

## Lecture 4

### Muta rotation, optical activity and physical properties of sugars

#### A. Isomerism

In organic chemistry, isomerism is defined as the existence of more than one compound with the same molecular formula. A close observation of the structure of monosaccharides (hexoses) indicate that they possess same molecular formula ( $C_6H_{12}O_6$ ) but with different physical and chemical properties. There are different types of isomerism

- **D-glucose and D-fructose** differ in the position of carbonyl group (aldehyde and ketone group). These two compounds are **functional isomers**.
- Another type of isomerism exhibited by compounds possessing asymmetric carbon atom like monosaccharides, is **stereoisomerism**. These stereoisomers differ in the spatial arrangement of atoms or groups. There are two types of stereoisomerisms - **geometrical and optical isomerism**.
  - **Geometrical isomers** (cis-trans) differ in the spatial arrangement of atoms across a double bond. Geometrical isomerism is not noticed among carbohydrates.
  - **Optical isomers** differ in the arrangement of atoms around an asymmetric carbon atom. The number of possible optical isomers can be calculated using the formula  $2^n$  where  $n$ =number of asymmetric carbon atoms. For example, glucose contains four asymmetric carbon atoms and the possible optical isomers of glucose are  $2^4 = 16$ .

#### Epimers, enantiomers and diastereomers:

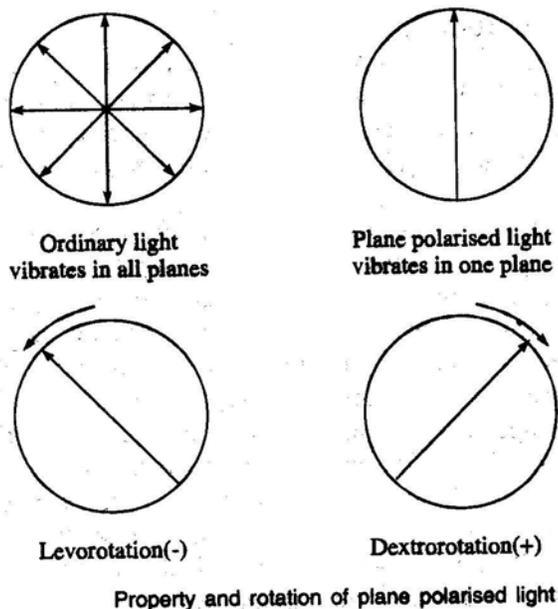
- **Epimers** are monosaccharides differing in configuration around a single carbon atom other than the carbonyl carbon. e.g. **Mannose and glucose** are epimers with respect to carbon 2. **Galactose and glucose** are epimers with respect to carbon 4.
- **Enantiomers** are non- superimposable mirror images of each other. They differ in the ability to rotate the plane polarized light. A solution of one enantiomer rotates the plane of such light to the right, and a solution of the other to the left. **D-glucose and L-glucose** are examples of enantiomers.
- **Diastereomers** are stereoisomers that are not mirror images of each other. **D-glucose, Dmannose, D-galactose** and other members of aldohexose are diastereoisomers.

## B. Optical activity

A ray of ordinary light vibrates in all directions at right angles to the direction in which the ray is travelling. When this light is passed through a Nicol prism, the emerged light vibrates in only one direction and such light is called as a '**plane polarized light**'

When a beam of plane polarized light is passed through a sugar solution, that is optically active, the plane-polarized light will be rotated either to the right (clockwise) or to the left (anticlockwise).

- When the plane polarized light is rotated to the **right**, the compound is **dextrorotatory** and is written as (+).
- If the plane polarized light is rotated to the **left**, the compound is **levorotatory** (-)



Optical activity is measured using polarimeter. Optical activity varies with the concentration of the sugar solution and length of the polarimeter tube where sugar solution is placed.

Specific rotation ( $\alpha$ ) of a sugar molecule is calculated by the formula :

$$(\alpha) = \frac{\text{Observed rotation}}{\text{Length of tube (dm)} \times \text{concentration}}$$

where  $T$  = temperature and  $D$  = D line of spectrum.

The specific rotation of some important sugars are given below:

D - glucose (dextrose) + 52.2	D - fructose (levulose) -92.0	D - galactose + 80.5
D - mannose + 14.6	L - arabinose + 104.5	Sucrose + 66.5

### C. Mutarotation

- Mutarotation refers to the change in optical rotation when an aqueous sugar solution is allowed to stand.
- Sugars having potential free aldehyde or keto group exhibit mutarotation.
- Many sugars exist in two crystalline forms. For example, when D-glucose is dissolved in water and allowed to crystallize out by evaporation of water, one form of D-glucose is obtained. If D-glucose is crystallized from acetic acid or pyridine, another form of D-glucose is obtained. These two forms exhibit different physical and chemical properties.
- A freshly prepared aqueous solution of  $\alpha$ -D glucose has a specific rotation of  $+113^\circ$ . If the solution of  $\alpha$ -D-glucose is allowed to stand, the specific rotation changes to  $+52.2^\circ$ .
- Similarly, a fresh solution of  $\beta$ -D-glucose has a specific rotation of  $+19^\circ$  which changes to  $+52.2^\circ$  on standing.
- This change in optical rotation is called **mutarotation**. On standing in solution, the hemiacetal ring opens and reforms to give a mixture of  $\alpha$  and  $\beta$ -D-glucose having a specific rotation of  $+52.2^\circ$ .