Lecture 8
Discipline: Bioorganic Chemistry
Lecturer: Associate Professor, Dr. Gulnaz Seitimova

Title: Classification of carbohydrates. Genetic series of aldoses and ketoses. Stereochemistry of monosaccharides, their mutarotation.

Objective: To introduce the structural diversity and classification of carbohydrates. To explain the genetic relationships among aldoses and ketoses. To provide an understanding of monosaccharide stereochemistry, including chirality, configuration, and optical activity. To describe the mechanism and significance of mutarotation in carbohydrate chemistry.

Main Questions: General definition and biological significance of carbohydrates. Classification of carbohydrates: monosaccharides, oligosaccharides, polysaccharides. Aldoses and ketoses: structural features and functional groups. Genetic (homologous) series of aldoses and ketoses. Chirality, asymmetric centers, and absolute configuration (D/L). Fischer projections and stereochemical relationships among sugars. Cyclization of monosaccharides; formation of α- and β-anomers. Mutarotation: mechanism and factors affecting it.

Key Notes and Theses

General Characteristics and Classification of Carbohydrates

Carbohydrates are the most abundant organic compounds in the plant world. Carbohydrates account for approximately three-fourths of the dry weight of plants. Animals (including humans) get their carbohydrates by eating plants, but they do not store much of what they consume. In fact, less than 1% of the body weight of animals is made up of carbohydrates.

Carbohydrates are polyhydroxy aldehydes or ketones, or compounds that yield them upon hydrolysis. They are essential for:

- energy metabolism (glucose),
- structural functions (cellulose, chitin),
- recognition processes (glycoproteins, glycolipids).

Classification:

1. Monosaccharides – simplest carbohydrates, cannot be hydrolyzed.
2. Oligosaccharides – 2–10 monosaccharide units (e.g., disaccharides: sucrose, lactose).
3. Polysaccharides – hundreds to thousands of units (starch, glycogen, cellulose).

Aldoses and Ketoses

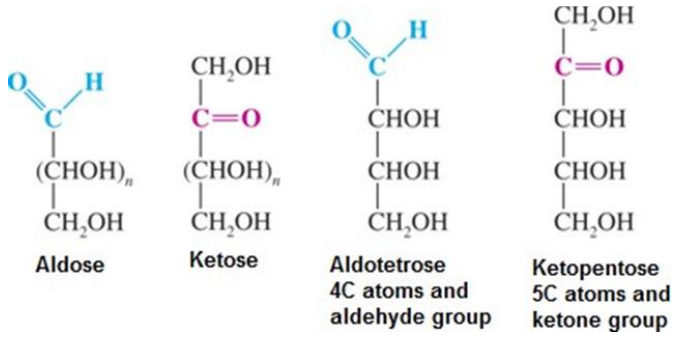
Monosaccharides are classified by:

- Number of carbon atoms (triose, tetrose, pentose, hexose, heptose).
- Functional group:
  - Aldoses – contain an aldehyde group (CHO) at C-1.
  - Ketoses – contain a ketone group (C=O) usually at C-2.

Examples:

- Glyceraldehyde – simplest aldose.
- Dihydroxyacetone – simplest ketose.
- Glucose – aldohexose.

- Fructose – ketohexose.



Genetic Series (Homologous Series) of Aldoses and Ketoses

The genetic relationship describes how monosaccharides of different lengths are related by chain extension or shortening.

Aldoses

Aldoses differ by one carbon atom in a homologous (genetic) series.

- Starting from D-glyceraldehyde, aldoses can be extended via the Kiliani–Fischer synthesis.
- Each chain extension introduces a new asymmetric center → doubling the number of stereoisomers.

Example (Aldose series):

D-Glyceraldehyde → D-Erythrose / D-Threose → D-Ribose / D-Arabinose / D-Xylose / D-Lyxose → D-Glucose / D-Mannose / D-Galactose

Ketoses

Ketoses also form a homologous series but begin with dihydroxyacetone, which is achiral.

- Extension produces ketotetroses, ketopentoses, ketohexoses, etc.
- Their stereochemistry arises from the chiral centers formed after chain length increase.

Example (Ketose series):

Dihydroxyacetone → Erythrulose → Ribulose / Xylulose → Fructose

Stereochemistry of Monosaccharides

Chirality and Asymmetric Centers

Monosaccharides (except dihydroxyacetone) contain one or more chiral centers, making them optically active.

- Number of stereoisomers = 2^n (n = number of chiral centers).

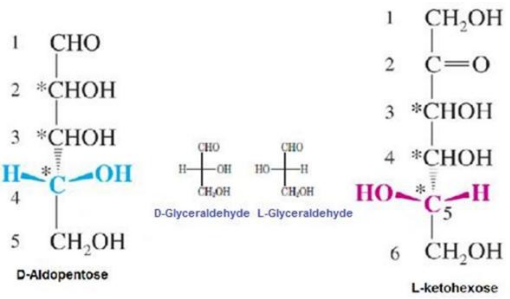
D- and L-Configuration

Based on orientation of the OH group on the asymmetric carbon farthest from the carbonyl group:

- D-series – OH on the right (Fischer projection).
- L-series – OH on the left.

Epimers

Sugars differing by configuration at a single carbon atom (e.g., D-glucose and D-mannose at C-2).



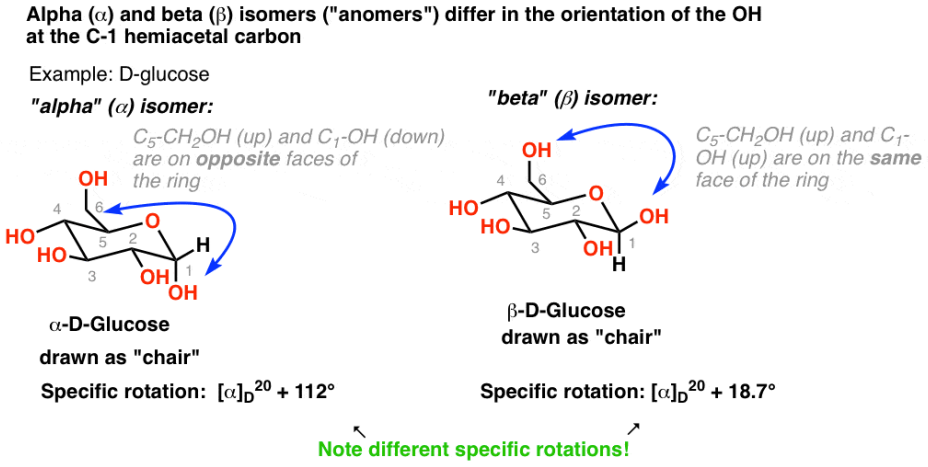
Cyclization and Anomer Formation

Monosaccharides in aqueous solutions exist predominantly in cyclic hemiacetal (aldoses) or hemiketal (ketoses) forms.

- Aldohexoses form pyranose rings (6-membered).
- Ketohexoses can form furanose rings (5-membered).

Cyclization creates a new chiral center at the anomeric carbon → formation of:

- α-anomer – OH group down (trans to CH_2OH).
- β-anomer – OH group up (cis to CH_2OH).



Mutarotation

Mutarotation is the change in optical rotation due to interconversion of α- and β-anomers via the open-chain form in aqueous solution.

Mechanism:

1. Cyclic form (α or β) ⇄ open-chain aldehyde/ketone ⇄ cyclic form (α or β).
2. Equilibrium leads to a mixture of anomers with characteristic optical rotation.

Example:

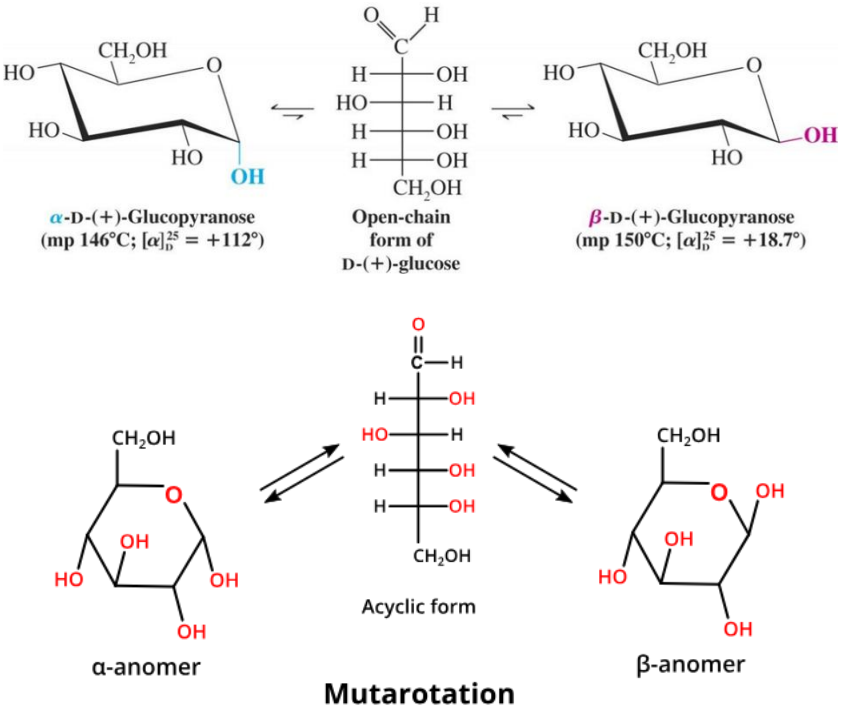
D-Glucose:

- α-D-glucopyranose → +112°
- β-D-glucopyranose → +18.7°
- Equilibrium: about +52.7°

Mutarotation is important for:

- sugar reactivity,

- enzyme specificity,
- structural stability in biological systems.



Questions for Knowledge Assessment

1. How are carbohydrates classified according to their structure and complexity?
2. What structural feature distinguishes aldoses from ketoses?
3. Explain the concept of the genetic series of monosaccharides.
4. Why does the number of stereoisomers increase along the aldose series?
5. What is the basis of the *D/L* classification of monosaccharides?
6. Describe the formation of *α*- and *β*-anomers.
7. What is mutarotation and how does it proceed mechanistically?
8. Provide an example of epimeric monosaccharides.
9. Why does glucose predominantly form the pyranose ring?

Recommended Literature

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