15. BIOMOLECULES

Synopsis: Biochemistry :

- The branch of science that deals with the study of the chemical composition and structure of living organisms and also various changes taking place within them.
- **Biomolecules** : The complex organic molecules which form the basis of life.
- Biomolecules build up living organisms and are also required for their growth and maintenances.
- The sequence that relates biomolecules to living organisms is
  Biomolecules $\rightarrow$ Organelles $\rightarrow$ Cells $\rightarrow$ Tissues $\rightarrow$ Organs $\rightarrow$ Living organism
- Biomolecules which form the basis of life are
  (i) Carbohydrates, (ii) Proteins, (iii) Nucleic acids (iv) Lipids, (v) Vitamins and Hormones.
- Most of the biochemical reactions takes in dilute neutral solutions (pH = 7) at bodytemperature and 1 atmosphere pressure involving complex mechanisms.
- The basic structural and function unit of living organisms is the “cell”.
- Glucose molecules supply energy to the cells by undergoing complex and controlled oxidation in presence of biocatalyst known as enzymes.
- In exergonic reactions Gibbs free energy change ΔG is negative. These reactions are spontaneous ($\Delta G < 0$ spontaneous).
- In endergonic reactions Gibbs free energy change ΔG is positive these reactions are non spontaneous ($\Delta G > 0$ non spontaneous).
- Endergonic reactions are made spontaneous by coupling it with exergonic reactions.
  Metalbolic process $A \rightarrow B$ $\Delta G > 0$ Endergonic nonfeasible
  Conversion of $S \rightarrow P$ $\Delta G < 0$ Exergonic feasible



$\Delta G < 0$, feasible

- $6CO_2 + 6H_2O \xrightarrow{\text{sun light}} C_6H_{12}O_6 + 6O_2$ $\Delta G = +2880$ kJ. It is a light reaction, it follows a dark reaction ATP hydrolysis.

$$\underset{\substack{\text{Adinosin}\\\text{Triphosphate}}}{ATP} \xrightarrow[\substack{\Delta G^\circ = -31 \text{ kJ mole}^{-1}}]{-H_3PO_4} \underset{\substack{\text{Adinocine}\\\text{diphosphate}}}{ADP} \xrightarrow[\substack{\Delta G^\circ = -31 \text{ kJ mole}^{-1}}]{-H_3PO_4} \underset{\substack{\text{Adinocine}\\\text{monophosphate}}}{AMP} \xrightarrow[\substack{\Delta G^\circ = -14 \text{ kJ mole}^{-1}}]{-H_3PO_4} \text{Adinocine}$$

- Glucose can be converted into disaccharide, polysaccharides like starch, cellulose or proteins or oils depending on the nature of plants and the reaction type.
  $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$ $\Delta H = -2880$ kJ mole^{-1}

i) CARBOHYDRATES

- In the beginning carbohydrates are considered as hydrates of carbon because of general formula $C_n(H_2O)_m$.
- Rhamnose ($C_6H_{12}O_5$) and deoxyribose ($C_5H_{10}O_4$) are carbohydrates but not represents the formula $C_n(H_2O)_m$.
- They are also called Saccharides due to similar taste like sugar derived from Latin word for sugar “Saccharum”.

- Formaldehyde (CH_2O), Acetic acid ($C_2(H_2O)_2$ will not behave like carbohydrates but represents the formula $C_n(H_2O)_m$.
- Based on structural evidence and chemical reactivity. They are defined as polyhydroxy aldehydes and polyhydroxy ketones.
- Depending upon their behaviour towards hydrolysis carbohydrates are divided into mono di and polysaccharides.
- Monosaccharides are simple carbohydrates which cannot behydrolysed to simpler carbohydrates.
  Ex. $(CH_2O)_n$ where n = 3 $\rightarrow$ 7 (glucose, fructose, ribose, galactose)
- Disaccharides give two units of monosaccharides on hydrolysis.
  Ex. Sucrose and maltose both have molecular formula $C_{12}H_{22}O_{11}$.
- ***Oligosaccharides*** on hydrolysis give 3 to 10 simple monosaccharides disaccarides also can be considered as oligosaccharides.
  Ex. Trisaccharides – raffinose $\xrightarrow{H_2O}$ Glucose + fructose + galactose.
  Stachycose ($C_{24}H_{42}O_{21}$) $\xrightarrow{H_2O}$ Glucose + fructose + 2 Galactose
- ***Polysaccharides*** carbohydrates which upon hydrolysis give (more than 10) many monosaccharide units.
  Ex. Starch, cellulose and glycogen $(C_nH_{10}O_5)_n$.
  n = 100 to 3000.
- More than 200 monosaccharides are known they are grouped as polyhydroxy aldehydes called **Aldoses** and polyhydroxy ketons called as **ketoses**.

Aldotriose	$CH_2OH - CHOH - CHO$	Glyceraldehyde
Aldotetrose	$CH_2OH - (CHOH)_2 - CHO$	Erythrose, threose
Aldopentose	$CH_2OH - (CHOH)_3 - CHO$	Arabinose, ribose, xylose, lyxose
Aldohexose	$CH_2OH - (CHOH)_4 - CHO$	Glucose, mannose, galactose, gulose, talose, lolose, allose, altrose
Ketotriose	$CH_2OH - \overset{\overset{O}{\|\|}}{C} - CH_2OH$	Dihydroxyacetone
Ketoterose	$CH_2OH - \overset{\overset{O}{\|\|}}{C} - CHOH - CH_2OH$	Erytrulose
Ketopentose	$CH_2OH - \overset{\overset{O}{\|\|}}{C} - (CHOH)_2CH_2OH$	Ribulose, Xylulose
Ketohexose	$CH_2OH - \overset{\overset{O}{\|\|}}{C} - (CHOH)_3CH_2OH$	Fructose, surbose, tagatoce

- **Sugars** monosaccharides and oligosaccharides are crystalline solids soluble in water and sweet in taste are called sugars.

- **Nonsugars** polysaccharides are amorphous solids insoluble in water and taste less called reducing sugars while others which do not reduced.
- **Reducing sugar** carbohydrates which contain aldehyde or keto group in hemiacetal form reduce Tollens and Fehlings solution are these reagents are called nonreducing sugars.
- **Glucose** (Dextrose : Grape sugar) 20% in fruits and grapes.
- Sucrose and starch on boiling with dil H_2SO_4 in alcoholic solution undergoes hydrolysis to give glucose.

$$\underset{\text{sucrose}}{C_{12}H_{12}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

$$C_{12}H_{22}O_{11} + nH_2O \xrightarrow[393]{H^+\ 2-3atm} n\underset{\text{glucose}}{C_6H_{12}O_6}$$

- The molecular formula of the glucose is $C_6H_{12}O_6$.
- Glucose has 5 – OH group is conformed by the acylation of glucose.
- Acylation of glucose with acetic anhydride or with acylchloride give glucose pentacetate.

$$CHO-(CHOH)_4-CH_2OH \xrightarrow{(CH_3CO)O} CHO-(CHOCOCH_3)_4-CH_2OCOCH_3$$

- Glucose has one carbonyl group. Presence of carbonyl group can be conformed by the reaction with hydroxylamine or with a molecule of hydrogen cyanide.

$$\underset{\text{D-glucose}}{CH_2OH-(CHOH)_4CHO} + \underset{\text{phynyl hydroxylamin}}{H_2N-NHC_6H_5} \longrightarrow HOCH_2-(CHOH)_4-CH=N-NHC_6H_5$$

D-glucose phenyl hydrazone

$$\underset{\text{D-glucose}}{CH_2OH-(CHOH)_4CHO} + HCN \longrightarrow HOCH_2-(CHOH)_4-CHOHCN$$

D-glucose cyanohydrin

- Glucose reduces ammonical silver nitrate (Tollen's reagent) to metallic silver.

$$CH_2OH(CHOH)_4-CHO + Ag_2O \longrightarrow \underset{\text{Gluconic acid}}{CH_2OH-(CHOH)_4-COOH}$$

- Glucose reduces Fehlings solution to reddish brown cuprous oxide.

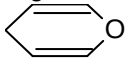
$$CH_2OH-(CHOH)_4-CHO + 2CuO \longrightarrow \underset{\text{Gluconic acid}}{CH_2OH-(CHOH)_4-COOH} + Cu_2O$$

- Tollens test, Fehlings test confirms that the carbonyl group is –CHO aldehyde group.
- Bromin water or an alkaline solution of iodine oxidises only the aldehyde group of glucose to gluconic acid.
- Glucose molecule has one primary alcoholic group (CH_2OH).
- Presence of CH_2OH group can be known with nitric acid test.
- Glucose with nitric acid gives saccharic acid.

$$CH_2OH-(CHOH)_4-CHO \xrightarrow{HNO_3} \underset{\text{Saccharic acid}}{HOOC-(CHOH)_4-COOH}$$

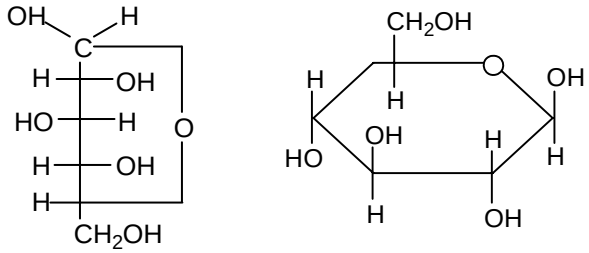
- Glucose on prolonged heating with HI gives hexane. It indicates that all six carbons of glucose are Pn linked linearly.

$$CH_2OH-(CHOH)_4-CHO \xrightarrow{HI} CH_3-(CH_2)_4-CH_3$$

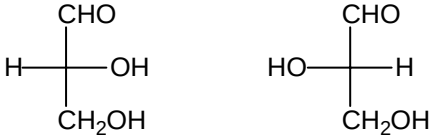
- Glucose with phenyl hydrazine gives a osazone called glucosagone it is dihydrazone.
- Glucose with concentrated sodium hydroxide first gives a yellow colour and then turns brown and finally resinifies. This is called is omers action
- Glucose with a dilute solution of sodium hydroxide gives a mixture of D-glucose D-mannose, D-fructose. This is Lobry de Bruyn Van Ekenstein rearrangement.
- Fructose and mannose also can give Lobry de Bruyn Van Ekenstein rearrangement.
- Due to reversible isomerisation fructose with keto group also can reduce Tollen's reagent.
- D-glucose and L-glucose differs in the position of –OH group at second carbon.
- Glucose open chain structure proposed by Bayer.
- – CHO group of glucose does not respond to Schiff's test and sodium bisulphate and ammonia. This can't be explained by the open chain structure of glucose.
- Pentacetate of glucose does not react with hydroxy lamine though it contains –CHO group.
- Concentrated solution of glucose at 30°C gives α-D glucose with melting point 146°C and specific rotation $(\alpha)_D = +111°$.
- Concentrated solution of glucose at above 98°C give B-D glucose with the melting point 150°C and specific rotation $(\beta)_D = +19.2°$.
- α_D and β_D forms of glucose differ from each other in stereochemistry at first carbon.
- The change in specific rotation of ether form of glucose in aqueous solution to that of equilibrium mixture is called mutarotation.
- α-D + glucose $\rightleftharpoons$ equilibrium mixture + 52.5° 36% α and 64% β $\rightleftharpoons$ β-D glucose +19.2°
- α_D and β_D forms of glucose with methanol and dry HCl gas gives α_D glucoside and β-D-glucoside respectively.
- Glucoside formation involves ring formation with C_1 and C_5 carbons.
- Glucoside formation makes the C_1 carbon (anomeric carbon) asymmetric.
- α-D glucoside and β-D glucoside differs in the configuration at C_1 carbon are called anomers.
- In α-D glucoside –OH group is at right and in β-D glucoside –OH grouped left.
- Super imposable mirror images are enantiomers.
- α-D glucoside and β-D glucoside are not mirror images of each other and they are not super imposable, so they are not enantiomers.
- Pyranose structure (α or β) is a six numbered cyclic configuration of glucose, it is similar to pyran.
- Pyran is six numbered ring containing 5 carbons and one oxygen. 
- Five membered ring structure of glucose is called furanose structure as it is similar to furan.
- Glucose is found to occur in pyranose structure.
- In Haward structure of glycopyranose the lower thickened edge of the ring is nearest to the viewer.

- The groups projected to the right in Fisher projection are below the plane of the ring and those on the left are above the plane of the ring.

  β-D glucopyranose

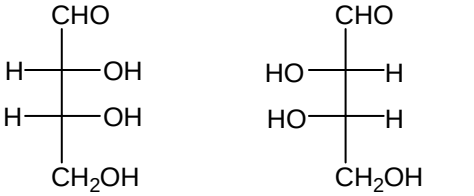


- The stereochemistry of all sugars is determined with respect to D- or L-glyceraldehyde.
- In Fischer projection OH group on C_2 is at right (+) configuration is D and OH is on C_2 is at left (–) configuration is L.

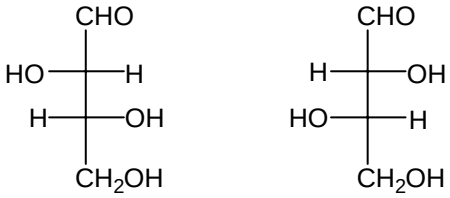


R(+) Glyceraldehyde S(–) glyceraldehyde

- In tetrose the –OH group at C_2 and C_3 are on the same side. The consider the highest numbered carbon atom as stereogenic centre.



Analogus to D-glyceraldehyde **Analogus to L-glyceraldehyde**



D - form **L - form**

- D form and L-forms are called diasterioisomers or diastereomers.
- Stereoisomers which are not mirror images are called diastereomers.
- Disaccharide on hydrolysis give two monosaccharide units may be same or different.

  Sucrose → glucose + fructose

  Lactose → glucose + galactose

  Maltose → glucose + glucose

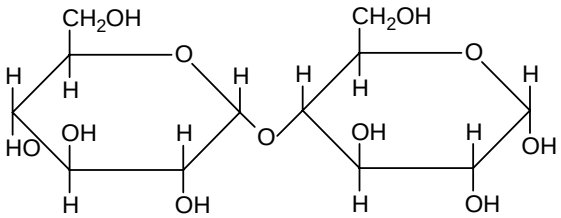
- Reducing and nonreducing nature of disaccharide depends on the position of linkages between the two monosaccharide units.

Sucrose $C_{12}H_{22}O_{11}$ Cane sugar :

- It is most common disaccharide widely present in plants.
- Sugar cane or beetroot contains sucrose.
- Colourless, crystalline, sweet substance with $[\alpha]_D = 65.5°$.
- Sucrose is dextro-rotatory, on hydrolysis gives dextro-rotatory glycose $[\alpha]_D = +52.5°$ and Laevorotatory fructose $[\alpha]_D = -92.4°$.
- The mixture of glucose and fructose is Laevorotatory.
- Hydrolysis of sucrose involves change in the rotation from D to L, This is called inversion of cane sugar or mixture is called invert sugar.
- Linkage present in sucrose is $C_1 - C_2$ linkage.

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

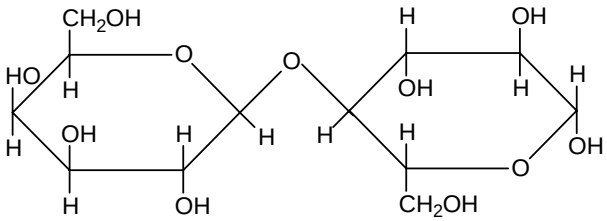
- Maltose is obtained from starch by the hydrolysis process in presence of diastate enzyme produced by germinated barlyseas.
- $(C_6H_{10}O_5)_n + n/2\ H_2O \rightarrow n/2\ C_{12}H_{22}O_{11}$ (maltose).
- Maltose is a reducing sugar contains C-1 to C-4 linkage.



- Maltose with the enzyme maltose produced by yeast gives two units of glucose both will have pyranose form.

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

- Present in milk and it is known as milk sugar.
- It is a reducing sugar on hydrolysis gives D-galactose and D-glucose.
- $C_{12}H_{22}O_{11} \xrightarrow{\text{emulsion}} C_6O_{12}O_6 + C_6H_{12}O_6$.
- Emulsion hydrolyses β-glycosidic linkages.
- Lactose contains $C_1 - C_4$ linkage.



Polysaccharides :

- Starch, cellulose, dexdrin, glycogen are polysaccharides.
- Monosaccharides are linked through glycoside linkages in polysaccharides.

Starch or Amylum $(C_6H_{10}O_5)_n$:

- Starch is present in wheat, maize, rice, potatoes, barley, sorghum which are obtained from plants.
- Starch is a amorphous while powder insoluble in cold water soluble in boiling water.
- Starch solution gives blue colour with iodine in cold condition colour disappears on heating.
- Starch on hydrolysis forms D-glucose

$$(C_6H_{10}O_5)_n \xrightarrow{n/2\ H_2O} \frac{n}{2}\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} \xrightarrow{H_2O} \underset{\text{D-glucose}}{C_6H_{12}O_6}$$

- Starch cannot be oxidised by Tollen's reagent or Fehling's solution.
- Starch does not forms osazone.
- In starch C_1 carbon is in glycoside form.
- Glycosides are acetyls in which anomeric hydroxyl group is replaced by an alkoxy group.
- In glycosides anomeric – OH group is replaced by some other groups connected with O, N, S. They are respectively called their glycoside.
- Starch contains polysaccharides amylose and amylopectin.
- Natural starch contains 10-20% of amylase and 90-80% of amylopectin.
- Amylase water soluble and it contains only D-glucose units they give blue colour with I_2 solution.
- Amylase contains $C_1 – C_4$ α-glucosidic linkage.
- Molecular mass of amylase is 10,000 to 50,000.
- Amylopectin branched chain polysaccharide water in soluble.
- Amylopectin doesn't give blue colour with I_2 solution.
- Amylopectin molecule contains 25-30, D-glucose units.
- In amylopectin α-D-glycosidic link between $C_1 – C_4$ of the molecule.
- Branched chains in amylopectin are due to $C_1 – C_6$ linkages through oxygen.
- Starch a major food material easily hydrolysis in saliva by amylase enzyme to give glucose final product.

Cellulose $(C_6H_{10}O_5)_n$:

- This is the structural component of vegetable matter.
- Wood has 40-50% and cotton has upto 90% cellulose.
- It is formed by photosynthesis.
- It contains large number of D-glucose units joined by β-1, 4 glycosidic linkages.
- In the hydrolysis of cellulose gives D-glucose as final product.
- Cellulose is digested in ruminant animals like cattle sheep in presence of enzyme cellulose.
- Cellulose is a colourless amorphous solid.
- Cellulose contains many hydrogen bond which makes the individual stands to align linearly.
- It will not reduce Tollen's reagent and Fehlings solution.
- It doesn't form osazone its molecular weight is about 50,000 – 5,00,000 or 300-2500 D-glucose units.

- Cellulose doesn't digest in human stomach due to the absence of enzyme cellulose.
- Cellulolytic bacteria present in the stomach (rumen) of ruminant mammals like cattle and sheep gives cellulose it breakdown the cellulose into glucose during digestion.