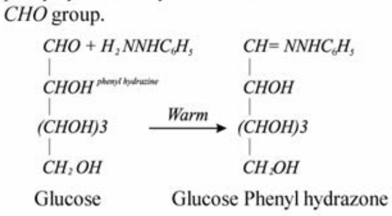
- Glucose reduces Tollen's reagent to metallic silver and also reduces Fehling's solution to reddish brown cuprous oxide and itself gets oxidised to gluconic acid. These reactions suggest that the carbonyl group is an aldehydic group.
- Acylation of Glucose with acetic anhydride gives glucose penta acetate. Hence Glucose molecule contains 5 'OH' groups



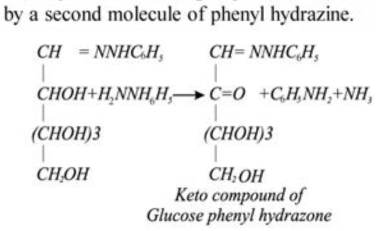
- On oxidation with HNO_3 both glucose and gluconicacid form saccharic acid, a dicarboxylic acid. It suggests the presence of primary alcoholic group $(-CH_2OH)$



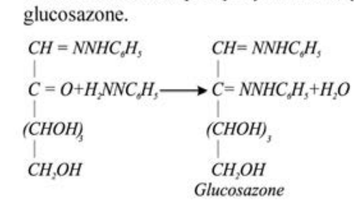
- D-Glucose on reaction with excess of phenyl hydrazine (3 moles of phenyl hydrazine per mole of glucose), forms a dihydrazone known as **osazone**.
  Fischer's mechanism : When glucose warmed with excess of phenyl hydrazine, first forms phenylhydrazone by condensation with – *CHO* group.



The adjacent – *CHOH* group is then oxidised by a second molecule of phenyl hydrazine.



The resulting carbonyl compounds reacts with a third molecule of phenyl hydrazine to yield glucosazone.



Note: All monosaccharides which differ in configuration only at C_1 and C_2 give the same osazone,
e.g., D-glucose, D-fructose, D-manose all form the same osazone

- With conc. NaOH solution, glucose first turns yellow, then brown and finally resinifies.
- With dil. NaOH solution, glucose under goes reversible isomerisation and gives a mixture of D-mannose and D-fructose. This reaction is known as **Lobry de Bruyn-Van Ekenstein rearrangement.**
  D-glucose ⇌ D-Manose ⇌ D-Fructose
  It is because of this isomerisation that D–fructose reduces Tollens' reagent and Fehling's solution, though fructose does not contain any aldehydic group.
  Same results were obtained if manose (or) fructose are treated with alkali. It is concluded that fructose with ketone group also reduces tollen's reagent due to this isomerisation
- **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