Quadrant II – Transcript and related materials

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Module Name: Structure of Monosaccharides

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Notes:

MONOSACCHARIDES

Carbohydrates are most abundant biomolecules in nature are primarily composed of carbon, oxygen and hydrogen.

Monosaccharides are the carbohydrates that cannot be further hydrolysed and therefore they are the monomer units of carbohydrates which combine to form polymers. They are also referred to as simple sugars. Their basic formula is $C_n(H_2O)_n$ where n=3-7. The smallest monosaccharides of n=3 are glyceraldehyde and dihydroxyacetone.

They are **polyhydroxy aldehydes or ketones** i.e., they contain either an aldehyde group or a ketone bonding pattern and also contain more than one hydroxyl (OH) group.

They are divided into different categories:

1. **Based on functional group**

- If the functional group is an aldehyde group (-CHO), they are known as **aldoses**. E.g., Glyceraldehyde and Glucose
- If the functional group is a keto group (C=O), they are known as **ketoses**. E.g., dihydroxyacetone and Fructose.

2. **Based on number of carbon atoms** they are further classified as trioses (3C), tetroses (4C), pentoses (5C), hexoses (6C) and heptoses (7C).

STRUCTURE OF MONOSACCHARIDES

1. **Asymmetric carbon atom/chiral centre:**

A carbon atom bonding with different groups or atoms is known as asymmetric carbon atom or chiral carbon. All carbohydrates except dihydroxyacetone have one or more asymmetric carbon atoms.

2. **Isomers of Monosaccharides:**

Isomers are two compounds with same molecular formula but different chemical structures. The number of isomers depends on the number of chiral centres (n). The general formula is 2^n. Example: Glucose has four asymmetric carbon atoms, i.e., n = 4, so $2^4 = 16$ isomers are possible for glucose.

(a) Epimers:

Monosaccharide isomers which differ in configuration around one specific carbon atom other than the carbon atom of carbonyl group. e.g., Glucose and mannose are epimers at C2 whereas glucose and galactose are epimers at C4.

(b) Enantiomers:

Enantiomers are pair of stereoisomers that are Non super-imposable mirror images of each other with regards to chiral carbon atoms. e.g., D and L sugars.

The type of sugar isomer as the D form or L form is determined by the orientation of the –H and –OH groups around the carbon atom adjacent to the terminal primary alcohol carbon (E.g., 5^{th} carbon in glucose).

D sugars contain the reference group on the right side of the last chiral centre from the functional group. If glucose is taken and the chiral centre furthermost from it is the 5th carbon atom and the reference group -OH is present on the right side of the straight chain, it is known as D-glucose. L series compounds are those compounds that contain the reference group on the left side of the last chiral centre from the functional group. If the -OH group is present at the left side on 5th carbon of the straight chain form of glucose then it is known as L-glucose.

- **OPTICAL ISOMERISM**

When a beam of plane polarized light is passed through a solution of optical isomer, it is deflected either towards the right or left. If it rotates towards right then the sugar is dextrorotatory (+) and it towards left then it is levorotatory (-).

There is no relation between the configurations of the sugar to the rotation of the plane polarized light. That is, the direction of rotation of polarized light is independent of the stereochemistry of the sugar, so it may be D (+)/ D (-) or L (+)/L (-).

- **Racemic mixture:**

A solution containing equal number of D (+) & L (-) forms of a sugar is known as a racemic mixture.

(c) Anomers:

Carbohydrates contain both aldehydic (carbonyl) and alcoholic groups within the molecule.

When an aldehydic group (or carbonyl carbon) reacts with an alcoholic group, then it results in the formation of a **hemiacetal** thus resulting in the formation of an additional chiral centre at the 1st carbon atom and this chiral centre is now known as the **anomeric carbon atom** and the sugars differing at this anomeric carbon atom are known as anomers. Similarly, when the keto group reacts with the alcoholic group it forms a **hemiketal**.

The ring can open and reclose allowing the rotation to occur around the carbon bearing reactive carbonyl group yielding wo possible configurations**- α and β of the hemiacetal and hemiketal**. If the -OH group on the anomeric carbon atom is towards the right (down in Haworth projection) then it is known as alpha (α) anomer. If the —OH group on the anomeric carbon atom is towards the left, then it is known as beta (β) anomer or β-sugar.

3. Ring structures of carbohydrates:

In aqueous solutions, monosaccharides that contain of 5-7 carbons can rearrange their bonding pattern to form cyclic structures. It is a reversible reaction in which the open-chain form is interconverted with the cyclic form. The rearrangement/cyclization reaction of a monosaccharide is due to hemiacetal/hemiketal formation.

A hemiacetal is a molecule that contains both an OR group and OH group that are bonded to the same carbon. An aldehyde or a ketone will react with an alcohol to form a hemiacetal.

Cyclic monosaccharides with five-member rings are called furanoses, and those with six member rings are called pyranoses.

Aldehydic group on 1st carbon atom of sugars can react with the alcoholic group on 4th carbon atom in pentoses and 4th or 5th carbon atoms in hexoses, forming a hemiacetal (as explained under anomers). This results in the formation of a cyclic ring structure. If the 1st and the 4th carbon atoms are involved in the hemiacetal formation, then the resultant ring structure is a five membered ring that resembles another compound known as furan. Hence the name of the resultant carbohydrate ring structure is furanose ring.

If the 1st and the 5th carbon atoms of the same sugar are involved in the hemiacetal formation then the resultant ring structure is a six membered ring that resembles another compound known as pyran. Hence the name of the resultant carbohydrate ring structure is pyranose ring.

Among the carbohydrates, trioses and tetroses do not involve in the ring formation owing to their short length. Pentoses always form the furanose ring structure, whereas hexoses can form both furanose and pyranose ring structures.