Carbohydrates Notes

${\bf Hankertrix}$

April 29, 2025

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1 Definitions

1.1 Carbohydrates

Carbohydrates are polyhydroxyl aldehydes or ketones with the general formula $(CH_2O)_n$.

1.1.1 Functions of carbohydrates

- Cellular fuel: Metabolism of sugars provide energy to run the cell and carbon atoms for biosynthesis.
- Cellular components: Sugars are components of biomolecules and other cellular structures.

1.2 Monosaccharides

Monosaccharides, or **simple sugars**, have from 3 to 7 carbon atoms, and one aldehyde or one ketone group. They cannot be broken down into simple sugars under mild conditions.

1.3 Aldose

Aldose is a sugar molecule that has an **aldehyde** group. The aldehyde group is always at the **end** of the carbon chain.

1.4 Ketose

Ketose is a sugar molecule that has a **ketone** group. The ketone group is always on the **second carbon** of the chain.

1.5 Oligosaccharides

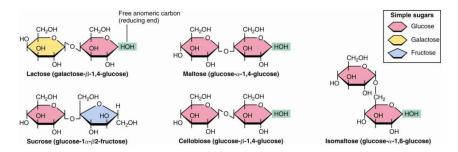
Oligosaccharides are made of 2 to 10 simple sugar residues.

1.6 Polysaccharides

Polysaccharides are polymers of monosaccharides. They contain **acetal and ketal** linkages, which are stable under physiological condition. **Enzymes** are needed to break the **glycosidic bonds** in polysaccharides.

1.7 Disaccharides

Disaccharides are also polymers of monosaccharides, but they are only made of 2 monosaccharides. They are two monosaccharides linked by a **glycosidic bond**, which is O-R bond, where the R group comes from the alcohol. The free substituted anomeric carbon is the **reducing** end, which means that **it itself gets oxidised**.



1.8 Epimer

Epimers are carbohydrates that differ in the location of the -OH group in **one** location.

1.9 Tautomer

Tautomers are structural isomers (constitutional isomers) of chemical compounds that readily interconvert, by relocating a proton (H^+) in a process called tautomerisation.

1.10 Mutarotation

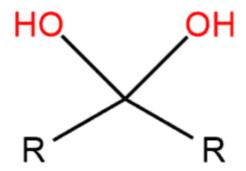
Mutarotation is the change in optical rotation of a chiral material due to the interconversion between the alpha (α) anomeric form of a carbohydrate to its beta (β) anomeric form and vice versa.

1.11 Reducing sugars

Reducing sugars refer to any sugar that is capable of acting as a reducing agent. This means that

1.12 Carbonyl hydrate

Carbonyl hydrate is the functional group shown below:



The mechanism is shown below:

1.13 Hemiacetal

Hemiacetal is the functional group shown below:

The mechanism is shown below:

Hemiketal is just the hemiacetal functional group with its **hydrogen** replaced with a \mathbf{R} group. Both hemiacetal and hemiketal are **unstable** and are usually in rapid equilibrium with carbonyl and alcohol in aqueous solutions at physiological pH (pH 7.4).

$$\stackrel{\mathsf{HO}}{\searrow_{\mathsf{H}}} \stackrel{\mathsf{OR}}{\longleftarrow} \stackrel{\mathsf{O}}{\longleftarrow_{\mathsf{H}}} + \mathsf{ROH}$$

1.14 Acetal

Acetal is the functional group shown below:

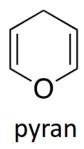
Ketal is just the acetal functional group with its **hydrogen** replaced with a R group. Both ketal and acetal are usually stable and are not in rapid equilibrium with carbonyl and alcohol in aqueous solutions at physiological pH (pH 7.4).

1.15 Anomers

Anomers are cyclic monosaccharides that differ from each other in the configuration of the C-1 or C-2 carbon. For aldoses, it is the C-1 carbon, and for ketoses, it is the C-2 carbon. When the -OH group is **below** the carbon atom, it is called the α -anomer, and when the -OH is **above** the carbon atom, it is called the β -anomer.

1.16 Pyranose

Pyranose is a cyclic carbohydrate (sugar) with 6 members. The name comes from pyran, which is shown below:



1.17 Furanose

Furanose is a cyclic carbohydrate (sugar) with 5 members. The name comes from furan, which is shown below:



furan

1.18 Monosaccharide derivatives

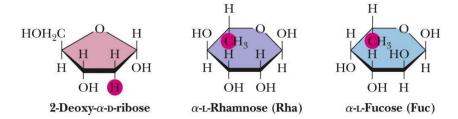
Monosaccharide derivatives are molecules with functional groups that are derived from monosaccharides.

1.18.1 Sugar alcohols

Sugar alcohols are formed by mild reduction of sugars. Sugar alcohols such as sorbitol, mannitol, and xylitol sweeten many "sugarless" gums and candies.

1.18.2 Deoxy sugars

Deoxy sugars are monosaccharides with one or more hydroxyl (-OH) groups replaced by hydrogens H. 2-Deoxy-D-ribose is a constituent of DNA.

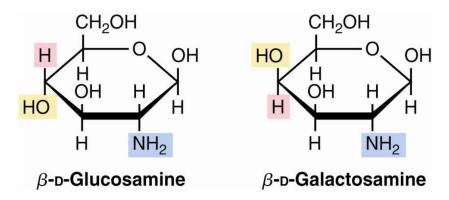


1.18.3 Sugar esters

Sugar esters are phosphate esters. The phosphate esters of glucose, fructose, and other monosaccharides are important metabolic intermediates. The ribose moiety of nucleotides such as ATP and GTP is phosphorylated at the 5' position.

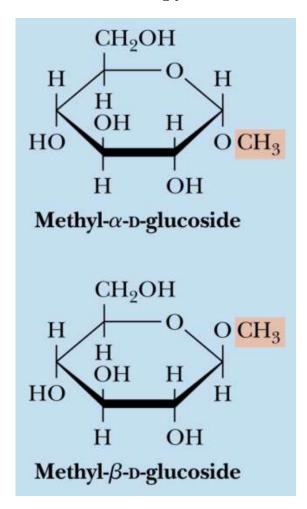
1.18.4 Amino sugars

Amino sugars are sugars with an amino group at C-2. They are found in many oligosaccharides and polysaccharides.



1.18.5 Glycosides

Glycosides are the product of the dehydration reaction between monosaccharides and alcohols. This reaction retains the α - or β -configuration at the C-1 carbon. The new bond is called a **glycosidic bond**.



2 Terminology of carbohydrates

The -ose ending indicates a carbohydrate, and simple sugars are known by common names like **glucose**, **ribose**, and **fructose** rather than systematic names. The number of carbon atoms in an aldose or ketose is specified by the prefixes tri-, tetra-, pent-, hex-, or hept-.

3 Fischer projection forms

- The stereochemistry at the chiral carbon **furthest away** (highest number) from the functional group (ketone or aldehyde) determines the **D** or **L** configuration.
- -OH group on the right \rightarrow **D-configuration**
- -OH group on the left \rightarrow **L-configuration**
- Most naturally-occurring carbohydrates are in the D-configuration.

3.1 Manipulation of Fischer projections

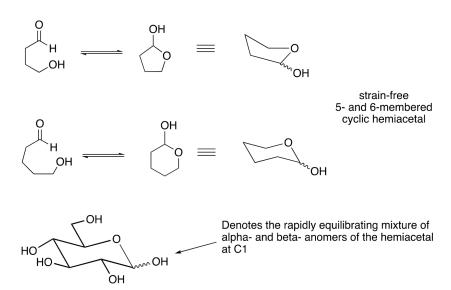
3.1.1 Fischer projections can only be rotated by 180°

3.1.2 Rotating 90° or 270° results in an enantiomer

These two compounds are enantiomers

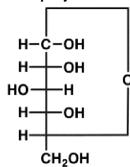
3.1.3 If one group of the Fischer projection is held steady, the other groups can be rotated either clockwise or counterclockwise

4 Intramolecular carbonyl addition

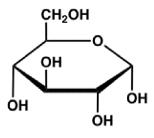


5 Haworth projection form

Haworth projection (1929) An improvement over the cyclic Fischer projection



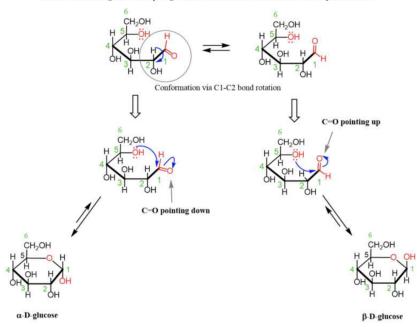
α-D-Glucopyranose (cyclic Fischer projection)



 α -D-Glucopyranose Haworth projection

6 Formation of anomers

Formation of $\alpha\text{-}D\text{-}glucose$ and $\beta\text{-}D\text{-}glucose$ anomers via intramolecular nucleophilic attack



7 Common sugars in biological chemistry

7.1 Pyranose

7.1.1 D-glucose

D-glucose

7.1.2 D-mannose

D-mannose (C2 epimer: C2-OH axial)

7.1.3 D-galactose

$$HO$$
 OH
 OH
 OH
 OH

D-galactose (C4 epimer: C4-OH axial)

7.2 Furanose

7.2.1 Ribose

Ribose is used in adenosine triphosphate (ATP), which is shown below:

7.3 Disaccharides

7.3.1 Lactose

It's also known as galactosyl-beta-1,4-glucose.

Disaccharide: galactosyl-beta-1,4-glucose Lactose (the sugar in mother's milk)

7.3.2 Cellobiose

It's also known as the glucosyl-beta-1,4-glucose.

7.3.3 Maltose

It's also known as the glucosyl-alpha-1,4-glucose.

7.4 Polysaccharides

7.4.1 Cellulose

It is made up of poly-beta-1,4-glucosyl units and is used as a structural polymer in plants.

7.4.2 Starch or glycogen

It is made up of poly-alpha-1,4-glucosyl units and is used as an energy storage polymer in plants and animals.