Ministry of Public Health of Ukraine
Poltava State Medical University
Department of biological and bioorganic chemistry

Carbohydrates 1. Structure and chemical properties of monosaccharides.

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Lecture plan

- **Functions of carbohydrates**
- **Classification and nomenclature of monosaccharides**.
- **Isomers of monosaccharides.**
- **Chemical reactions of monosaccharides**

Carbohydrates

- The carbohydrates are the biomolecules consisting of carbon (C), hydrogen (H) and oxygen (O) atoms, usually with a hydrogen–oxygen atom ratio of 2:1 (as in water) with the empirical formula Cm(H2O)n
- The carbohydrates are polyhydroxy (contain many hydroxyl (-OH) groups) derivates of aldehydes or ketones.
- Carbohydrates are classified into three majour classes based on the number of monomer units and the degree of the polymerization:

 - **monosaccharides** (simple sugar, can’t be hydrolyzed): glucose, fructose, ribose

 - **oligosaccharides** (short chains of monosaccharides residues – 2-20 units): sucrose, lactose.

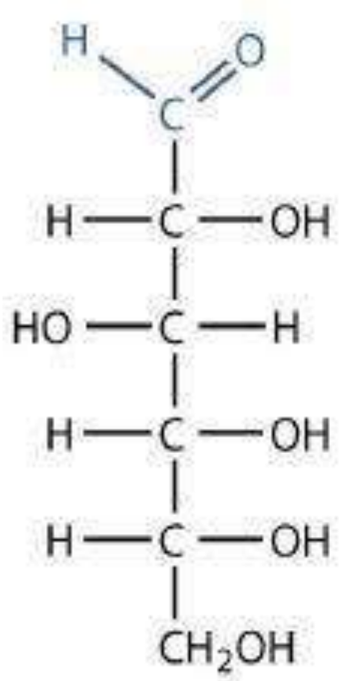
 - **polysaccharides** (long polymers with more than 20 monosaccharides): starch, glycogen, cellulose.

Functions of carbohydrates

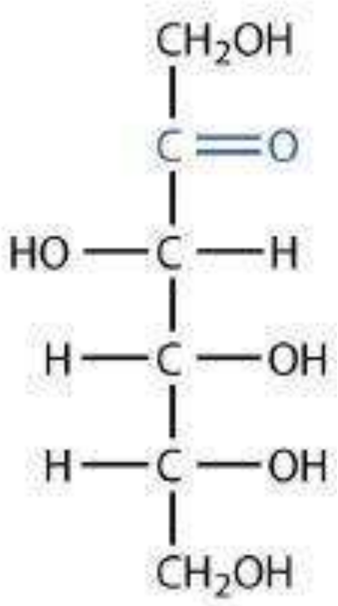
- The primary role of carbohydrates is to supply energy to all cells in the body. Many cells prefer glucose as a source of energy versus other compounds like fatty acids. Some cells, such as red blood cells, are only able to produce cellular energy from glucose (anaerobic oxidation, because they don't contain mitochondrias). The brain is also highly sensitive to low blood-glucose levels because it uses only glucose to produce energy and function. Glucose can cross blood brain barieer. About 70 percent of the glucose entering the body from digestion is redistributed (by the liver) back into the blood for use by other tissues. Cells that require energy remove the glucose from the blood with a transport protein in their membranes.
- Some glucose is converted to ribose and deoxyribose, which are essential building blocks of important macromolecules, such as RNA, DNA, and ATP. Glucose is additionally utilized to make the molecule NADPH, which is important for protection against oxidative stress and is used in synthesise of lipids, amino acids, participate in detoxification of poisons.
- Glucose, galactose are components of lipids (glycolipids), complex proteins such as glycoproteins and proteoglycans of connective tissue.
- The polysaccharide glycogen contributes to the storage of glucose in the body.
- Glycosaminoglycans are heteropolysaccharides of connective tissue: they support the body's shape, maintain the balance of water and minerals, etc.

Classification and nomenclature of monosaccharides

- Monosaccharides can be classified by the **number *x* of carbon atoms** they contain: **triose (3), tetrose (4), pentose (5), hexose (6), heptose (7),** and so on.
- Monosaccharides are also classified as **aldoses or ketoses**. Those monosaccharides that contain an aldehyde functional group are called aldoses; those containing a ketone functional group on the second carbon atom are ketoses.
- Combining these classification systems gives general names that indicate both the type of carbonyl group and the number of carbon atoms in a molecule. Thus, monosaccharides are described as aldotetroses, aldopentoses, ketopentoses, ketoheptoses, and so forth. Glucose and fructose are specific examples of an aldohexose and a ketohexose, respectively.

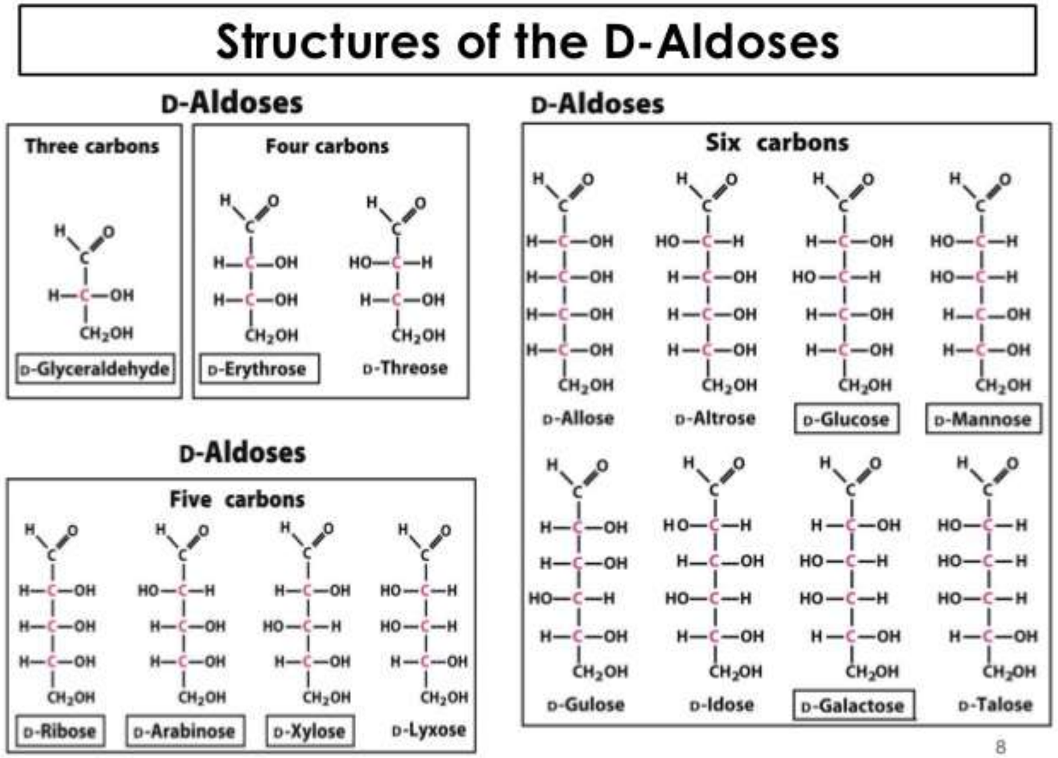


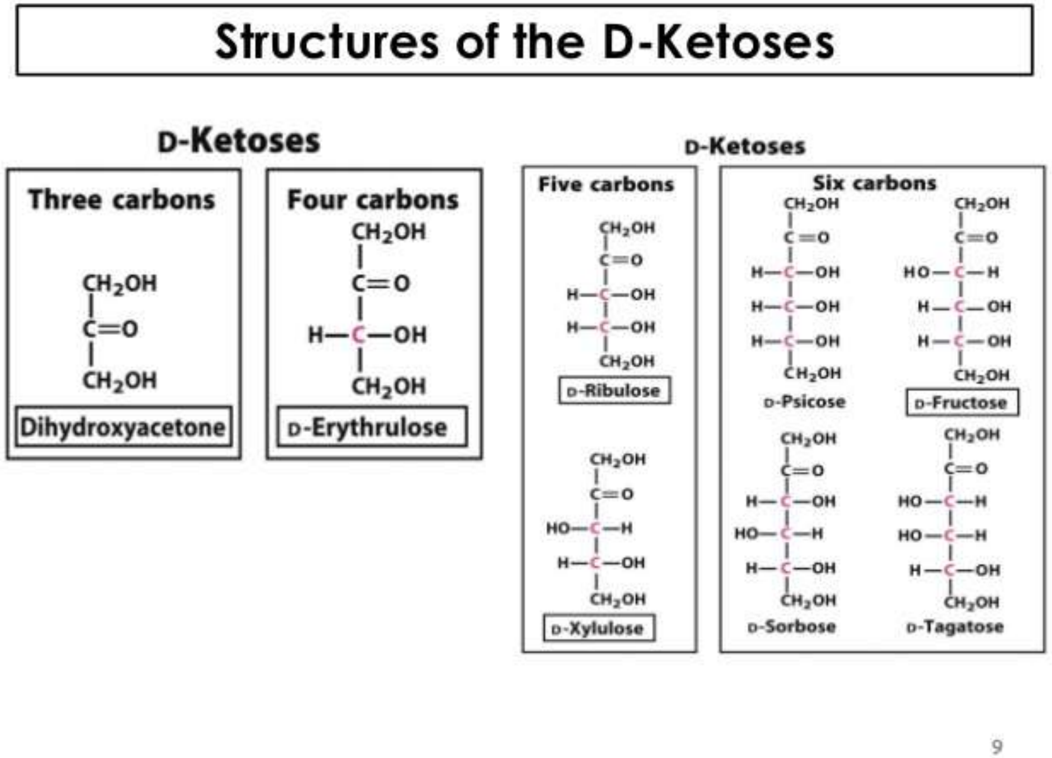
Glucose
(an aldohexose)



Fructose
(a ketohexose)

Examples of monosaccharides



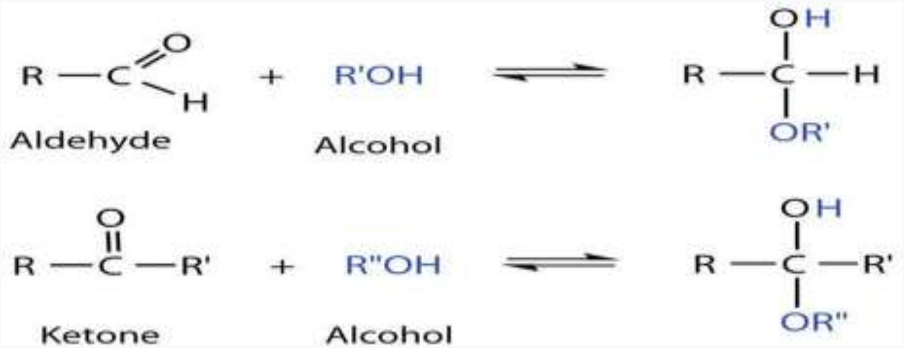


https://www.slideshare.net/MuhammadFazalurRehma3/carbohydrates-59234998

Cyclization of monosaccharides

Formulas of monosaccharides can be presented in the form of linear formulas (Fisher's projection) and in the form of cycles (Heworth's projection).

Linear forms can be converted into cyclic ones, since monosaccharides are aldehydo and keto derivatives of polyhydric alcohols, the functional groups of which can react with each other, forming hemiacetal.

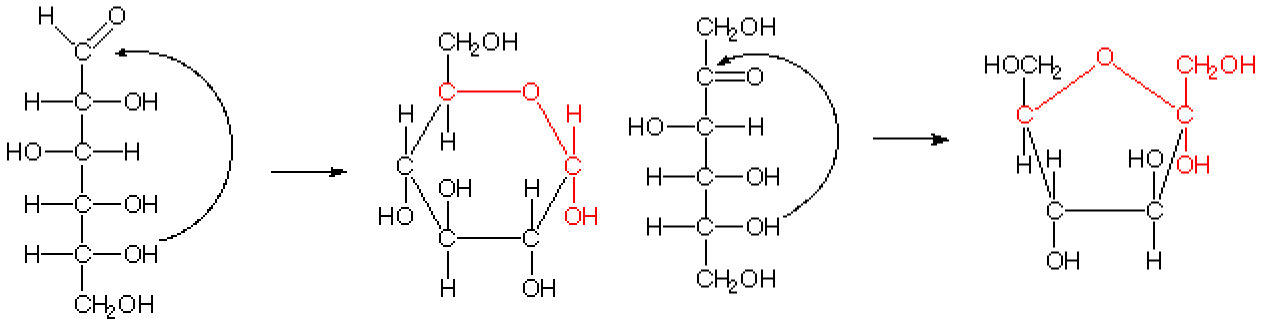


Monosaccharides can exist as a linear chain or as ring-shaped molecules; in aqueous solutions they are usually found in ring forms.

Glucose in a ring form can have two different arrangements of the hydroxyl group (-OH) around the anomeric carbon (carbon 1 that becomes asymmetric in the process of ring formation).

If the hydroxyl group is below carbon number 1 in the sugar, it is said to be in the alpha (α) position, and if it is above the plane, it is said to be in the beta (β) position.

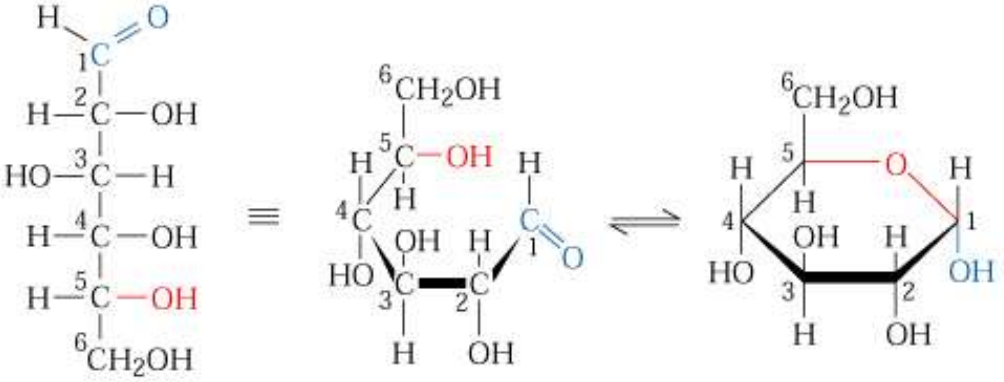
- The cyclic hemiacetal that has a five-membered ring is called a furanose. This name is derived from that of the five-membered, oxygen-containing heterocyclic compound furan. Thr hemiacetal with six-mmembered ring ai a known as pyranose after heterocycle - pyran



Pyran cycle

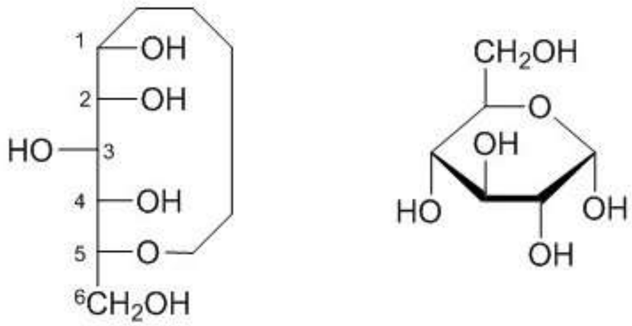
Furan cycle

https://chem.libretexts.org/Courses/Sacramento_City_College/SCC%3A_Chem_309_-_General_Organic_and_Biochemistry_(Bennett)/Text/14%3A_Carbohydrates/14.4%3A_Cyclic_Structures_of_Monosaccharides



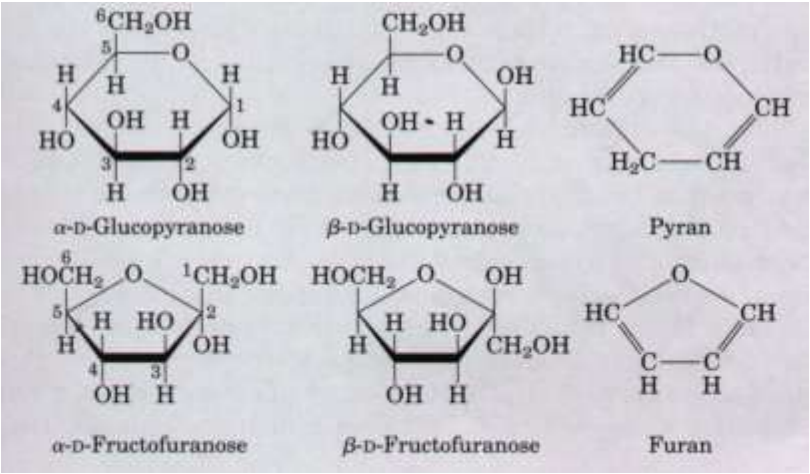
D-Glucose
(linear form)

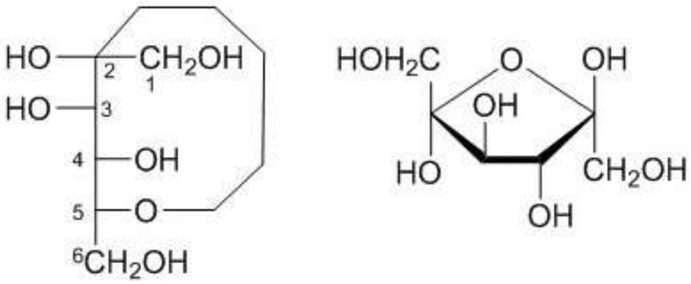
α-D-Glucopyranose
(Haworth projection)



α-D-glucopyranose (α-D-Glc*p*)

pyran





α-D-glucofuranose (α-D-Glc*f*)

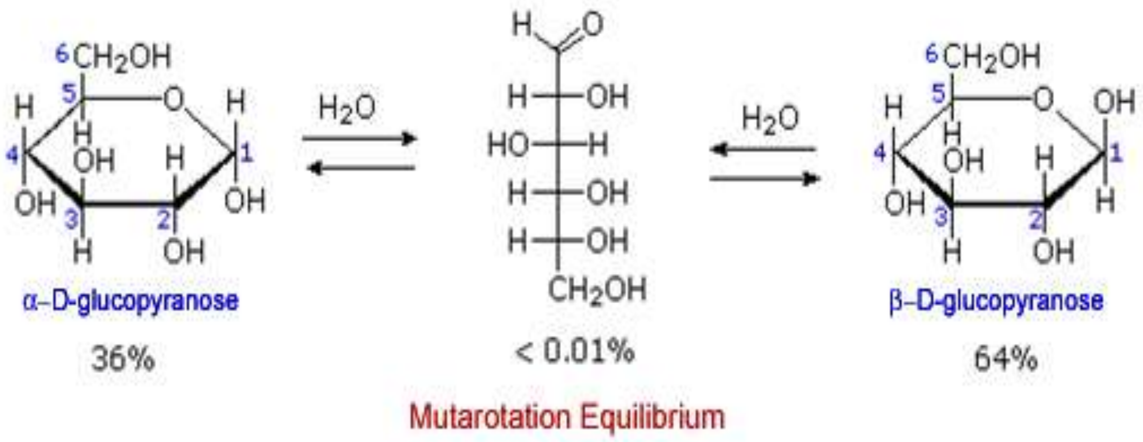
furan

http://www.bioinfo.org.cn/book/biochemistry/chapt11/bio1.htm

https://www.sciencedirect.com/topics/medicine-and-dentistry/tetrose

Mutarotation

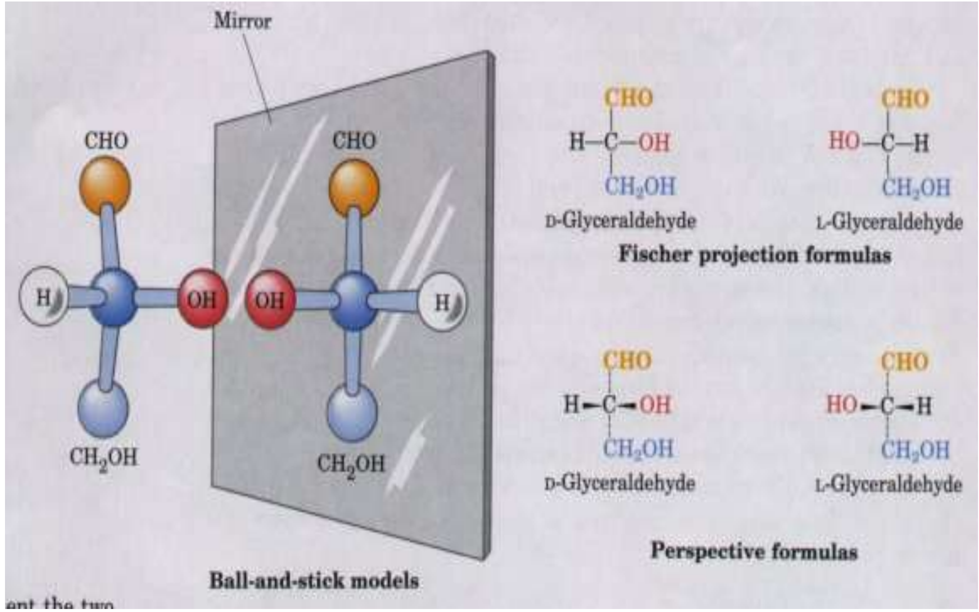
- Mutarotation is the change in the optical rotation because of the change in the equilibrium between two anomers, when the corresponding stereocenters interconvert. Cyclic sugars show mutarotation as α and β anomeric forms interconvert. The optical rotation of the solution depends on the optical rotation of each anomer and their ratio in the solution.



https://www.pinterest.com/pin/489273946990104263/

Isomers of monosaccharides

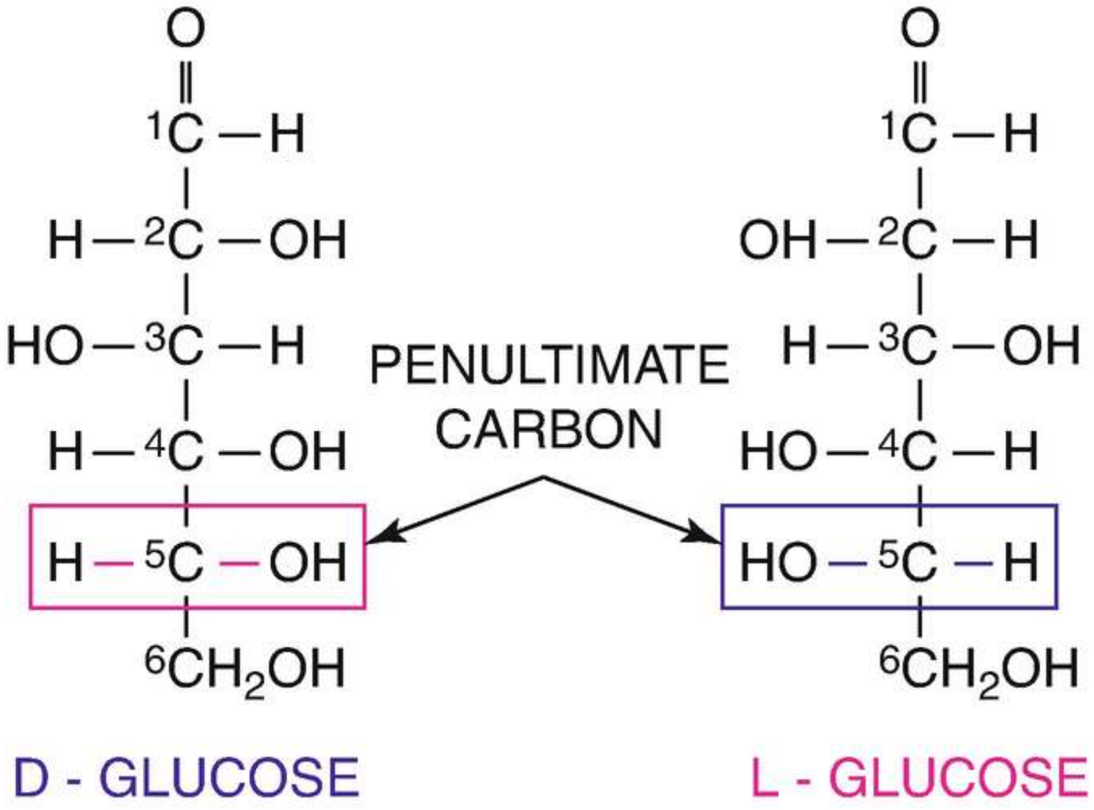
- All the monosaccharides except dihydroxyacetone contain one or more asymmetric (chiral) carbon atoms and thus occur in optically active isomeric forms. The simplest aldose, glyceraldehyde, contains a chiral center (the middle carbon atom) and therefore has two different optical isomers, or enantiomers. By convention, one of these two forms is designated the D isomer of glyceraldehyde; the other is the L isomer. To represent three-dimensional sugar structures on paper, we often use Fischer projection formulas.
- In general, a molecule with n chiral centers can have 2n stereoisomers. Glyceraldehyde has 21 = 2; the aldohexoses, with four chiral centers, have 24 = 16 stereoisomers. The stereoisomers of monosaccharides of each carbon chain length can be divided into two groups, which differ in the configuration about the chiral center most distant from the carbonyl carbon; those with the same configuration at this reference carbon as that of D-glyceraldehyde are designated D isomers, and those with the configuration of L-glyceraldehyde are L. isomers. When the hydroxyl group on the reference carbon is on the right in the projection formula, the sugar is the D isomer; when on the left, the L isomer. Of the 16 possible aldohexoses, 8 are D forms and 8 are L. Most of the hexoses found in living organisms are D isomers.



http://www.bioinfo.org.cn/book/biochemistry/chapt11/bio1.htm

Isomers of monosaccharides

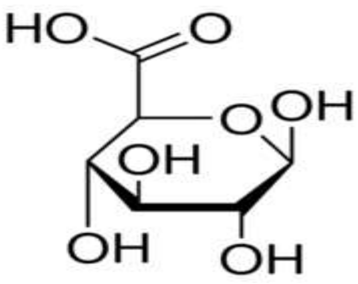
- Carbon atoms are numbered beginning from the reactive end of the molecule, the CHO (aldehyde) or “C” double bonded “O” (carbonyl) end of the molecule.
- Each carbon atom is then numbered in order through the end of the chain.
- When numbering stereoisomers that have more than three carbon atoms we look at the position of the OH group on the penultimate or next to last carbon atom because this determines whether it is an L or D stereoisomer.



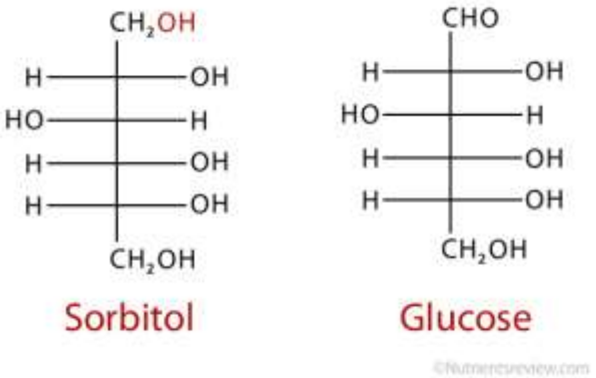
https://link.springer.com/chapter/10.1007/978-981-13-1035-5_6

Chemical reactions of monosaccharides

- **Hexose compounds can undergo a number of chemical reactions:**
- **Oxidation** to acids e.g. glucose, oxidation of CH2OH to COOH produces glucuronic acid:

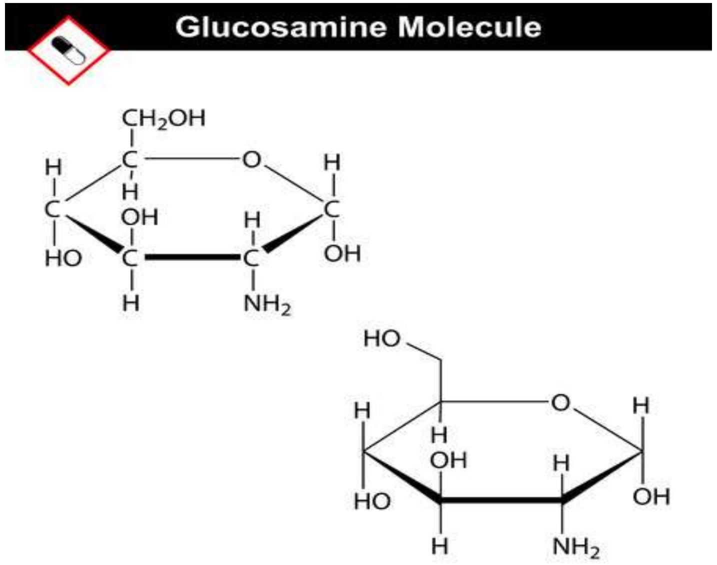


- **Formation of alcohols**, for example glucose forms sorbitol:



https://www.nutrientsreview.com/carbs/sugar-alcohols-sorbitol.html

- **Combine with NH3** to produce hexosamines, for example, glucosamine. Glucuronic acid an hexosamine are examples of monomers of glycosamonoglycans.



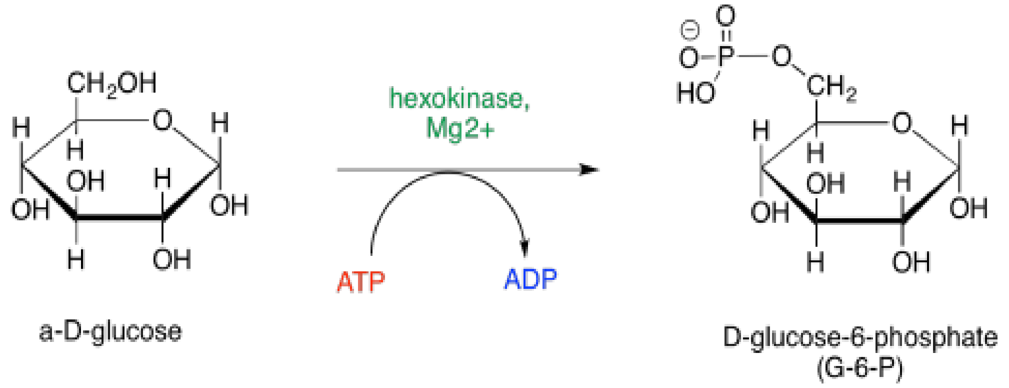
https://www.123rf.com/photo_43890932_stock-vector-glucosamine-structure-component-of-cartilage-tissue-of-joints-structural-chemical-formulas-2d-vector.html

Chemical reactions of monosaccharides

Phosphorylation to hexose phosphates, for example, glucose-l-phosphate and glucose-6-phosphate.

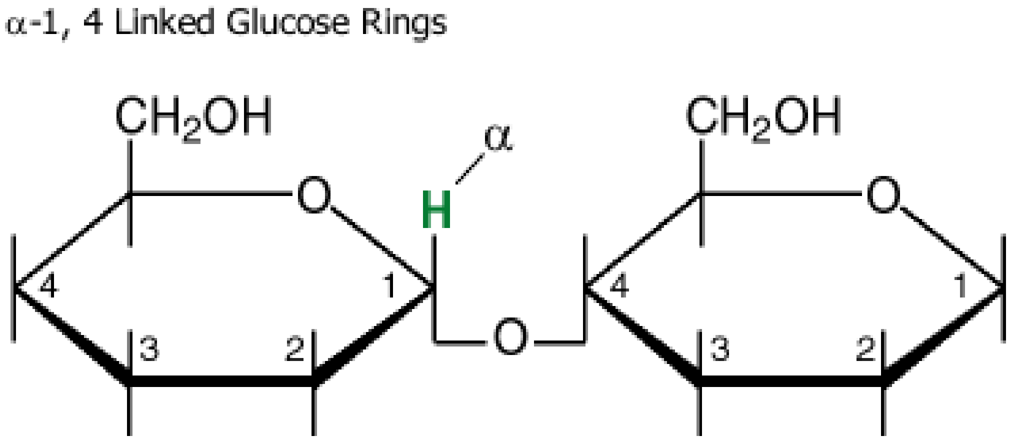
Phosphorylation of glucose is important, because:

- glucose phosphate ester is unable to leave the cell, since the molecule is negatively charged and repels from the phospholipid surface of the membrane,
- the presence of a charged group ensures the correct orientation of the molecule in the active center of the enzyme,
- the concentration of free (non-phosphorylated) glucose in the cell decreases, which facilitates the diffusion of its new molecules from the blood.

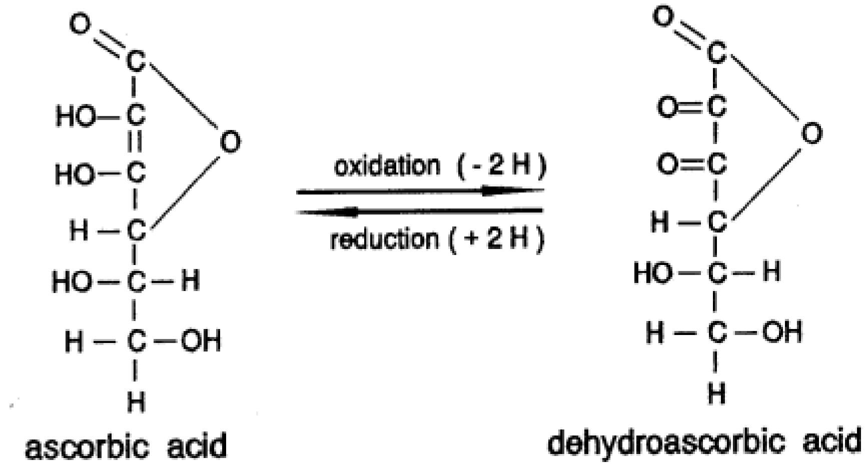


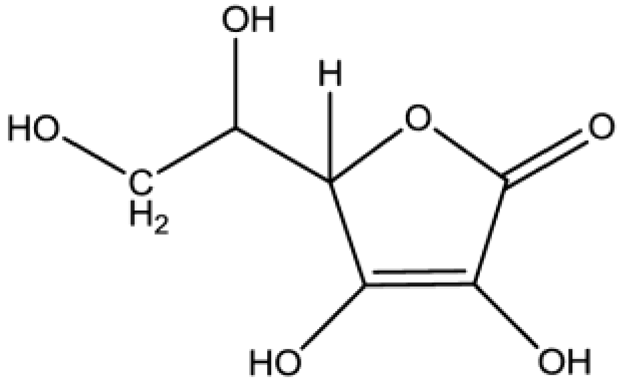
Chemical reactions of monosaccharides

- **Glycoside formation** to produce di, tri, tetra, oligo and polysaccharides, nucleotides.
- Combining the H of a hydroxyl group on a sugar with an alcohol group or another hydroxyl group causes an Esterification or Condensation reaction to yield a glycoside. This occurs at C atom one, the anomeric C atom.



Ascorbic acid





Ascorbic acid (vitamin C):

- takes part in the antioxidant protection of cells;
- takes part in **hydroxylation reactions d**uring the following processes: collagen synthesis (formation of hydroxyproline, hydroxylysine),

synthesis of catecholamines (dopamine, adrenaline), synthesis of steroids, serotonin

http://sites.science.oregonstate.edu/chemistry/courses/ch130/old/VITCTEXT.htm

https://www.researchgate.net/figure/Structural-formula-of-ascorbic-acid_fig1_325442290

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Semyonova T.V. Bioorganic chemistry: Manual /Semyonova T.V. – Simferopol, 2004. – 128p.
Jelena Dodonova. Bioorganic chemistry (Set of lectures)/ Jelena Dodonova. - Vilnius, 2016.-301 p.