Unit 14

Biomolecules

- **Biomolecules** are complex, lifeless organic molecules (compounds) which combine in a specific manner to produce life, *e.g.*, carbohydrates, proteins, amino acids, fats, etc.
  These biomolecules interact with each other or constitute the molecular logic of life processes. In addition, some simple molecules like vitamins and mineral salts also play an important role in the functions of organisms.

CARBOHYDRATES

- **Carbohydrates** are polyhydroxy aldehydes or ketones or compounds which produce such units on hydrolysis and contain at least one chiral C-atom in their molecules. They are primarily derived from plants and most of them have the general formula $C_x(H_2O)_y$ *e.g*, glucose, fructose, sucrose, etc.

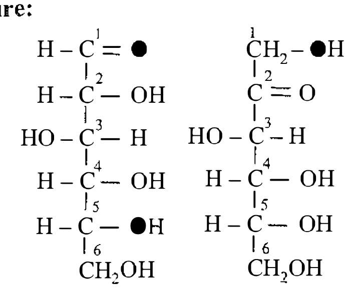
Classification

Carbohydrates

- **Monosaccharides** (Simple Sugar)
  These can not be broken into lower sugars on hydrolysis
  General formula : $C_nH_{2n}O_n$
  $n = 3$ to 7
  - **Aldoses** (Polyhydroxyl aldehydes) *e.g.*, Glucose
  - **Ketoses** (Polyhydroxy ketones) *e.g.*, Fructose
- **Oligosaccharides**
  Upon hydrolysis yields 2 – 10 molecules of monosaccharides
  - **Disaccharides** *e.g.*, Sucrose, Maltose
  - **Trisaccharides** *e.g.*, Raffinose
  - **Tetrasaccharides** *e.g.*, Stachyose
  - **Pentasaccharides** *e.g.*, Verbascose
- **Polysaccharides**
  Upon hydrolysis gives more than 10 monosaccharides
  - **Homopolysaccharides** (Same basic sugars) *e.g.* Starch, Glycogen
  - **Heteropolysaccharides** (Contain different basic sugars groups) *e.g.*, Chondroitin sulphates

Monosaccharides (Glucose and Fructose)

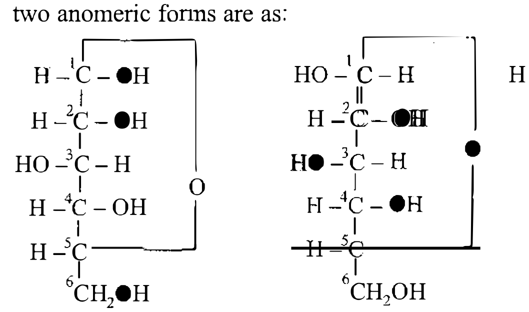
- **Structure:**



D-(+)-glucose   *D*-(–)-fructose

> Glucose also exists in ring form.
  – The five membered ring containing an oxygen is called the **furanose form.**
  – The six membered ring containing an oxygen atom is called the **pyranose form**.

> **Anomers** refer to a pair of stereoisomers which differ in configuration only around C_1. Cyclic structures for two anomeric forms are as:



α-*D*-(+)-glucopyranose   β-*D*-(+)-glucopyranose

- Cyclic structures are also known as **hemi-acetal** structures.
- *D*-(+)-glucose exists in two anomeric forms *i.e.*, α-*D*-(+)-glucopyranose and β-*D*-(+)-glucopyranose shown above. When these are separately dissolved in water, they undergo a change in specific rotation till it becomes constant after some time. The change in specific rotation of isomers in aqueous solution is called **mutarotation**.

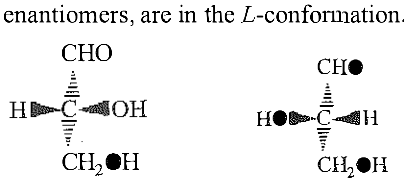
$$\alpha\text{-}D\ (+)\ \text{glucose} \rightleftharpoons \text{Equilibrium} \rightleftharpoons \beta\text{-}D\ (+)\ \text{glucose}$$

$$[\alpha]_D^t = +112^\circ \qquad [\alpha]_D^t = +52.7^\circ \qquad [\alpha]_D^t = +19^\circ$$

Physical and Chemical Properties

	Property	Glucose	Fructose
1.	Molecular formula	$C_6H_{12}O_6$	$C_6H_{12}O_6$
2.	Nature	Polyhydroxy aldehyde	Polyhydroxy ketone
3.	Melting point	146 °C	102 °C
4.	Optical activity of natural form	Dextrorotatory	Laevorotatory
5.	Solubility in ethyl alcohol	Almost insoluble	More soluble
6.	Oxidation (a) with bromine water (b) with conc. nitric acid	 Gluconic acid Saccharic acid (glucaric acid)	 No reaction Mixture of glycollic acid, tartaric acid and trihydroxy glutaric acid
7.	Reduction	Sorbitol	Mixture of sorbitol and mannitol.
8.	Calcium hydroxide	Forms calcium glucosate, soluble in water	Forms calcium fructosate, insoluble in water
9.	Molisch's reagent	Forms a violet ring	Forms a violet ring
10.	Fehling's solution	Gives red precipitate	Gives red precipitate
11.	Tollens' reagent	Forms silver mirror	Forms silver mirror
12.	Phenylhydrazine	Forms osazone	Forms osazone
13.	Resorcinol + HCl (dil.)	No colouration	Gives red or brown colour or precipitate
14.	Freshly prepared ammonium molybdate sol. + few drops of acetic acid	Light blue colour	Bluish green colour on heating
15.	Alcoholic α-naphthol + HCl (conc.)	No colouration	A purple colour (violet) on boiling

- ***D* and *L* configuration**
  - Carbohydrates can exist in either of two conformations, as determined by the orientation of the hydroxyl group about the asymmetric carbon farthest from the carbonyl. With a few exceptions, those carbohydrates that are of physiological significance exist in the *D*-conformation. The mirror image conformations, called enantiomers, are in the *L*-conformation.



D-Glyceraldehyde *L*-Glyceraldehyde

Structures of Glyceraldehyde Enantiomers

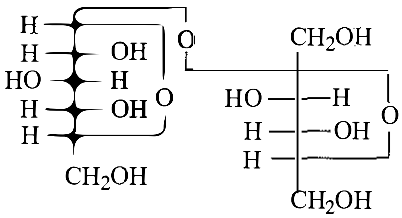
  - By convention, a monosaccharide is said to have *D*-configuration if the hydroxyl group attached to the asymmetric carbon atom adjacent to the — CH_2OH group is on the right hand side irrespective of the positions of the other hydroxyl groups. On the other hand, the molecule is assigned *L*-configuration if the — OH group attached to the carbon adjacent to the — CH_2OH group is on the left.

Oligosaccharides (Sucrose or Cane sugar or Table sugar ($C_{12}H_{22}O_{11}$))

- It is **dextrorotatory** in nature.
- The molecular formula of sucrose is ($C_{12}H_{22}O_{11}$) Upon hydrolysis with dilute mineral acid (HCl) or by enzyme, invertase it forms equimolar mixtures of *D*-(+)-glucose and *D*-(–)-fructose.

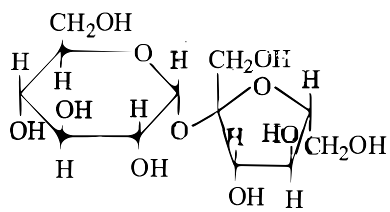
$$\underset{\substack{(+)\text{-Sucrose} \\ [\alpha]_D = +66.5^\circ}}{C_{12}H_{22}O_{11(s)}} + H_2O \xrightarrow{\text{Hydrolysis}} \underbrace{C_6H_{12}O_{6(aq)} + C_6H_{12}O_{6(aq)}}_{\substack{\text{invert sugar} \\ (+)\text{-Glucose } [\alpha]_D = +52.7^\circ \text{ and} \\ (-)\text{-Fructose } [\alpha]_D = -92.4^\circ}}$$

- The mixture is overall laevorotatory. Thus, the hydrolysis of sucrose brings about a change in the sign of optical rotation, from dextro (+) to laevo (–) and such a change is known as inversion and the equimolar mixture of *D*-(+)-glucose and *D*-(–)-fructose which sucrose gives on hydrolysis is called **invert sugar**.
- **Structure**



Glucose unit Fructose unit

Fischer structure for sucrose

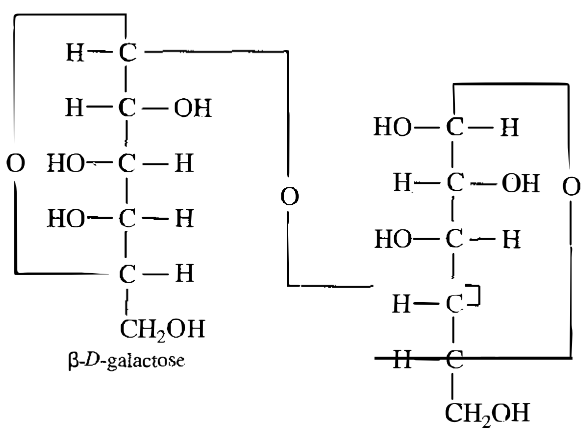


Glucose unit Fructose unit

Haworth structure for sucrose

Lactose ($C_{12}H_{22}O_{11}$)

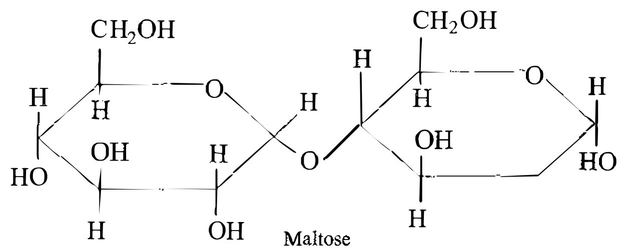
- Lactose occurs in milk and is also called milk sugar. Hydrolysis of lactose with dilute acid yield equimolecular mixture of *D*-glucose and *D*-galactose. It is a reducing sugar. It gets hydrolysed by emulsin, an enzyme which specifically hydrolyses β-glycosidic linkages.



Maltose or Malt Sugar, ($C_{12}H_{22}O_{11}$)

- It is obtained by partial hydrolysis of starch by diastase, an enzyme present in malt.

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{\text{Diastase}} \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}}$$



On hydrolysis one mole of maltose yields two moles of *D*-glucose. It is a reducing sugar. The two glucose units are linked through an α-glycosidic linkage between C-1 of one unit and C-4 of another . Both glucose units are in pyranose form.

Polysaccharides

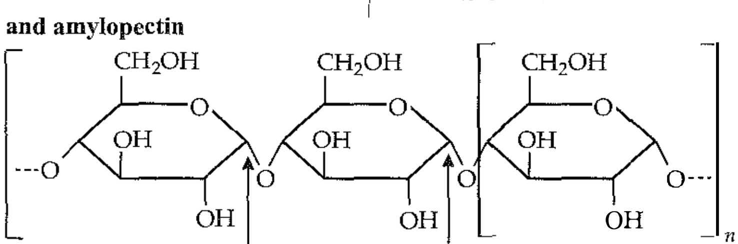
Starch

- Starch is a polysaccharide. It is the most important source of energy for human beings. Starch is hydrolysed to glucose by enzyme amylase present in saliva.
- It is a polymer of α-glucose and consists of two components - **amylose** and **amylopectin.**

	Amylose	Amylopectin
1.	It is water soluble.	It is insoluble in water.
2.	It is 15-20% of starch.	It is 80-85% of starch.
3.	It is long straight chain polymer.	It is long branched chain polymer.
4.	It has 200-1000 α-*D*-glucose units held by C_1-C_4 glycosidic linkage.	It has 25-30 α-*D*-glucose units joined by C_1-C_4 glycosidic linkage. These chains are connected with each other by 1,6-linkage.
5.	It gives blue colour with iodine.	It does not give blue colour with iodine.

- Starch is the most valuable constituent of food as rice, bread, potato and corn flour, etc. It is very important in manufacture of glucose, dextrin, adhesives and in paper, textile industries.

- **Structure of amylose and amylopectin**



α-1, 4-Glycoside bonds Repeating monomer

Structure of amylose