

МІНІСТЕРСТВО ОХОРОНИ ЗДОРОВ'Я УКРАЇНИ
ХАРКІВСЬКИЙ НАЦІОНАЛЬНИЙ МЕДИЧНИЙ УНІВЕРСИТЕТ

**CARBOHYDRATES: MONOSACCHARIDES. STRUCTURE AND
FUNCTIONS OF DI- AND POLYSACCHARIDES.**

Methodical instructions for 1st year students' self-work
in Biological and bioorganic chemistry

**ВУГЛЕВОДИ: МОНОСАХАРИДИ. СТРУКТУРА І ФУНКЦІЇ ДИ- ТА
ПОЛІСАХАРИДІВ**

Методичні вказівки для самостійної роботи студентів 1-го курсу
з біологічної та біоорганічної хімії

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Compiled by:

A.O. Syrovaya,
V.N. Petyunina,
V.O. Makarov,
S.V. Andreeva,
L.V. Lukianova,
S.N. Kozub,
T.S. Tishakova,
O.L. Levashova,
E.V. Savelieva,
N.N. Chalenko,
O.S. Kalinenko,
O.A. Zavada,
N.V. Kopoteva,
M.A. Vodolazhenko
H.A. Chistiakova

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Укладачі:

Г.О. Сирова,
В.М. Петюніна,
В.О. Макаров,
С.В. Андрєєва,
Л.В. Лук'янова,
С.М. Козуб,
Т.С. Тішакова,
О.Л. Левашова,
О.В. Савельєва,
Н.М. Чаленко,
О.С. Каліненко,
О.О. Завада,
Н.В. Копотєва,
М.О. Водолаженко
Г.О. Чистякова

Subject I “Carbohydrates: monosaccharides. Structure and functions of di- and polysaccharides”

1. Number of hours – 4.

2. Material and methodological support.

a) Tables:

- Graph structure of the subject;
- Classification of carbohydrates;
- Glycosidic OH-group;
- Ring-chain tautomerism;
- Tautomeric transformations of D-glucose;
- Disaccharides (lactose, maltose, sucrose);
- Composition of vegetable starch;
- Pentoses (ribose, arabinose, xylose);
- Ascorbic acid;
- Непарин Гепарин;
- Glycolysis Гліколіз;
- Chondroitin-6-sulfate;
- Hyaluronic acid.

b) Reactants and equipment: rack with test tubes, graduated pipets, burner; solutions: 0,5% glucose, fructose, starch, 1% sucrose, maltose, lactose, 5% CuSO₄, 10% NaOH, concentrated HCl, 1 drop of diluted I₂ solution.

Educational literature:

1. Biological and Bioorganic chemistry: in two books: Textbook. Textbook 1. Bioorganic chemistry / B.S. Zimenkovsky, V.A.Muzyhenko, I.V. Nizhenkovska, G.O. Syrova; edited by B.S. Zimenkovsky, I.V. Nizhenkovska. – K.: AUP “Medicina”, 2017. – 288 p.

2. Fundamentals of bioorganic chemistry: manual / A. O. Syrovaya, E. R. Grabovetskaya, V. N. Petiunina. – Kharkiv : KhNMU, 2016. – 191 p.
3. Carbohydrates: oligo- and polysaccharides: Methodical instructions for 1st year students' / compiled by A.O. Syrovaya, L.G. Shapoval, V.N. Petyunina, E.R. Grabovetskaya, N.M. Tkachuk, V.A. Makarov, S.V. Andreeva, S.A. Nakonechnaya, L.V. Lukyanova, R.O. Bachinsky, S.N. Kozub, T.S. Tishakova, O.L. Levashova, N.V. Vakulenko, N.N. Chalenko. – Kharkiv: KhNMU, 2013. – 30 p.
4. Carbohydrates: monosaccharides. Structure and functions of di- and polysaccharides: methodical instructions for 1st year students' self-work / compiled by A.O. Syrovaya, V.N. Petyunina, V.O. Makarov et al. – 2nd edition, revised, corrected and expanded – Kharkiv: KhNMU, 2018. – 28 p.
5. Text of Lectures.

3. Substantiation of the subject.

Carbohydrates are probably the most abundant and widespread organic substances in nature, and they are essential constituents of all living things. They participate in metabolic and energy-releasing processes in the human and animal body. Carbohydrates as main components of food provide energy for life functions. Carbohydrates are the precursors for synthesis of other compounds in the body, for example, fats, amino acids, steroids.

Carbohydrates and their derivatives are used in applied medicine: 40% solution of glucose, glycosides (for example, digitalis – as cordial agent and dextran as blood substitute).

Disorders of carbohydrate metabolism are characteristic for many diseases such as diabetes mellitus, lactose and fructose intolerance, galactosemia, glycogen storage diseases, damages of liver and nervous system.

Knowledge about the structure of mono- and polysaccharides and their properties can be used in practice of future doctors and in medico-biological investigations.

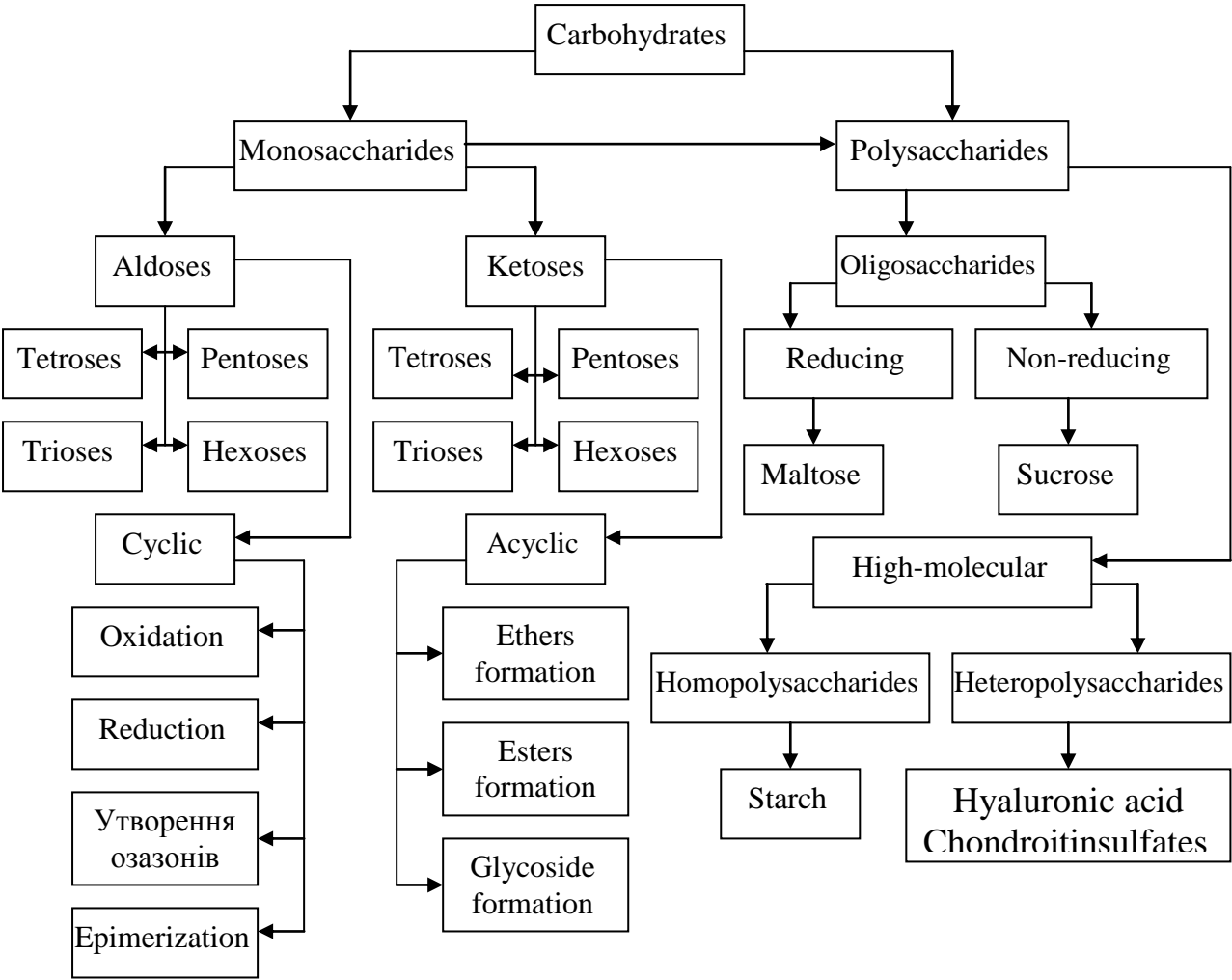
4. The purpose of the subject:

1. To know the classification of monosaccharides by number of carbon atoms and functional groups, depending on the ring size and location hemiacetal hydroxyl.
2. To study the most stable conformation of the hexoses.
3. To learn the properties associated with the existence of a hemiacetal (glycoside) hydroxyl in monosaccharide molecules
4. To be able to illustrate properties of monosaccharides linked to the presence of carbonyl and hydroxyl groups (oxidation, reduction, the formation of ethers, esters, hexoses epimerization in an alkaline medium).
5. To know the monosaccharide composition, structure, conformation of the most important disaccharides (maltose, lactose, cellobiose, sucrose).
6. To learn Find out the fractional composition of starch, linear and spatial structure of amylose and amylopectin and glycogen – glycogen.
7. To learn the basic chemical properties of starch: hydrolysis, the compound inclusion.
8. To know the composition and structure of the major heteropolysaccharides: hyaluronic acid, heparin, chondroitin sulfate.

5. Practical skills:

1. To be able to predict the properties of important monosaccharides.
2. To be able to carry out the reaction for monosaccharides.
- 3 To be able to predict the properties of the polysaccharides.
4. To be able to carry out qualitative reaction for the polysaccharides.

6. Graph structure of the subject.



7. Plan of students' work.

№	Stages	Time	Training and visual aids	Location
1.	Motivational characteristics and plan of the subject. Answers to the students' questions	25 min		Class room
2.	Control of students' knowledge baseline	20 min	Tests for initial control	
3.	Students' knowledge correction by solving of educational tasks (individual work)	60 min	Methodical instruction for students, lecture notes, reference data, posters. Manuals, reference materials, tables.	
4.	Laboratory work	35 min	Reactants and equipment	
5.	Control of knowledge	25 min	Tests for control	
6.	Analysis and conclusions. Home work	15 min		

8. Tasks for self-work:

- list of questions to be study:

1. Classification of carbohydrates. Isomerism. Tautomeric forms of monosaccharides. Mutarotation.

2. Chemical reactions of monosaccharides with the participation of carbonyl-group: oxidation-reduction reactions (qualitative reactions for the detection of aldehyde group).

3. Glycoside formation, their role in the structure of oligo- and polysaccharides, nucleosides, nucleotides and nucleic acids. Phosphate esters of glucose and fructose, their significance in carbohydrate metabolism.

4. Ascorbic acid as derivative of hexoses, biological role of vitamin C.

5. Oligosaccharides: structure, properties. Disaccharides (sucrose, lactose, maltose), their biomedical significance.

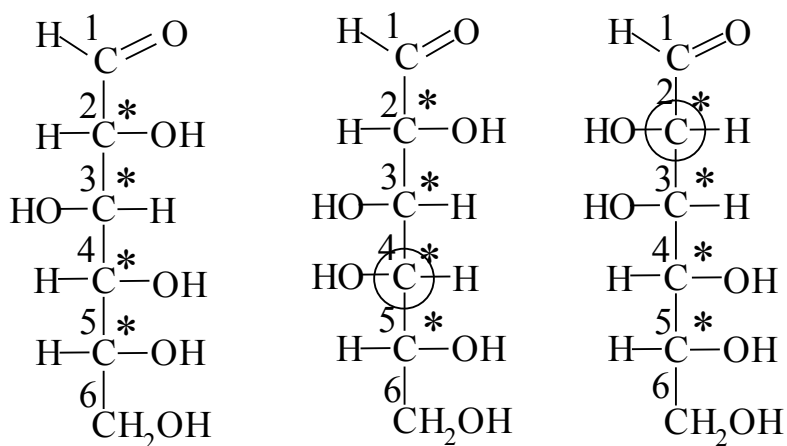
6. Polysaccharides. Homopolysaccharides: starch, glycogen, cellulose, dextran – structure, hydrolysis, biomedical significance. Qualitative reaction of starch.

7. Heteropolysaccharides: determination, structure. Structure and biomedical significance of glucosaminoglycans (mucopolysaccharides) – hyaluronic acid, chondroitin sulfates, heparin.

Teaching tasks and examples of their solution

Task №1. What isomers are characteristic for monosaccharides? What is the difference between optical isomers?

Example of solution: Pentoses and hexoses are the most common in nature. Usually they have unbranched chains, so quantity of the isomers is expected to be quite small. However, monosaccharides contain several asymmetric carbon atoms and therefore they show optical isomerism. Thus, aldohexoses have four asymmetric carbon atoms and 16 optical antipodes. They are divided into eight pairs of D- and L-hexoses which differ in the arrangement of substituents around asymmetric carbon atoms and have the same properties, except for sign of rotation.



Isomers which have different arrangement of hydroxyl groups at some chiral centers have not only different optical activity but also differ in some physical and chemical properties and named differently (glucose, galactose, mannose, etc.).

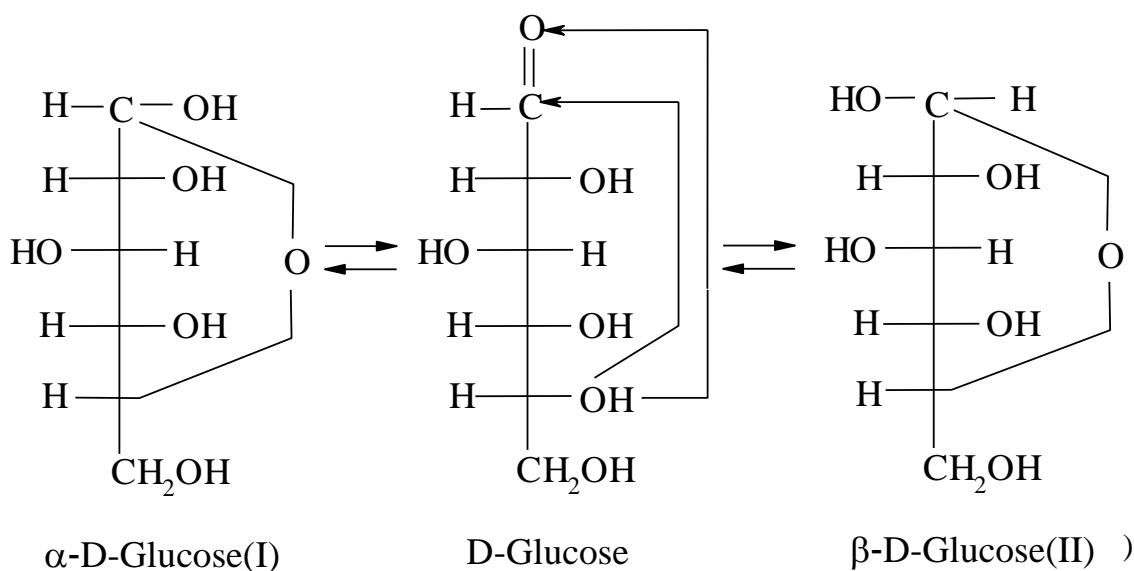
The aldehyde and keto-formulas clearly explain the reactions of these substances. However, there are some properties which can not be explained by the structure of these formulas. Aldoses do not give some characteristic aldehyde

reactions. Glucose, e.g., under normal conditions does not produce coloration with Schiff's reagent. At the same time, some reactions (formation of glycosides) can not be explained by oxo forms.

Task №2. What is the essence of tautomeric transformations of monosaccharides, what is their influence on the chemical properties?

Example of solution: Aldehyde or keto structure is one of tautomeric forms of monosaccharides and most of saccharides exist as cyclic tautomeric forms which are internal hemiacetals of polyhydric aldehydes and ketones.

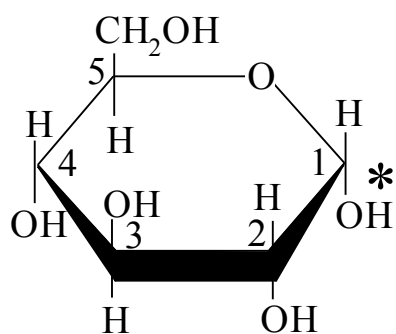
Tautomeric transition of aldehyde or ketone form into cyclic one is the formation of internal hemiacetal due to displacement of hydrogen atom from hydroxyl group at the fifth or fourth carbon atom to a carbonyl group. As a result the carbon atoms become connected through oxygen with the formation of six- or five-membered ring:



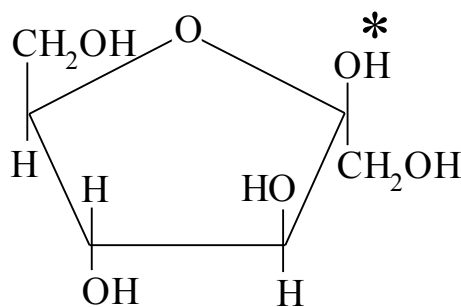
The formation of the cyclic form is accompanied by formation of new hydroxyl group which is absent in the open-chain form. It is called hemiacetal hydroxyl group.

Its properties differ from the other hydroxyl groups because of two reasons. First of all, it is in equilibrium with the carbonyl group and second of all, it is bound with carbon connected to oxygen of the cycle which attracts electronic density. Carbon atom which is linked to a hemiacetal hydroxyl group is asymmetric, thus the existence of two cyclic isomers is possible. They are named as α - and β -anomers - the forms in which the location of hemiacetal hydroxyl group is the same as the location of hydroxyl at the asymmetric carbon atom which defines belonging of the saccharide to D- and L-series.

English chemist Haworth offered to represent cyclic forms of monosaccharides in the form of regular polygons that lie perpendicular to the plane of the figure:

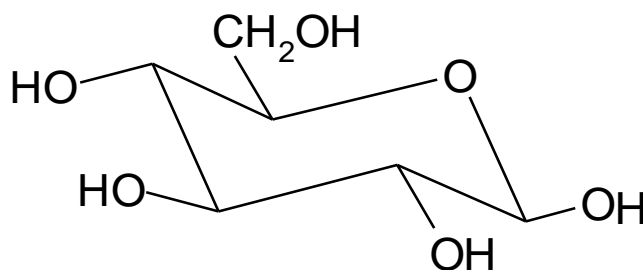


α -D-glucopyranose



β -D-fructofuranose

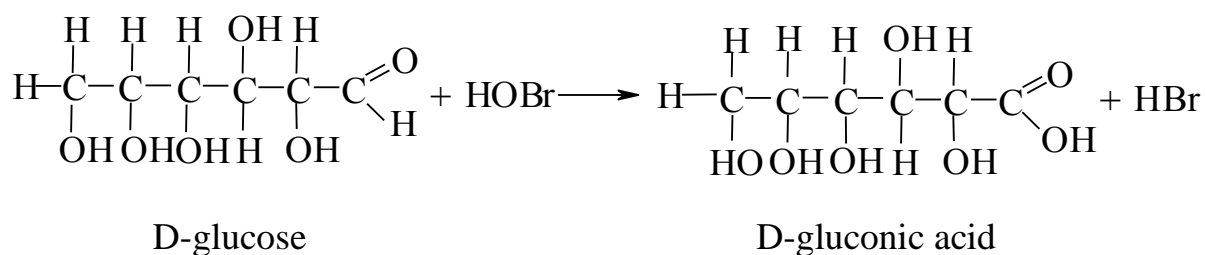
Cyclic monosaccharides can exist in the same conformations as other cycles, which consist of tetragonal carbon atoms, e.g., chair conformation.



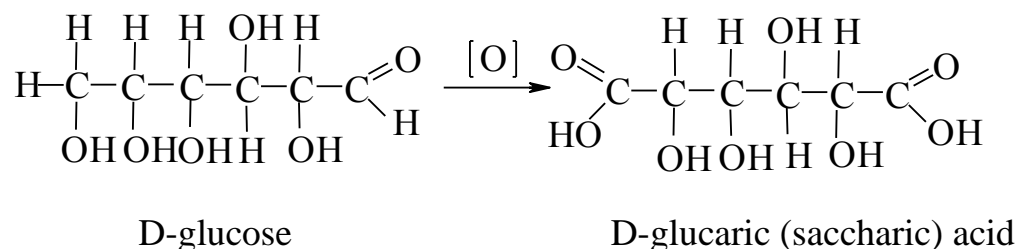
Task №3. What biologically important products can be obtained by oxidation and reduction of glucose?

Example of solution: The presence of different functional groups in monosaccharides, as well as their ability to tautomeric transformations results in high reactivity and variety of chemical properties of monosaccharides. They easily enter oxidation reactions. Products depend on the strength of the oxidizing agents and the pH.

Glucose on reaction with bromine water in neutral medium is oxidized into hydroxy acid with same number of carbon atoms:



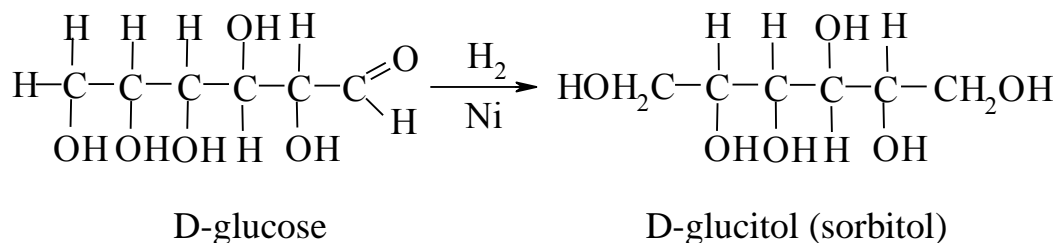
Stronger oxidizing agents (e.g., concentrated nitric acid) oxidize not only aldehyde group but also the primary alcohol group into carboxyl groups. The products are dibasic hydroxy acids:



The most pronounced transformations of monosaccharides take place in alkaline medium. Interaction with the ammoniacal silver nitrate or copper(II)

hydroxide results in breaking of the carbon chain with formation of mixture of different hydroxy acids.

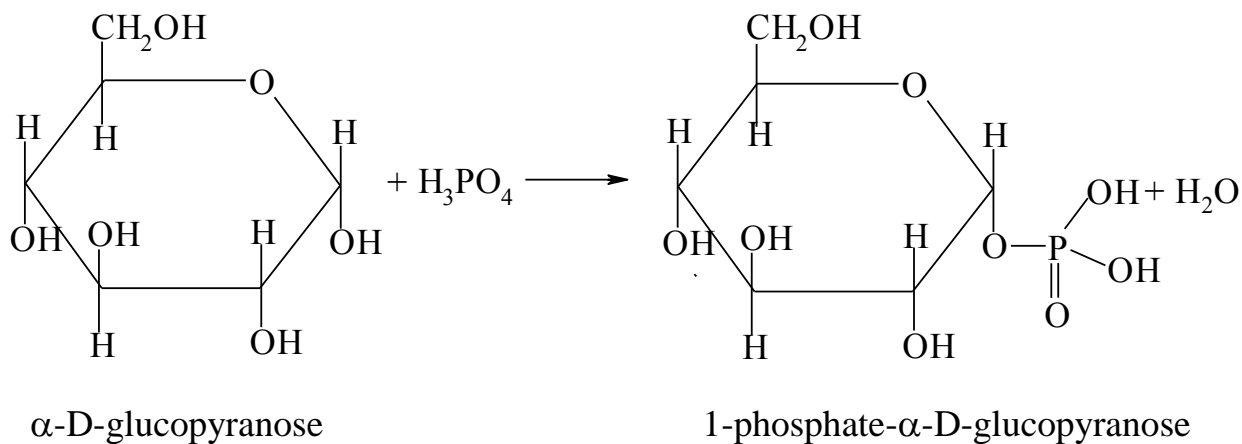
Reduction with hydrogen in the presence of metallic nickel converts monosaccharides into polyhydric alcohols:



Glucose is reduced into hexatomic alcohol sorbitol, which is used as a sugar substitute for diabetics.

Task №4. Write the reaction of monosaccharides with phosphoric acid.

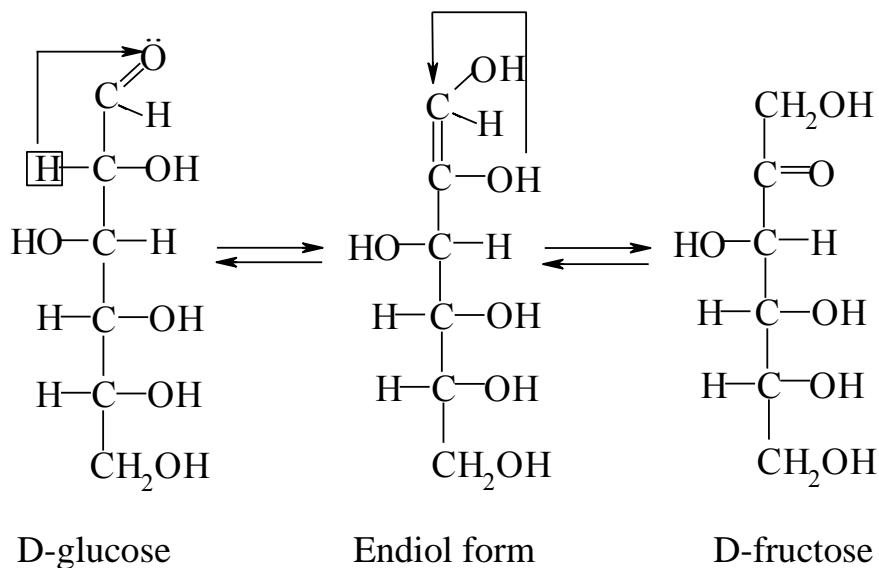
Example of solution: The alcoholic hydroxyls of glucose participate in the formation of ethers with alcohols and esters with acids. Phosphoric acid esters of monosaccharides are of great biological importance.



Phosphate formation is the first step of the biochemical transformations of monosaccharides.

Task №5. What transformations of monosaccharides occur in alkaline medium?

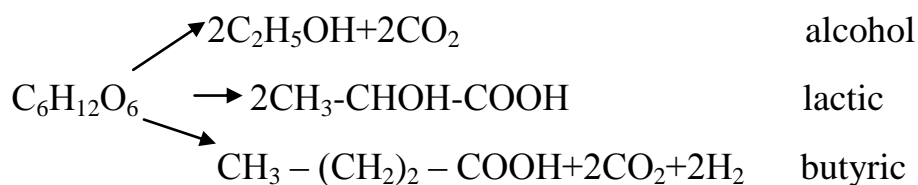
Example of solution: In alkaline medium monosaccharides undergo isomerization via the formation of the enol form:



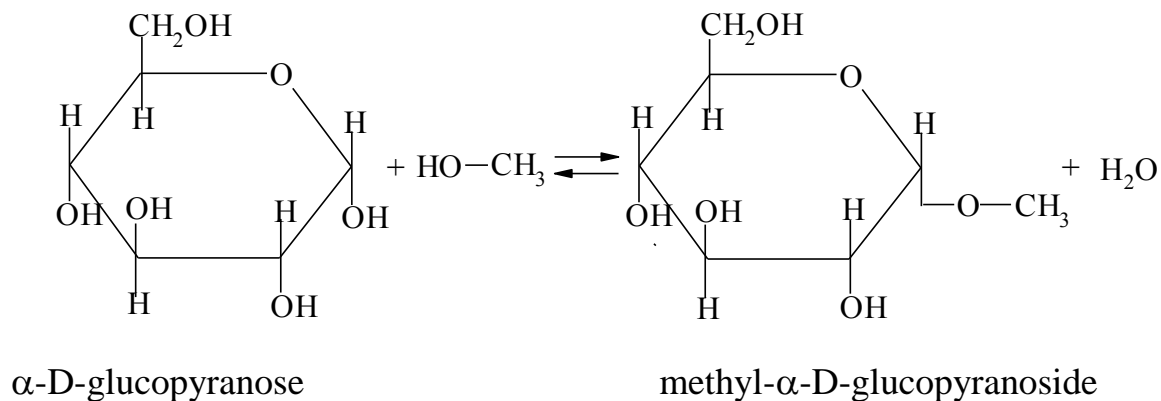
Isomerization of monosaccharides and their derivatives takes place in important biochemical transformations.

Task №6. What transformations of monosaccharides take place under the action of microorganisms?

Example of solution: Conversion of monosaccharides by the action of microorganisms is called fermentation. Depending on the process conditions and the type of microorganisms there are several types of fermentation:



The highest reactivity of the hemiacetal hydroxyl group as compared to other hydroxyl groups allows, under certain conditions (boiling of glucose in alcohol solution containing 2% of dry hydrochloric acid), to obtain acetals of saccharides – glycosides.



Some natural glycosides serve as medicines, e.g., cardiac glycosides.

Task №7. What is the biological role of monosaccharides?

Example of solution: Ribose and deoxyribose are of great biological importance. They are the components of ribonucleic and deoxyribonucleic acids.

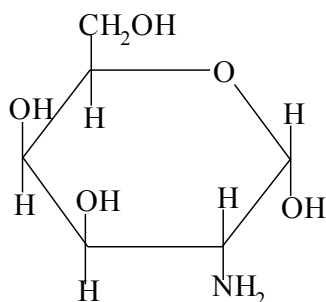
The most common aldohexose is glucose. It is also known as grape sugar, as it is contained in the grape juice. Glucose is also contained in other sweet fruits. There are about 0.1% of glucose in blood.

Fructose is the representative of ketohexoses. This one is the sweetest of all carbohydrates. In large quantity it is found in honey.

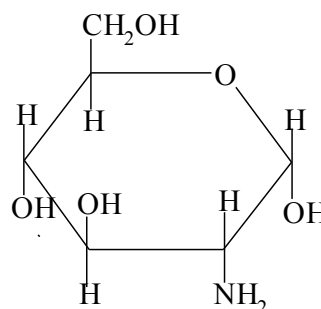
Task №8. Give the structure of the amino sugars. Characterize their properties.

Example of solution: Derivatives of monosaccharides obtained by substitution of alcoholic hydroxyl with amino group are called amino saccharides. They possess strong reducing properties. Residues of amino saccharides enter the composition of

certain polysaccharides.



2-deoxy-2-amino- α -D-galactopyranose
(galactosamine)



2-deoxy-2-amino- α -D-glucopyranose
(glucosamine)

Task №9. Which polysaccharides are called oligosaccharides? Give examples. Characterize bonds between the monosaccharide units and chemical properties.

Example of solution: All polysaccharides can be regarded as anhydrides of simple sugars which are obtained by removal of one or more molecules of water from two and more monosaccharides molecules. Polysaccharides are divided into two subgroups: oligosaccharides - relatively low-molecular weight carbohydrates, which give a small number of molecules of monosaccharides on hydrolysis (name is derived from the Greek "oligos" - few) and high-molecular weight polysaccharides which are composed of hundreds and thousands of monosaccharide residues.

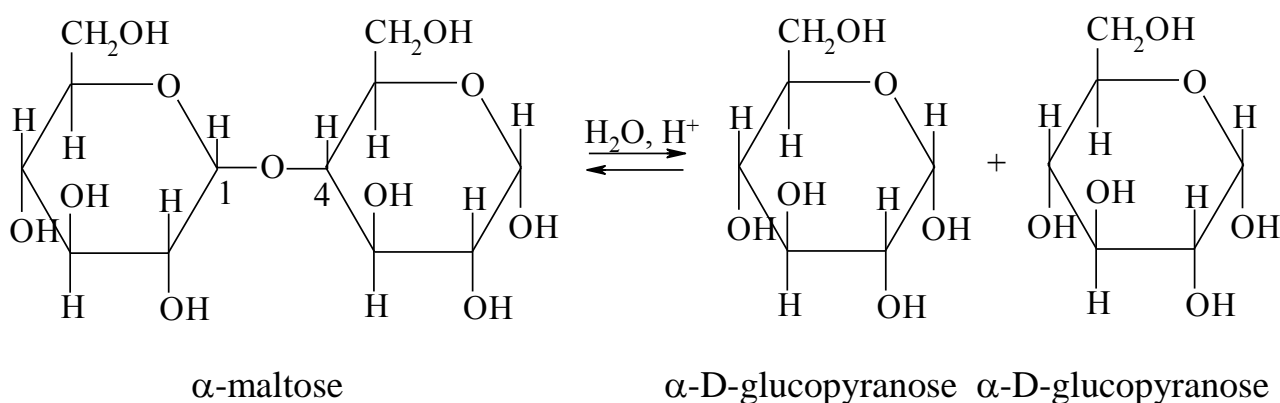
Oligosaccharides exhibit a number of properties which are similar to those of simple carbohydrates: they are highly soluble in water and have a sweet taste.

Disaccharides are the most important. They all are glycosides, that is, a molecule of water is released from two molecules of monosaccharides with obligatory participation of hemiacetal (glycosidic) hydroxyl group. Hydroxyl group of the second molecule which participates in the formation of a glycosidic bond may be either alcoholic or hemiacetal one. In the first case the disaccharide molecule has one hemiacetal hydroxyl, and therefore such compounds have similar properties with

monosaccharides, i.e. they can be easily oxidized, so they are known as reducing disaccharides.

If the disaccharide molecule is formed involving hemiacetal hydroxyls of both monosaccharides they are known as non-reducing disaccharides.

The reducing disaccharides are able to tautomerism due to the presence of hemiacetal hydroxyl group in the molecule. Therefore, they enter chemical reactions that are characteristic for monosaccharides (oxidation with silver oxide, osazones formation, etc.). The most important reducing disaccharides are maltose (malt sugar) and lactose (milk sugar).

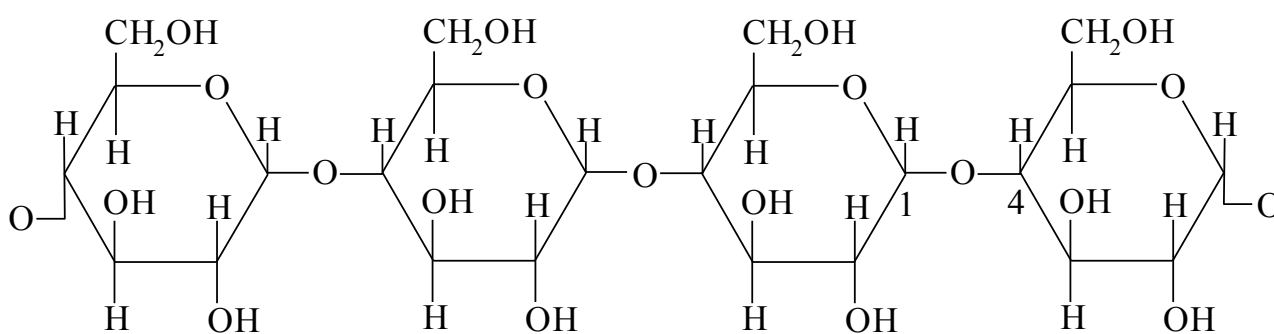


In maltose molecule two residues of α -D-glucose are linked by 1,4-glycosidic bond; lactose consists of residues of D-galactose and D-glucose in β -form.

Sucrose is an example of non-reducing sugars. It consists of residues of D-glucose and D-fructose. Sucrose has no free glycosidic hydroxyl, so it can not be transformed into the open carbonyl form and therefore does not reduce silver oxide and copper(II) hydroxide. Like all polysaccharides, sucrose is capable of hydrolyzing and exhibits the properties of polyols.

Task №10. Which compounds are called homopolysaccharides?

Example of solution: Polysaccharides are high-molecular weight substances, which are composed of hundreds or thousands of monosaccharide residues. These residues may be identical (homopolysaccharides) or different (heteropolysaccharides). Starch and cellulose are the main homopolysaccharides. These polysaccharides are hydrolyzed into glucose. The composition of both compounds is expressed as $(C_6H_{10}O_5)_n$. Glucose residues are joined by glycosidic linkages in the long chains, wherein one molecule provides its hemiacetal hydroxyl and second molecule provides its alcoholic hydroxyl group:

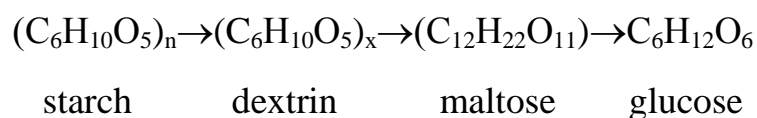


amylose

Cellulose and starch are practically deprived of reducing properties, as they have only one hemiacetal hydroxyl group per several hundreds or even thousands of glucose residues.

Task №11. What are the products of partial and complete hydrolysis of starch?

Example of solution: At rapid heating starch breaks into simpler molecules which are called dextrans with the same molecular formula as that of the starch, but with a smaller number of units. Further refluxing with mineral acids gives subsequent cleavage with formation of maltose initially and then glucose. Thus, a simplified starch hydrolysis can be represented as follows:

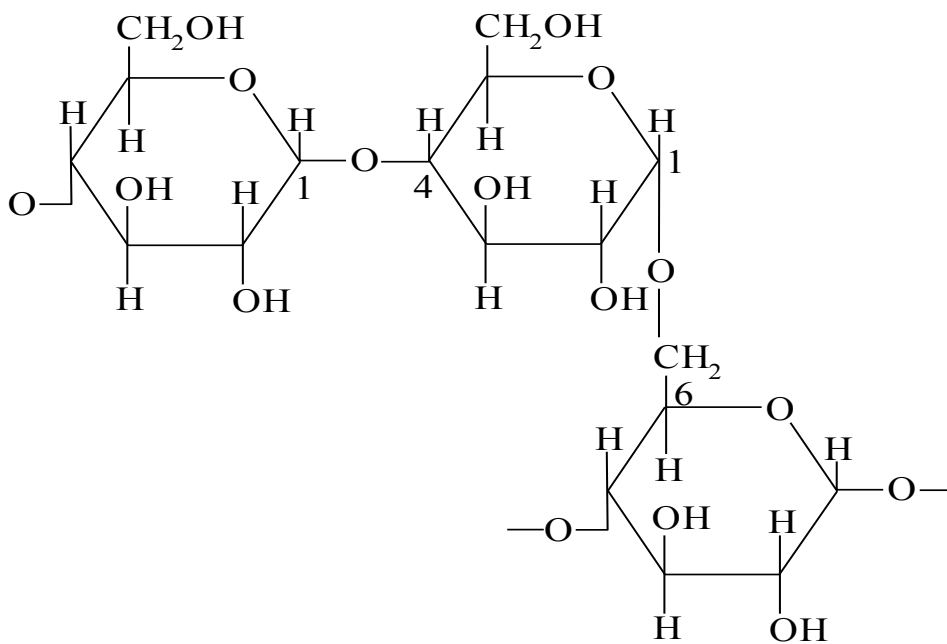


Task №12. Give the structures of the vegetable and animal starch.

Example of solution: Analysis of the structure of starch showed that it is not a unified substance, but it is a mixture of the two fractions - amylose and amylopectin. In most plants starch is comprised of 15-20% of amylose and 80-85% of amylopectin. Amylose molecule is constructed from α -D-glucose units linked by 1,4-glycosidic bonds.

Amylose molecule contains from 200 to 1000 glucose units and has a spatial structure, forming a spiral coil which consists of six glucose residues. This spatial structure is a consequence of the axial location of hemiacetal hydroxyl group in glucose. Inside spiral amylose molecule there is a channel with a diameter of about 5 nm. This channel can include molecules of suitable size, forming a special kind of complexes, the so-called inclusion compounds. Complex of amylose with iodine can serve as example of such compounds. It is blue in color, and its formation is used for the qualitative determination of starch.

Amylopectin is branched polysaccharide with a molecular weight of over one million (polymerization degree is 6000). Amylopectin, as well as amylose, consists of α -D-glucose, but its molecule has more than 30 branches due to 1,6-glycosidic linkages. Due to branched structure amylopectin has spherical shape.

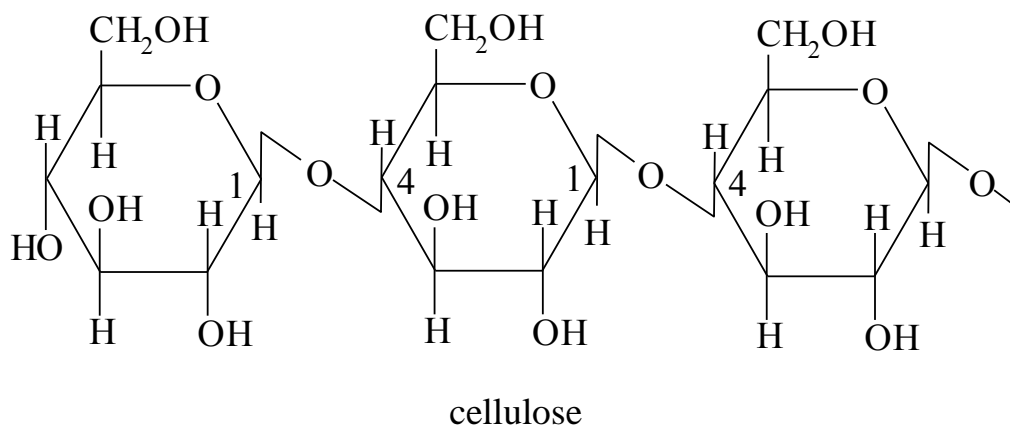


amylopectin

Animal starch - glycogen is contained in all animal organisms. Its molecules are very similar to those of amylopectin, but glycogen molecules are much more branched. Glycogen is well soluble even in cold water. Glycogen serves as storage carbohydrate in the organism. Its content in liver is about 20% and about 4% in muscles. All the processes of life, primarily the work of the muscles, are accompanied by the breakdown of glycogen, this process leads to release of energy.

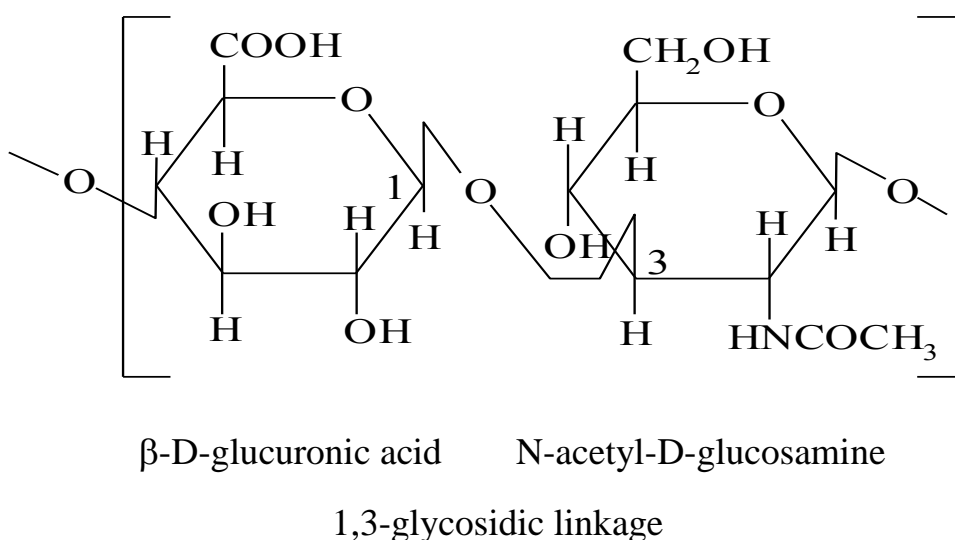
Task №13. Give the composition and structure of cellulose.

Example of solution: Cellulose is the most abundant naturally occurring polysaccharide. It forms walls of the plant cells, gives the mechanical strength and elasticity to the plant tissues. The average molecular weight of the cellulose of plant origin is in the range of 100,000 to 1,000,000. Cellulose consists of residues of β -D-glucose linked by 1,4-glycosidic bonds and has a linear structure:



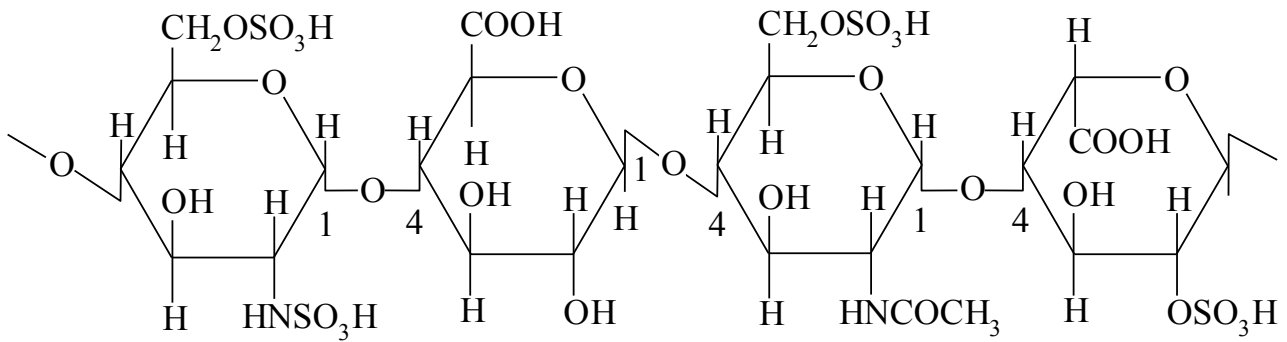
Task №14. What are heteropolysaccharides? What are their constituent parts?

Example of solution: Heteropolysaccharides are polysaccharides built from the residues of different monosaccharides. They are widely distributed in nature in the form of complexes with proteins. Hyaluronic acid is contained in connective tissue, vitreous body of the eye, synovial fluid. On hydrolysis it produces glucosamine, glucuronic acid and acetic acid. The structural components of hyaluronic acid are glucuronic acid and N-acetylglucosamine linked by 1,3-glycosidic bonds:



Heteropolysaccharide - heparin is in the organs and tissues of animals and humans. Especially there are a lot of heparine in the liver, lungs, heart, and skeletal

muscles. It was isolated in a crystalline state, and is widely used as substance for preventing blood coagulation (anticoagulant). Heparin molecule includes glucuronic acid, L-iduronic acid and partially sulfated glucosamine:



heparin

Revision exercises

№ 1

1. Write the formula of α -D-glucopyranose (Haworth formula). Specify atom which determines its belonging to the D-series.
2. What are the monosaccharide units in cellulose? Write a fragment of cellulose structure and specify the linkage between the monosaccharides.
3. Write the reduction reaction of alkaline copper(II) hydroxide solution with glucose. What is the use of this reaction?

№ 2

1. Write the formula of β -D-glucopyranose and its 6-phosphate (Haworth formulas). Specify atom which determines its belonging to the D-series.
2. Write the hydrolysis of sucrose. Name the product. Specify the glycosidic bond in sucrose molecule.
3. What property of glucose is the basis of its interaction with Fehling's reagent? Specify the composition of the reagent.

№ 3

1. Write the formula of α -D-galactopyranose (Haworth formula). Specify atom which determines its belonging to the D-series.
2. What are mucopolysaccharides? Write the structure of the components of chondroitin-6-sulfate and specify the nature of the linkage between them.
3. Write the reaction of glucaric acid formation from D-glucose. Specify the conditions.

№ 4

1. Write the formula of β -D-galactopyranose (Haworth formula). Specify atom which determines its belonging to the D-series.

2. Show the structure of chondroitin-4-sulfate. Name monomers.
3. Which properties of glucose are shown in "silver mirror" test?

№ 5

1. Write open-chain formulae of D-mannose and D-xylose. Specify atom which determines its belonging to the D-series.
2. Write the reaction equation of glycoside formation from disaccharide maltose and ethanol.
3. Which reaction can prove the existence of several hydroxyl groups in hexose?

№ 6

1. Show phenomenon of ring-chain tautomerism on example of D-ribose (furanose cycle). Which biopolymers contain D-ribose?
2. Name fractions of vegetable starch. How do they differ in structure?
3. Which polysaccharides are called homopolysaccharides? Name the monosaccharide units of dextran and specify the nature of bonds between them. Give structure of the fragment of the main chain.

№ 7

1. Write the formula of β -D-ribofuranose (Haworth formula). Specify atom which determines its belonging to the D-series.
2. Write formula of disaccharide consisting of D-glucuronic acid and N-acetylglucosamine linked by 1,3-glycosidic bond. Which biopolymer is composed of such disaccharides?
3. Write the reaction of D-glucuronic acid decarboxylation. Name the product obtained.

№ 8

1. Write the formula of β -D-deoxyribofuranose (Haworth formula). Specify atom which determines its belonging to the D-series.
2. Give the structure of amylopectin. Which products are obtained by its hydrolysis?
3. Write the reaction of oxidation of D-galactose into D-galactonic acid. Specify the conditions.

№ 9

1. Write the formula of β -D-deoxyribofuranose (Haworth formula). Specify atom which determines its belonging to the D-series.
2. Give the structure of sucrose and explain the reason for the absence of reducing properties.
3. Give an equation for the formation of D-gluconic acid from D-glucose. What is the oxidizing agent?

№ 10

1. Write open-chain formulae of D-ribulose and D-xylulose. Specify atom which determines its belonging to the D-series.
2. What are the monosaccharide units of glycogen? Write the structure of the glycogen molecule and show the chain branching.
3. What property of glucose is shown in Trommer reaction?

№ 11

1. Write the formula of β -D-fructofuranose (Haworth formula). Specify atom which determines its belonging to the D-series.
2. Write the hydrolysis of lactose (milk sugar). Name the products and bond in the molecule of lactose.
3. Write the reaction of glucose reduction with ammoniacal silver oxide solution. What is the use of this reaction?

№ 12

1. Write the formula of α -D-fructofuranose (Haworth formula). Specify atom which determines its belonging to the D-series.
2. Write the hydrolysis of sucrose. Name the resulting monosaccharides. Does sucrose possess reducing properties?
3. Write reaction equation of glucose with Fehling's reagent.

№ 13

1. Write the formula of 1,6-diphosphate- β -D-fructofuranose in the open-chain form and in Haworth formula. Specify atom which determines its belonging to the D-series.
2. Write the hydrolysis of maltose (malt sugar). Name the products and bond in the molecule of maltose.
3. How to obtain pentoses from hexuronic acids?

№ 14

1. Write 2- α -D and 2- β -D-glucosamine in pyranose ring as Haworth formulas. Specify atom which determines its belonging to the D-series.
2. Write the hydrolysis of cellobiose. Name the products and bond in this molecule.
3. What reaction can show reducing properties of glucose?

№ 15

1. Write 2- α -D and 2- β -D-galactosamine in pyranose ring as Haworth formulas. Specify atom which determines its belonging to the D-series.
2. Write formula of disaccharide consisting of D-glucuronic acid and N-acetylglucosamine linked by 1,3-glycosidic bond. Which biopolymer is composed of such disaccharides?
3. What reaction can prove the presence of some hydroxyl groups in glucose?

SUGGESTED READINGS

1. Biologically important classes of bioorganic compounds. Biopolymers and their structural components: Theoretical course of biological and bioorganic chemistry, Module 1 / A.O. Syrovaya, E.R. Grabovetskaya, N.M. Tkachuk et al. – Kharkov: KhNMU. – 2013.– 183 p.

2. Zurabyan S.E. Fundamentals of bioorganic chemistry / S.E. Zurabyan – M.: Geotar-Med. – 2003. – 320 p.

3. Biological and Bioorganic Chemistry: in two books: Textbook. Textbook 1. Bioorganic Chemistry / B.S.Zimenkovsky, V.A.Muzychenko, I.V.Nizhenkovska, G.O.Syrova; edited by B.S.Zimenkovsky, I.V.Nizhenkovska. —K. :AUP «Medicina», 2017. — 288 p.

Навчальне видання

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Упорядники:

Сирова Ганна Олегівна,
Петюніна Валентина Миколаївна,
Макаров Володимир Олександрович,
Андрєєва Світлана Вікторівна,
Лук'янова Лариса Володимирівна,
Козуб Світлана Миколаївна,
Тішакова Тетяна Станіславівна,
Левашова Ольга Леонідівна,
Савельєва Олена Валеріївна,
Чаленко Наталія Миколаївна,
Каліненко Ольга Сергіївна,
Завада Оксана Олександрівна,
Копотева Наталія Василівна,
Водолаженко Марія Олександрівна,
Чистякова Галина Олексіївна.

Відповідальний за випуск: Водолаженко М.О.

Комп'ютерний набір та верстка: Водолаженко М.О.