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:

\[
(\alpha) = \frac{\text{Observed rotation}}{\text{Length of tube (dm) x concentration}}
\]
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 α-D glucose has a specific rotation of +113°. If the solution of α- D-glucose is allowed to stand, the specific rotation changes to +52.2°.
- Similarly, a fresh solution of β- D-glucose has a specific rotation of +19° which changes to +52.2° on standing.
- This change in optical rotation is called mutarotation. On standing in solution, the hemiacetal ring opens and reformed to give a mixture of □ and D-glucose having a specific rotation of +52.2°.