BIOMOLECULES

The hydrates of carbon was originally defined as carbohydrates, with general formula of $Cn(H_2O)y$. But this defination has found several limitations today.

(i) Carbon do not forms hydrates

(ii) There are number of organic molecules having $Cn(H_2O)y$ formula but are not carbohydrates.

e.g. (a) Formaldehyde (HCHO) : CH_2O

(b) Acetic acid CH_3COOH : $C_2H_4O_2$ etc.

(iii) A number of carbohydrates do not have $Cn(H_2O)$ formula.

e.g. (i) Rhamnose - $C_6H_{12}O_5$

(ii) Deoxyribose - $C_5H_{10}O_4$

MODERN DEFINITION :

Polyhydroxy aldehyde or Ketone or substances which gives these on hydrolysis is called carbohydrates. They have at least one chiral carbon is general

CLASSIFICATION :

TYPE : 1

Carbohydrates

(1) Monosaccharides	(2) Oligosaccharides	(3) Polysaccharides
Simplest carbohydrates which can't be hydrolysed into simpler molecules Gen. formula = $(CH_2O)_n$ n = 3 to 7.	* oligo = few Carbohydrates which on hydrolysis gives 2 to 10 molecules of carbohydrates	Carbohydrates which on hydrolysis gives number of carbohydrates. e.g. $(C_6H_{10}O_5)n$ n = 100 to 3000

TYPE : 2

Carbohydrates

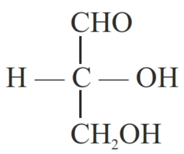
(i) Sugar	(ii) Non-Sugar
All the Mono and Oligosaccharides have sweet taste and these are collectively called sugars. They are crystalline in nature.	Polysaccharides are tasteless and are called non-sugar. They are amorphous in nature.

TYPE : 3

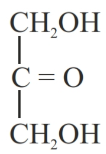
Carbohydrates

(i) Reducing	(ii) Non-Reducing
All those carbohydrates which has aldehydic or ketonic group in their hemiacetal and hemiketal structures have the ability to reduce Tollen's Reagent or Fehling solution. They are called Reducing sugar. * All Monosaccharides whether aldose or ketose are reducing sugars.	The carbohydrates which can not reduce Tollen's reagent or Fehling solutions are called as Non-reducing. * All Polysaccharides are non reducing. e.g. Starch, Cellulose, dextrins, Glycogens etc.

Simplest Triose : The simplest monosaccharides are triose.



Aldotriose
Glyceraldehyde



Aldoketose
Dihydroxy acetone

GLUCOSE

* They are also called as Grape sugar or Dextrose. It is present in sweet fruits.
  Molecular formula — $C_6H_{12}O_6$
  It is aldohexose sugar

PREPARATION OF GLUCOSE :

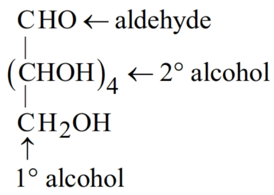
(i) From Sucrose (Cane - Sugar) : By acidic hydrolysis.

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

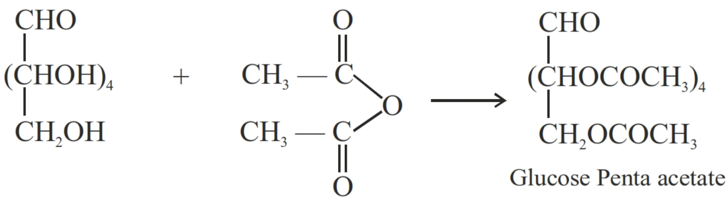
(ii) From Starch : Commercial method.

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} \xrightarrow[\text{393K.Boil}]{nH_3O^+} n\ \underset{\text{Glucose}}{C_6H_{12}O_6}$$

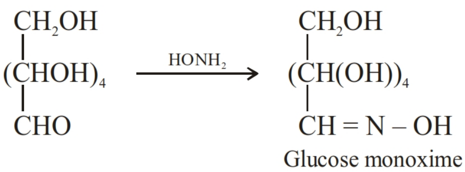
CHEMICAL REACTION OF GLUCOSE :



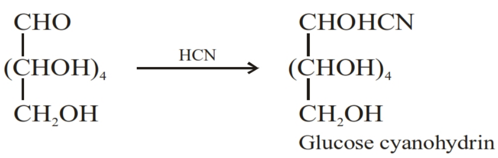
1. Reaction with Acetic anhydride : Acetylation



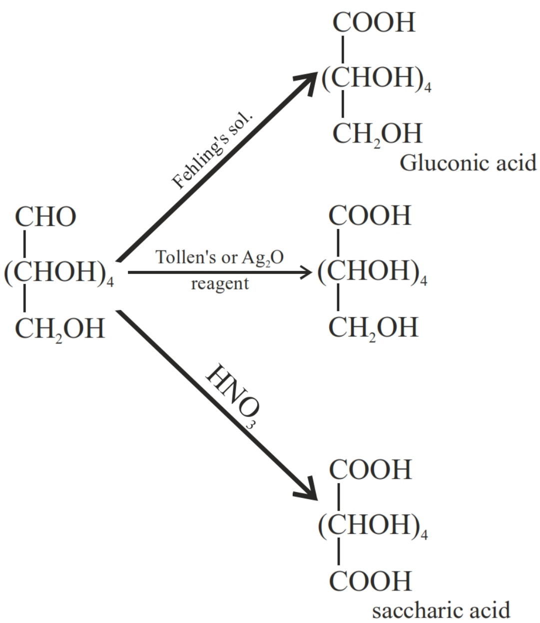
2. Reaction with hydrosylamines :



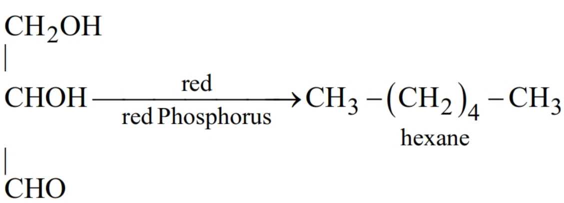
3. Reaction with HCN :



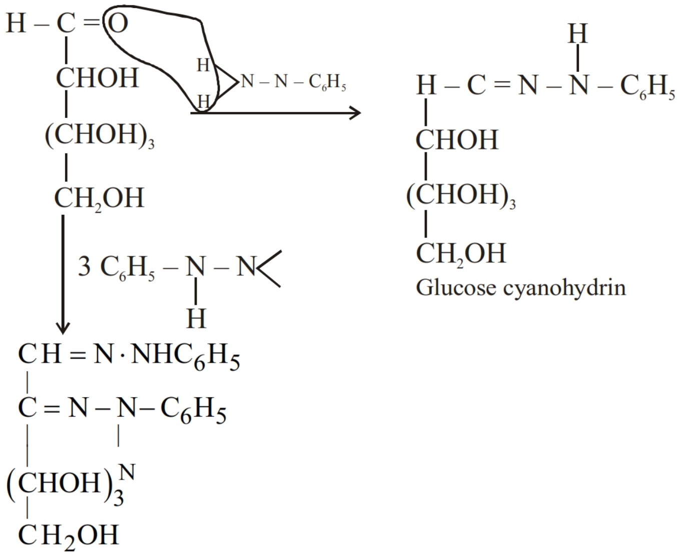
4. Oxidation :



5.Reduction :



6. Reaction with Phenyl hydrazine :



Glucose dihydrazone (Osazone)

7. Action of Alkali : Lobry de Bruyn-van Ekenstein reaction

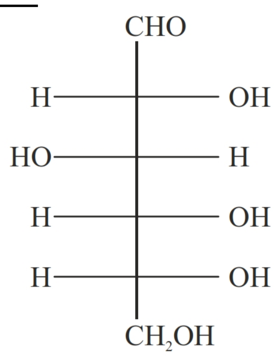
D — Glucose $\rightleftharpoons$ D — Mannose $\rightleftharpoons$ D — Fructose

On adding concentrated solution of NaOH this occurs.

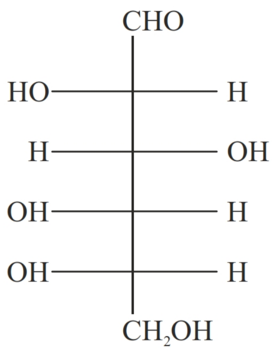
$\Rightarrow$ It is probably on account of this isomerisation, that fructose reduces Fehling's solution and Tollen's Reagent in alkaline medium.

Structure of Glucose

Open-chain strs :



D-Glucose



L-Glucose

Limitationof open-chain strs :

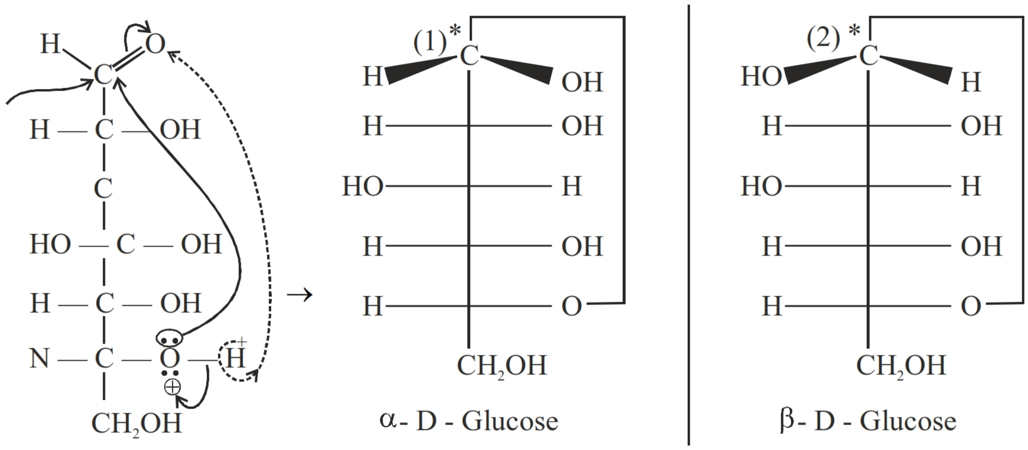
(i) Glucose doesn't undergo characteristic reaction of aldehydes such as
   (a) Glucose does not reacts with $NaHSO_3$ (sodium bisulphate)
   (b) Glucose does not responds to schiff's test.

(ii) Glucose doesn't reacts with G.R.

Cyclic structures of Glucose :

$\alpha - D$ and $\beta - D$ Glucose : (Hemiacetal structures)

- In α-D-Glucose OH group is towards right while in β-D-Glucose the OH group is towards left at C_1.



Anomers :

"The stereo isomers which differs in configuration at "C_1" is called anomers".

The "Cl" is also called as anomeric carbon or Glycosidic carbon.

Note : 'α' and 'β - D' Glucose are not enantiomers, since the configuration at other carbon remains same.

Mutarotation :

When Glucose is crystallized from a concentrated solution at 300 K, α form of D-Glucose is isolated. But, from a hot saturated solution (aqueous) at a temperature in excess of 100°C, the β-Glucose is obtained.

Term	α	β
M.pt :	146°C	150°C
Sp. rotation :	+111°	+19.2°

If eithe of the two forms is dissolved in water and allowed to stand, the specific rotation of the solution slowly changes and reaches a constant value of +52.5°.

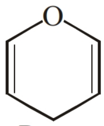
"The spontaneous change in specific rotation of an optically active compound is called muta rotation".

$$\underset{\text{glu cos e}}{\alpha - D - (+)} \rightleftharpoons \underset{\text{Mixture}}{\text{Equilibrium}} \rightleftharpoons \underset{\text{Glucose}}{B - D + ve}$$

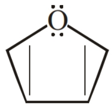
Haworth structures of Glucose : The molecules of glucose and fructose can exist in any of the two cyclic structures.

(a) Pyranose structure
Six membered ring
Derived from pyran

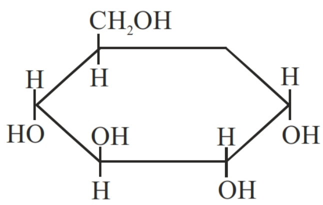
(b) Furanose structure
5 Membered Ring
Derived from furan



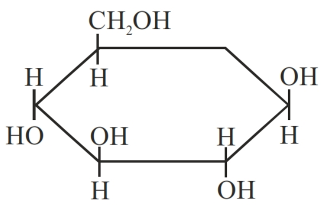
Pyran



Furan



α –D Glucose



β –D Glucose

OLIGOSACCHARIDES

These are carbohydrates which gives 2 to 10 molecules of monosaccharides.

* In some standard text (particularly in Biology) n = 2 to 7 has been frequentaly used.

Example

(1) Disaccharides : Sucrose, Maltose, Lactose

(2) Trisaccharides : Raffinose

(3) Tetrasaccharides : Stachyrose

Disaccharides :

Gives two molecules of same or different monosaccharides.

General formula :

Formula : $C_{12}H_{22}O_{11}$

Examples and its monomers :

(1) Sucrose $\xrightarrow[H_3O^+]{\text{Invertase}}$ Glucose + Fructose

(2) Maltose $\xrightarrow[\text{Maltase}]{H_3O^+}$ Glucose + Glucose

(3) Lactose $\xrightarrow[\text{Lactase}]{H_3O^+}$ Glucose + Galactose

- The disaccharides can be reducing or non reducing. If carbonyl group is free, sugar is reducing.

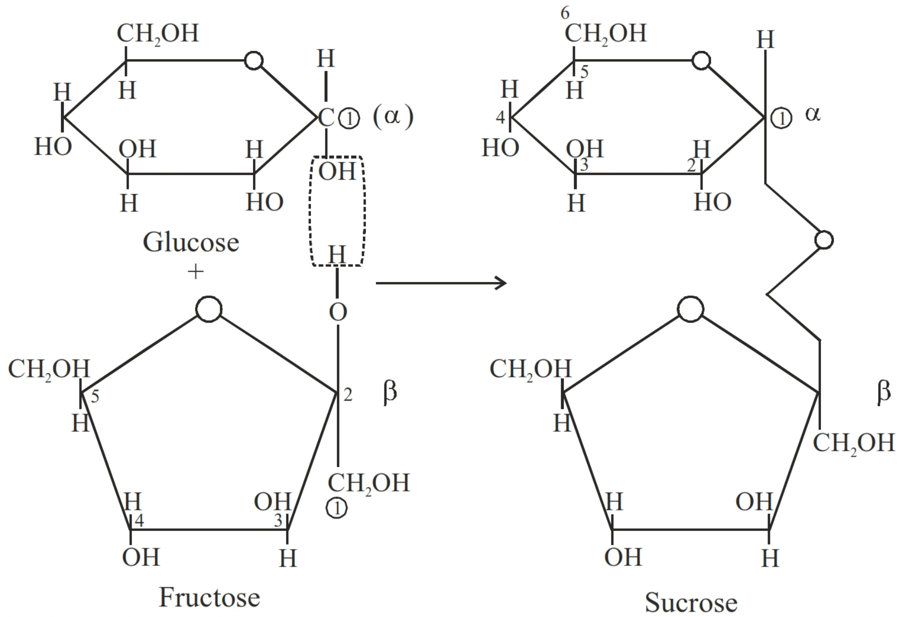
Sucrose or cane sugar or Table Sugar :

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

Specific rotation + 66.5° +52.5° –92.4°

Since the laevorotation of fructose is more than the dextro rotation of glucose, the resulting solution will be laevo rotatory. This overall process is called inversion of sugar.

Haworth Structure of Sucrose :



- Determination of ring size by spectral methods has revealed that, in sucrose glucose is in its pyranose form and fructose it is furanose form.
- There is thus, α,β glucosidic bond between glucose and fructose as monomers.

Polysaccharides :

Polysaccharides are formed when large number of monosaccharide joins together with simultaneous elimination of water molecules.

Some common polysaccharides are :

(i) Cellulose (ii) Starch (iii) Glycogen (iv) Dextrin

Starch :

(i) It is also called as Amylum.

General formula - $(C_6H_{10}O_5)_n$

where, $n \cong 100$ to 300

It is the chief food storage material in plants.

(ii) Starch is white amorphous powder which is sparingly soluble in water.

(iii) Hydrolysis of starch :

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} \xrightarrow[\text{or Diastase}]{H_3O^+} \underset{\text{Maltose}}{C_{12}H_{22}O_{11}} \xrightarrow{\text{Maltose}} \text{D-Glucose}$$

(iv) Starch does not reduce Fehling solution or Tollen's reagent and does not form osazone. This clearly suggests that all hemiacetal hydroxy group of glucose unit at C_1 is involved in glycosidic linkage.

(v) Starch is a mixture of two poly saccharides Amylose and Amylopectins.

Natural starch has

Amylose : 10 to 20%

Amylopectin : 80 to 90%

Cellulose :

(i) It is the major constituent material of plant cell wall. In general, wood contains 50% cellulose and cotton contains 90-95% cellulose.

(ii) It is a colourless, amorphous solid which can be decomposed by heating.

(iii) It is almost linear and its individiual monomeric units are joined through multiple H-bond.

(iv) Cellulose does not reduce Fehling solution, Tollen's reagent and does not forms osazone.

(v) Large population of cellulotic bacteria is present in the stomach of ruminant mammals. These bacteria causes decomposition of cellulose in stomach cellulose is digested as glucose in ruminant mammals.

(vi) Human does not have any system to digest cellulose.

(vii) Structure of Cellulose : Cellulose is a straight chain polymer of D-glucose which are joined by $\beta-$ Glucosidic bond b/w C_1 of one glucose and C_4 of other glucose.

PROTEINS

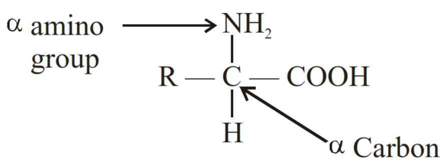
Proteins are vital chemical substance essential for the growth and maintenance of life. Chemically proteins are condensation polymers in which the monomeric unit is α amino acids. All proteins contain the elements like carbon, hydrogen, oxygen nitrogen and sulphur in major.

Hydrolysis of Proteins

$$\text{Protein} \xrightarrow{\text{Hydrolysis}} \text{Peptides} \xrightarrow{\text{Hydrolysis}} \alpha-\text{Amino acids}$$

α Amino acids :

α amino acids are the building block of proteins.



The total of 2O amino acids has been isolated by hydrolysis of various proteins.

Classification of α Amino acids :

Amino acids

Essential	Non-essential
The amino acids which can't be synthesised in human body is called essential amino acids * They arey 10.	The amino acids which can be synthesised in human body is called non-essential amino acids. * They are also 10.

α - Amino acids

(a) Neutral	(b) Alkaline	(c) Acidic
Has one NH_2 group and one COOH group.	Two NH_2 group and one COOH group	Has two COOH group and one NH_2 group

Zwitterion ion structure :

α - amino acid largely exists as dipolar ion.

$$R-\underset{\displaystyle NH_2}{\underset{|}{CH}}-COOH \rightleftharpoons R-\overset{\displaystyle NH_3}{\overset{|}{CH}}-COO^-$$

Zwitter ion

Electrical behaviour of Amino acids :

(a) In acidic solution : α amino acid exist as cations and thus will migrat towards the cathode under electrical field.

$$R-\underset{\displaystyle NH_2}{\underset{|}{CH}}-\overset{\displaystyle O}{\overset{\|}{C}}-O-H+\underset{\text{Acid}}{H^+} \rightleftharpoons R-\underset{\displaystyle \oplus NH_3}{\underset{|}{CH}}-COOH$$

The cation will migrat towards cathode.

(b) In alkaline solution : α Amino acid exist as

$$R-\underset{\displaystyle CH_2}{\underset{|}{CH}}-\overset{\displaystyle O}{\overset{\|}{C}}-OH+\underset{\text{Base}}{H^-} \rightleftharpoons R-\underset{\displaystyle NH_2}{\underset{|}{CH}}-\overset{\displaystyle O}{\overset{\|}{C}}-O^-$$

Anion

The anion will migrat towards +ve electrode i.e. Anode.

Iso electric point :

The pH at which amino acid has no net migration towards any of the electrode under influence of electric field is called isoelectric point.

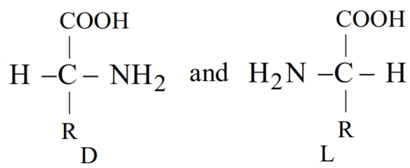
Each amino acid has a characteristic isoelectric point.

Amino acid	Iso electric point (pH)
(1) Neutral	Slightly less than 7($\cong$ 6.1)
(2) Acidic	3.2 to 3.5
(3) Alkaline	7.6 to 10.8

At isoelectric point amino acids have least solubility.

D, L Nomenclature of Amino acids :

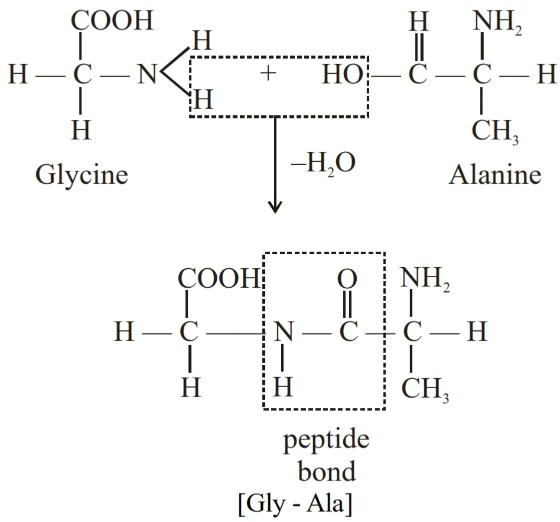
Au amino acids except glycine is chiral and has two stereo isomeric forms.

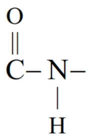


All naturally occuring amino acid belongs to L series.

Peptide bond :

Peptides are organic amides formed by the condensation of amino group of one α amino acid and carboxylic acid of other amino acid, by simultaneous elimination of water.



* Thus  linkage is called the peptide bond.

Poly peptides :

If large number of α amino acids are joined together by peptide bonds, the polyamide is formed. Such polyamides are called polypeptides.