

Reactions and derivatives of monosaccharides, disaccharides, O- and N-glycosidic bonds, examples

Monosaccharides are derivatives of hydrocarbons, or of furan and pyran heterocycles, from which their basic division into **furanoses** and **pyranoses** is derived. They are a basic component of the food of animals, including humans. They contain **several chiral carbons**, which allows the formation of epimers and enantiomers (right- and left-handed antipodes that turn the plane of polarized light to the opposite side in solution).

See the *Carbohydrates* page for more detailed information.

Reactions of monosaccharides

Mutarotation

A so-called mutarotation can occur within one carbohydrate cycle. It is a condition where a carbohydrate **changes its optical rotation** upon dissolution. This is made possible by the fact that the C-1 carbon of the aldose is the chiral center of the cyclic molecule. We call the corresponding isomers **anomers**.

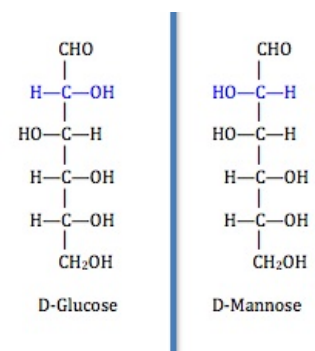
Epimerization

An isomerization reaction that takes place in a weakly basic environment. In the presence of an optically active substance (e.g. glucose), **its configuration changes**. D-glucose can thus transition to D-mannose, which only differs in configuration at C-2. An epimer of glucose is also D-galactose, which is distinguished by its configuration at C-4. Such pairs are then called **epimers**.

Redox reaction

The reduction of monosaccharides at the C-1 position (in the presence of Ni, Pt) produces the sugar alcohol **glucitol** (reduction of glucose → sorbitol).

Oxidation takes place preferentially on the first carbon, when the aldehyde group is oxidized to form a carboxyl. This is how sugar acids are formed → **aldonic acid** (in the case of glucose – gluconic acid). Oxidation can also take place on the last carbon to form **uronic** (glucuronic) acid, or it can take place on both carbons at the same time and thus aldaric (glucaric) **acid is formed**.



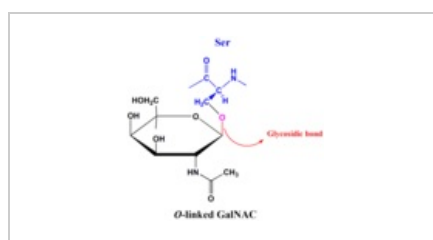
Epimers D-glucose and D-mannose

Esterification

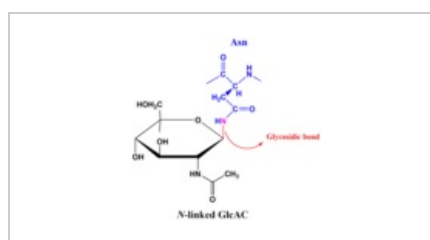
Reaction of monosaccharides (hydroxyl groups) with acids. In the body, the most common reaction of monosaccharides is with phosphoric acid (phosphorylation), which produces, for example, glucose-6-phosphate.

Glycosidic Bond

Acetate **bond of carbohydrates with -OH group** (e.g. alcohols, lipids, other carbohydrates - formation of oligo- and polysaccharides) or with **-NH₂** (e.g. nitrogenous bases in DNA and RNA). All monosaccharides with a carbonyl group can react with -OH to form a **hemiacetal**. The reaction taking place is a nucleophilic addition. The hemiacetal can further react with another nucleophilic group to form a total acetal to form a glycoside and water. This stabilizes the sugar and loses its reducing effects. The bond is called **O-glycosidic**. **The N-glycosidic bond** is formed by the reaction of a monosaccharide **with the -NH₂ or -NH group**. The resulting compounds are called nucleosides. In the human body, they occur in conjunction with phosphoric acid (phosphoric esters of nucleoside → nucleotides). It forms the basis for ATP, ADP, etc.



O-glycosidic bond



N-glycosidic bond

Carbohydrate Report

If a monosaccharide finds itself in a strongly acidic environment, a furan derivative is formed from the given monosaccharide, or pyran. Furfural is formed from ribose by dehydration , **5-hydroxymethyl-furfural** is formed from glucose by dehydration . This product can subsequently react with phenols and aromatic amines, condensation occurs and a colored condensation product is formed. We use these reactions to identify **carbohydrates** and distinguish aldoses from ketoses and pentoses from hexoses.

reaction	card	reagents used	result and evaluation
Molischova	general carbohydrate test	H 2 SO 4 , naphthol	purple product (monosaccharides faster than oligo-/polysaccharides)
Bialova	distinguishing pentoses from hexoses	HCl, orcinol , FeCl 3	<i>pentoses</i> – blue-green colouring <i>hexoses</i> – brown colouring
Selivanova	distinguishing aldohexoses from ketohexoses	HCl, resorcinol	red coloring <i>ketosis</i> – 1-2 min. <i>aldoses</i> – more than 3 min. <i>disaccharides</i> (containing ketohexose) – 3 min.
Schiff	proof of the free aldehyde group	Schiff's reagent	the reaction of the reagent with an aldehyde produces a violet-red product, the reaction with aldoses is slower
Benedict's	reducing properties of carbohydrates	alkaline environment, Benedict's reagent	reduction of Cu 2+ to Cu + occurs <i>monosaccharides</i> – orange-red Cu 2 O precipitate <i>reducing disaccharides</i> – orange-red Cu 2 O precipitate <i>non-reducing disaccharide y</i> – no color change
Barfoed's	reducing monosaccharides from reducing disaccharides	acetic acid, copper acetate	they reduce Cu 2+ at higher temperatures to form a red-orange Cu 2 O precipitate <i>monosaccharides</i> – fast course <i>disaccharides</i> – slow progress
Lugol's	starch	polyiodide ions	dark blue coloration

We can demonstrate the reducing properties of carbohydrates due to their ability to **reduce heavy metal ions** (at higher temperatures) that are bound in a complex. **The Tollens** and **Fehling** reactions, as well as **the Barfoed** and **Benedict tests** (see table) , are based on this principle .

They reduce all monosaccharides (aldoses and ketoses). In an alkaline environment, ketoses isomerize to aldoses, which can be reduced. Disaccharides containing free hemiacetal hydroxyl (lactose, maltose) also give a positive reaction. Starch hardly reduces, only its terminal glucose containing hemiacetal.

In medicine, we use these tests for a simple **urine examination** (e.g. when a metabolic disorder of carbohydrates is suspected)

Derivatives of monosaccharides

Esther

They are formed by the reaction of a saccharide (-OH) with an acid. The most important carbohydrate esters in the body are esters formed by reaction with trihydrogenphosphoric acid (phosphates). Such esters include, for example, **glucose-6-phosphate** , **fructose-6-phosphate** , **fructose-1,6-bisphosphate** , which participate in, for example, the process of glycolysis . Phosphorus esters can also be found in **nucleotides and nucleic acids**.

Amino derivatives

Derivatives that have the -OH group at C-2 replaced by an amino group, which is usually acetylated. The compound **N-acetylamino derivative** (acetic acid amide) is thus formed. Among the most important amino derivatives are **N-acetyl-D-glucosamine** and **N-acetyl-D-galactosamine** , which are characteristic of heteropolysaccharides and glycolipids .

Uronic acids

Oxidation products of hydroxyl at C-6. They can thus form compounds - glycosiduronates. Uronic acids include, for example, **D-glucuronic** acid , which is a typical structural component of heteropolysaccharides. It also plays an important role in detoxification reactions in the liver.

Aldonic acids

They are formed by oxidation of the aldehyde group at C-1. A metabolically important aldonic acid is **D-gluconic acid** , which is formed as a metabolite of the oxidation part of the pentose cycle .

Aldiols

They are also called sugar alcohols. They are formed by the reduction of the carbonyl group of a saccharide. Both D-glucose and D-fructose enable the formation of **D-sorbitol** , which is used as an artificial sweetener.

Disaccharides

300px|náhled|vpravo|O- a N- glykosidová vazba (https://www.wikiskripta.eu/images/thumb/0/0c/O-_a_N-_glykosidov%C3%A1_vazba.jpg/450px-O-_a_N-_glykosidov%C3%A1_vazba.jpg)

Disaccharides are carbohydrates that are formed by the condensation of 2 monosaccharides with the removal of water. Individual units are connected by O-glycosidic bonds. The opposite process is hydrolysis. Disaccharides taken in with food are broken down in the digestive system using glycosylases (e.g. maltase , lactase).

Representatives of disaccharides

Maltose – a disaccharide composed of two glucose units. It is a reducing sugar (bond: α 1,4). Maltose is obtained by hydrolysis of starch.

Lactose – a disaccharide composed of glucose and galactose. It is also a reducing sugar (bond: β 1,4). It is contained in the milk of mammals (4.8% cow's, 6% human).

Sucrose – disaccharide composed of glucose and fructose. It is a non-reducing sugar (bonds α , β 1,2), as it does not have a free hemiacetal. The most widespread disaccharide that all plants contain (cane sugar).

Links

related articles

- Carbohydrates in human nutrition

Resources

- MATOUŠ, Bohuslav, et al. *Fundamentals of medical chemistry and biochemistry*. 1st edition. Prague: Galén, 2010. 540 pp. ISBN 978-80-7262-702-8 .
- <https://el.lf1.cuni.cz/p9og07ou0x7/>

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