Министерство здравоохранения республики Беларусь УО «Витебский государственный медицинский университет»

L.G. Hidranovich, O.A. Khodos

БИООРГАНИЧЕСКАЯ ХИМИЯ ЛАБОРАТОРНЫЕ ЗАНЯТИЯ BIOORGANIC CHEMISTRY LABORATORY CLASSES

рекомендовано учебно-методическим объединением по высшему медицинскому, фармацевтическому образованию в качестве учебнометодического пособия для студентов учреждений высшего образования, обучающихся по специальности 1-79 01 01 «Лечебное дело»

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THEMATIC PLAN OF THE LECTURES IN BIOORGANIC CHEMISTRY

No	The theme of the lecture			
1	Introduction. Chemical bonds and mutural influence of atoms in or-			
	ganic compounds.			
2	Spatial structure of organic compounds.			
3	Classification and the mechanisms of the reactions in organic chem-			
	istry. Reactivity of saturated, unsaturated and aromatic hydrocar-			
	bons.			
4	Reactivity of alcohols, phenols, thiols, amines. Acid-base properties			
	of organic compounds.			
5	Reactivity of aldehydes and ketones, carboxylic acids and their de-			
	rivatives.			
6	Poly- and heterofunctional compounds, which are origin of the most			
	important medicament groups and which participate in the processes			
	of ability to live.			
7	Carbohydrates. Monosaccharides.			
8	Carbohydrates. Oligosaccharides and polysaccharides.			
9	Natural amino acids. Peptides and proteins.			
10	Nucleic acids.			
11	Lipids.			
12	Low molecular weight bioregulators. Steroids.			

THEMATIC PLAN OF THE LABORATORY CLASSES IN BIOORGANIC CHEMISTRY

$N_{\underline{o}}$	The themes of the laboratory classes			
1	Classification and nomenclature of organic compounds.			
2	Introduction. Chemical bonds and mutual influence of atoms in organic			
	compounds.			
3	Spatial structure of organic compounds.			
4	Reactivity of saturated, unsaturated and aromatic hydrocarbons. Labora-			
	tory work.			
5	Reactivity of alcohols, phenols, thiols, amines. Acid-base properties of			
	organic compounds. Laboratory work.			
6	Reactivity of aldehydes and ketones. Laboratory work.			
7	Carboxylic acids and their derivatives. Laboratory work.			
8	Poly- and heterofunctional compounds, which are origin of the most			
	important medicament groups and which participate in the processes of			
	ability to live. Laboratory work.			
9	Control-test № 1.			
10	Biologically important heterocyclic compounds. Alkaloids. Laboratory			
	work.			
11	Carbohydrates. Monosaccharides. Laboratory work.			
12	Carbohydrates. Oligosaccharides and polysaccharides. Laboratory work.			
13	Natural amino acids. Structure, properties, functions. Laboratory work.			
14	Peptides and proteins. Laboratory work.			
15	Purine and pyrimidine bases. Nucleosides. Nucleotides. Nucleic acids.			
	Laboratory work.			
16	Control-test № 2. «Biopolymers and their structural units».			
17	Saponified lipids. Peroxide oxidation of lipids. Laboratory work.			
18	Non-saponified lipids. Steroids.			

Introduction

The purpose of teaching of bioorganic chemistry.

Bioorganic chemistry is the sphere of science studying structure and mechanisms of functioning of biologically active molecules on the base of theoretical organic chemistry. The discipline is related to pharmacology, physiology and other medical and biologic disciplines.

The principal purpose of discipline studying is the formation of systematized knowledge about the relationship between structures and chemical properties of biologically important organic compounds as bases for understanding the essence of metabolism and its regulation at molecular level.

Goals of bioorganic chemistry.

The principal goals of bioorganic chemistry teaching at medical universities are the formation of modern ideas about the following:

- structures of natural biologically significant compounds;
- major factors influencing thermodynamic stability of organic molecules;
- mechanisms and features of poly- and heterofunctional organic compounds chemical transformations in vitro as bases for the following understanding processes of enzyme catalysis in vivo;
- principles of biological macromolecules synthesis and self-organizing in vitro and in vivo.

After <u>finishing the course of bioorganic chemistry a student must possess</u> the knowledge of:

- a place of bioorganic chemistry in the system of natural sciences as a branch of chemical sciences studying organic compounds that participate in processes of ability to live;
- a role of bioorganic chemistry in professional training of a doctor and specificity of bioorganic approach to studying processes of ability to live;
- modern physical and chemical methods of investigation of organic compounds structure and their properties;
- modern structural theory, types of chemical bonds, the relationship between the nature of substances, their structure, their reactivity and their biological importance;
- principles of symmetry, chirality and stereoisomerism of natural hetero-functional organic compounds;
- major factors influencing thermodynamic and conformational stability of organic molecules, principles of self-organizing of bioorganic macromolecules and their functioning;
- the newest chemical discoveries and prospects of their use in professional work.

A student must be able to use:

- the basic fundamental laws of chemistry necessary for an explanation of processes proceeding in a live organisms;
 - rules of the international chemical (IUPAC) nomenclature;
- the electronic effects of substituents leading formation of the reaction centers in a molecule and typical reactivity on the main functional groups and the possible mechanisms of transformations of organic compounds in vitro and in vivo;
- the general chemical laws that is the base of processes proceeding in an organism;
- chemical properties and biological importance of the main families of organic compounds participating in processes of ability to live.

A student must gain the following skills:

- carrying out of qualitative tests for determination of the main functional groups, unsatiration, the asid-base and reducing properties of organic compounds;
- usage of reference-book of physical and chemical sizes and tabulated data;
- carrying out of the elementary chemical experiments with following analysis and registration of results in the form of a report;
- prevention of accidents in chemical laboratory.

ACCIDENT PREVENTION.

- 1. Make all laboratory experiments with little quantity of substances. Strictly observe methods of the experiments.
- 2. It is forbidden categorically to taste chemical substances and take them with hands. Smell chemical substances very carefully directing the air from the aperture of the test-tube towards the nose by hand movement.
- 3. Use only clean and dry test-tubes for the experiments.
- 4. Warm the test-tube gradually and carefully. Use the test-tube holder to warm the test-tube. Don't direct the aperture of the test-tube to yourself or other students.
- 5. Carry out all experiments with concentrated acids and bases in the exhaust-hood. Don't admit them to be hitted on the skin to avoid the burn.
- 6. Carry out the experiments with volatile and flammable liquids (benzene, acetone, ethyl ethanoat, ethoxyethane) in the exhaust-hood far from the fire and working hot plates. Don't inhale vapour of volatile compounds to avoid the poisoning.
- 7. Take no risks with toxic substances (benzene, toluol, aniline, benzaldehyde, hydroxylamine). Don't inhale their vapour, avoid hitting the skin.
- 8. Don't pour concentrated acids, bases and reaction mixtures in the washbowl. Pour them into the special phial.
- 9. Inform the teacher if the accident took place. Use the first-aid kit in the laboratory or see a doctor.

THEME 1

Classification and nomenclature of organic compounds.

1. Training and educational goals:

- 1. To form knowledge of:
- classification of organic compounds according to the structure of carbon skeleton and according to the nature of functional groups;
- principal rules of substitutive nomenclature IUPAC and radicofunctional nomenclature.
- 2. To form skills in:
- finding functional groups of biologically important compounds and classifying them according to the structure of functional groups:
- using chemical nomenclature rules to name biologically important compounds.

2. Program questions:

- 1. Classification of the organic compounds according to the structure of carbon skeleton and according to the nature of functional groups.
- 2. IUPAC nomenclature of organic compounds. The parent structure, senior group, locants, prefixes and suffixes.
 - 3. Radicofunctional nomenclature.

3. Literature:

- 1. Bioorganic chemistry: учебное пособие для иностранных студентов / О.Н. Ринейская [и др.]. Минск: Новое знание, 2018. р. 6-13.
- 2. Hidranovich, L.G. Bioorganic chemistry lecture course / L.G. Hidranovich. Vitebsk, 2004. p. 4-16
- 3. Chernykh, V.P. Organic chemistry. Basic lecture course: The study guide for students of higher schools / V.P. Chernykh, L.A. Schemchuk. Kharkiv, 2011. p. 4-13.

4. Homework:

- 1. Prepare the theoretical material according to the program questions of the theme 1.
- 2. Solve the problems \mathbb{N}_2 (c), (d), \mathbb{N}_2 3 (a), (h), (i), \mathbb{N}_2 4 (d), (h), (i), (k) presented on the pages 9-12.

5. Problems.

1. Convert the line structures of following compounds to the condensed structures.

2. Classify each of the following compounds.

a)
$$CH_2-CH_2$$
 b) H_3C-N $O-C-CH$ Atropine CH_2-CH_2 b) H_3C-N $O-C-CH$ CH_2-OH Atropine $COOH$ $O-C-CH$ $O-C-C$

f)

g) H_2N -CH-COOH h) (i) H_2N -CH-COOH CH_2 -CH $_2$ -CH $_3$ (i) H_2N -CH-COOH CH_2 -CH $_3$ (ii) CH_2 -CH $_3$ (iii) CH_3

- 3. Give systematic IUPAC names for each of the following:
- (a) $H_3C-S-CH_2-CH_2-CH-COOH$ b) $HOOC-CH=C-CH_2-COOH$ NH₂ COOH
- (c) CH_3 - CH_2 - CH_2 - CH_2 - CH_3 (d) CH_3 -S- CH_2 - CH_2 - CH_3

(g)
$$CH_3$$
- C - CH_2 - $COOH$ (h) CH_3

$$CH_3$$

$$OH$$

$$OH$$

$$CH_3$$

$$CH$$

$$OH$$

$$CH$$

$$CH$$

$$CH$$

$$CH$$

$$CH$$

$$\begin{array}{c} \text{OH} \\ \text{CH--CH}_2\text{--NH}_2 \\ \text{(i)} \\ \text{OH} \end{array}$$

- 4. Write a structural formula for each of the following compounds:
 - (a) 4-isopropylheptane
 - (b) 4-methyl-2-pentanol
 - (c) 5,6-dichlorocyclohexene
 - (d) 2-chloro-3-hexyn-1-ol
 - (e) 2-phenylethanol
 - (f) 4-nitrobenzoic acid
 - (g) 2,4,6-trinitrophenol
 - (h) Benzoyl chloride
 - (i) 2-amino-1-(3,4-dihydroxyphenyl)-1-ethanol
 - (j) N,N-diethylhexanamide
 - (k) Methyl benzoate

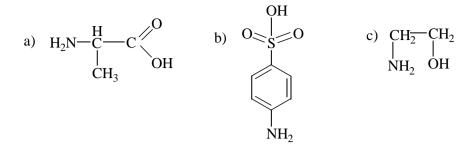
6. Approximate version of the card for the final control of the class:

Variant

1. Show functional groups, name them and families of organic compounds:

12

2. Give systematic IUPAC names for each of the following compounds:



- **3.** Write a structural formula for each of the following compounds:
 - a) 2-hydroxypropanoic acid;
 - b) 4-aminobenzenesulfonic acid

THEME 2

Chemical bonds and mutual influence of atoms in organic compounds.

1. Training and educational goals:

- 1.To form knowledge of:
- electronic structure of π , π -and p, π -conjugated systems;
- conjugation energy as a criterion for thermodynamic stability evaluation:
- aromaticity and its criteria;
- electronic effects (inductive and mesomeric effects).
- 2.To form skills in:
- finding and classifying conjugated system types in organic compounds;
- using aromaticity criteria to prove thermodynamic stability of biologically important organic compounds;
- determining the type and sign of electronic effects;
- finding electron donating (ED) and electron withdrawing (EW) groups.

2. Program questions:

- 1. Electronic structure of carbon atoms and heteroatoms of nitrogen and oxygen.
 - 2. Hybridization of atomic orbitals.
- 3. Chemical bonding in organic compounds. Covalent bond formation and its properties. Main characteristics of the σ and π -bonds in organic compounds. Hydrogen bonds.
- 4. Conjugation. Electronic structure of π , π and p, π conjugated systems. Conjugated systems with an open chain: 1,3-dienes; polyenes, allylic radical. Conjugation (resonance) energy (E_R).

- 5. Aromaticity of carbocyclic (benzenoid and nonbenzenoid) and heterocyclic compounds.
- 6. Electronic effects: inductive effects and resonance (mesomeric) effects. Electron donating (ED) and electron withdrawing (EW) groups.
 - 7. Electron density delocalization in the molecule. Reaction centres.

3. Literature:

- 1. Bioorganic chemistry: учебное пособие для иностранных студентов / О.Н. Ринейская [и др.]. Минск: Новое знание, 2018. р. 14-25.
- 2. Hidranovich, L.G. Bioorganic chemistry lecture course / L.G. Hidranovich. Vitebsk, 2004. p. 16-33.
- 3. Chernykh, V.P. Organic chemistry. Basic lecture course: The study guide for students of higher schools / V.P. Chernykh, L.A. Schemchuk. Kharkiv, 2011. p. 14-30.

4. Homework:

- 1. Prepare the theoretical material according to the program questions of the theme 2.
- 2. Solve the problems N_2 1 (d), (e), N_2 2 (f), (i), N_2 3 (d), (g) presented on the pages 14-15.

5. Problems.

1. Define the hybridization type of carbon atoms and heteroatoms (pyridine and pyrrole type) in following compounds:

a)
$$CH_2 = C - N$$
 CH_3

b)

C)
 $CH_2 - CH - C$
 H
 CH_3

C)
 $CH_2 - CH - C$
 H

C)
 $CH_2 - CH - C$
 H

C)
 $CH_2 - CH - C$
 H

C)
 $CH_2 - CH - C$
 H
 CH_2
 CH_2

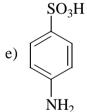
2. Find the conjugation in following compounds, define the type of conjugation and show the electronic structure of the conjugated systems. Designate electron's movement with curved arrows.

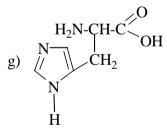
- a) CH₂=CH-CH₃
- b) CH₂=CH-CH=CH-CH₃
- c) CH₂=CH-CH₂-CH=CH₂

- d) CH₂=CH-O-CH₃
- e) CH_3 - CH_2 - CH_2 C

3. Define the sign (negative or positive) of inductive and resonance (mesomeric) effects of functional groups and heteroatoms in following compounds. Show these effects with arrows. Indicate ED and EW groups.

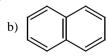
- b) CH₃-CH₂-O-CH₃ c) CH₂=CH-Cl





Prove the aromaticity of the following compounds: 4.











6. Approximate version of the card for the final control of the class:

Variant

1. Define the type of conjugation and show the electronic structure of the conjugated systems. Designate electron's movement with curved arrows.

$$CH_2=CH-CH_2$$
 — C OH

2. Define and explain are the following compounds aromatic or not:

3. Define the sign (negative or positive) of inductive and resonance effects of functional groups and heteroatoms. Show these effects with arrows. Indicate ED and EW groups.

THEME 3 Spatial structure of organic compounds.

1. Training and educational goals:

- 1. To form knowledge of:
- stereochemical concepts of conformation, configuration, chirality, enantiomerism and diastereomerism;
- conformational isomerism of alkanes and cycloalkanes;
- configurational isomerism;
- notions about the relationship of spatial structure and biological activity.
- 2. To form skills in:
- drawing Newman projection formulas of biologically important compounds to characterize the energy of the conformations;
- performing conformational analysis of cyclohexane and its derivatives;
- determining chirality of organic compounds;
- drawing the standart Fischer projection formulas of stereoisomers (enantiomers, σ-diastereomers);
- drawing the π -diastereomers of alkenes.

2. Program questions:

- 1. Configuration and conformation of organic compounds. The relationship between spatial structure of organic compounds and the hybridization type of carbon atom.
- 2. Conformations of open chain compounds. Newman projection formulas. Torsional and Van Der Waals strains in the molecules. Characteristic of energy of conformations.
- 3. Conformations of cyclic compounds. Five-membered and six-membered cycles. Stability of conformations. Chair conformations of cycohexane and its derivatives. Axial and equatorial bonds. 1,3-diaxial interaction, ring inversion.
- 4. Chirality. Chiral molecules. The chiral carbon atom. Stereoisomerism of molecules, with one stereocentre. Enantiomerism. Optical activity. The D-, L-system of a stereochemical designation. Notion of the R-, S-system of a stereochemical designation.
- 5. Stereoisomerism of molecules with more than one stereocentre: enantiomers and diastereomers. Meso compounds. Racemate.
 - 6. π -Diastereoisomerism. Stereochemistry and biological activity.

3. Literature:

- 1. Bioorganic chemistry: учебное пособие для иностранных студентов / О.Н. Ринейская [и др.]. Минск: Новое знание, 2018. p. 26-40.
- 2. Hidranovich, L.G. Bioorganic chemistry lecture course / L.G. Hidranovich. Vitebsk, 2004. p. 33-54.
- 3. Chernykh, V.P. Organic chemistry. Basic lecture course: The study guide for students of higher schools / V.P. Chernykh, L.A. Schemchuk. Kharkiv, 2011. p. 14-30.

4. Homework:

- 1. Prepare the theoretical material according to the program questions of the theme 3.
- 2. Solve the problems \mathbb{N}_2 1 (b), \mathbb{N}_2 2 (b), (c), \mathbb{N}_2 5 (a), \mathbb{N}_2 8 (c), \mathbb{N}_2 9 (b) presented on the pages 17-19.

5. Problems.

- 1. Write the Newman projection formulas of all staggered and eclipsed conformations for:
 - a. 1,2-diiodoethane;
 - b. 2-methylbutane (along C2–C3 bond);
 - c. 2-aminoethanol
 - d. butandioic acid (along C2–C3 bond)

2. Write the condensed structural formulas of each of the following:

3. In each of the following structures, indicate whether the substituent is in an axial or an equatorial position.

4. Convert each of the following structures into its two chair conformations. In each case indicate which one should be the more stable conformation.

- 5. Write the structure of the preferred conformation of:
- (a) 1-Isopropyl-2-methylcyclohexane
- (b) cis-1-Bromo-2-isopropylcyclohexane
- (c) trans-1-Methyl-3-isopropylcyclohexane
- (d) cis-1-Chloro-4-isopropylcyclohexane
- 6. Identify each of the following compounds is either the *cis-* or the transisomer:

(a)
$$H_3C$$
 OH H_4C C(CH₃):

$$H_3C$$
 OH H_4C C(CH₃):
$$H_4C$$
 OH H_4C COOH

$$H_4C$$
 OH H_4C COOH

$$H_4C$$
 OH H_4C COOH

- 7. Write the two chair conformations of all trans-1,2,3,4,5,6-hexachlorocyclohexane.
- 8. Draw the standard Fischer projection formulas of stereoisomers that correspond to each of the following compounds. Indicate enantiomers and diastereoisomers.
 - a) 2-hydroxypropanal;
 - b) 2-aminopropanoic acid;
 - c) 2-amino-3-hydroxybutanoic acid;
 - d) 2,3-dihydroxybutandioic acid.
- 9. Assign the R- or S- and D- or L- configuration to the stereocentre in each of the following:

a) HO
$$\stackrel{\text{H}}{\longrightarrow}$$
 O $\stackrel{\text{COOH}}{\longrightarrow}$ O $\stackrel{\text{COOH}}{\longrightarrow}$ NH₂ CH₃ CH₃ CH₃ CH₃ CH₃ CH₅

- 10. Draw the stereoisomers for the following compounds:
- a) CH₃-CH=CH-COOH
- b) COOH-CH=CH-COOH

6. Approximate version of the card for the final control of the class:

Variant

1. Write the Newman projection formulas of all staggered and eclipsed conformations for:

butanoic acid (along $C_2 - C_3$ bond)

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- **2.** Write the chair conformations for trans-1,3-dimethylcyclohexane. Indicate which one should be the most stable conformation.
- **3.** Draw the standard Fischer projection formulas of stereoisomers that correspond to the following compounds. Indicate diastereoisomers and enantiomers.

THEME 4

Reactivity of saturated, unsaturated and aromatic hydrocarbons.

1. Training and educational goals:

- 1. To form knowledge of:
- organic reaction terminology (a substrate, a reagent, products of the reaction, a reaction centre, the rate of the reactions, the mechanism of the reactions);
- homolytic and heterolytic cleavage of the covalent bond;
- reactivity of alkanes; the mechanism of free-radical substitution reactions:
- reactivity of alkenes; the mechanism of electrophilic addition reactions;
- reactivity of aromatic hydrocarbons; the mechanism of electrophilic substitution reactions;
- 2. To form skills in:
- predicting the possibility of homolytic and heterolytic cleavage of bonds;
- writing the mechanisms of the reactions (S_R, A_E, S_E) ;
- carrying out the characteristic and qualitative reactions for hydrocarbons.

2. Program questions:

- 1. Chemical reaction as a process. Terms: reactants (a substrate, a reagent), products (the product of interest, the by- product), a reaction center, an activation energy, the rate of the reaction, the mechanism of the reaction. Classification of organic reactions according to the result (substitution, addition, elimination reactions; rearrangements; oxidation-reduction reactions) and mechanisms such as radical reactions, ionic reactions (electrophilic, nucleophilic).
- 2. Types of reagents: radical, nucleophilic, electrophilic, acidic, basic. Types of bond cleavage in organic compounds and forming species: free radicals as the

result of homolysis, carbocations and carboanions as the result of heterolysis). Electronic and steric structures of these intermediates. Factors of their relative stability.

- 3. Reactivity of saturated hydrocarbons. Free–radical substitution reactions as homolytical reactions with participation of C–H bonds at a sp³ hybridized carbon atom. The mechanism of free radical substitution reactions on the example of the halogenation of alkanes. Free-radical substitution reactions as regionselective reactions. Ways of free radicals formation. Notion of chain processes. The role of free radical oxidation reactions in biological processes. Active forms of oxygen, peroxides.
- 4. Electrophilic addition reactions to alkenes as heterolytical reactions with participation of π -bond between two sp² hybrid carbon atoms. The mechanism of the hydration reaction. The acidic catalysis. The effect of static and kinetic factors on regional reactions of addition reactions. Markovnikov's rule.
- 5. Electrophilic addition to conjugated systems: hydration of α , β unsaturated carboxylic acids. Qualitative reactions for the unsaturated hydrocarbons (for the double bond).
- 6. Electrophilic aromatic substitution reactions as heterolytical reactions with participation of the π -electron cloud of an aromatic system. The mechanism of the reaction. The role of catalysts in the electrophile formation.
- 7. Electrophilic aromatic substitution reactions. Effect of substituents in an aromatic ring on its reactivity in electrophilic (aromatic) substitution. Orienting effect of substituents. Halogenation and alkylation reactions in vivo.

3. Literature:

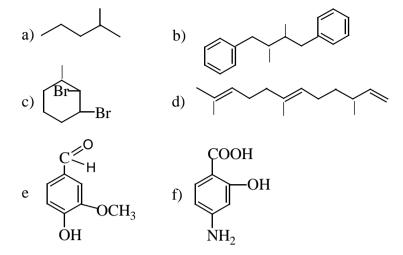
- 1. Bioorganic chemistry: учебное пособие для иностранных студентов / О.Н. Ринейская [и др.]. Минск: Новое знание, 2018. р. 46-52.
- 2. Hidranovich, L.G. Bioorganic chemistry lecture course / L.G. Hidranovich. Vitebsk, 2004. p. 75-91.
- 3. 3. Chernykh, V.P. Organic chemistry. Basic lecture course: The study guide for students of higher schools / V.P. Chernykh, L.A. Schemchuk. Kharkiv, 2011. p. 61-138.

4. Homework:

- 1. Prepare the theoretical material according to the program questions of the theme 4.
 - 2. Prepare the laboratory work protocol.
- 3. Solve the problems N_0 3 (b), N_0 5 (c), N_0 6 (d), N_0 7 (d) presented on the pages 21-24.

5. Problems.

1. Give systematic IUPAC names for each of the following:



- 2. Write a structural formula for each of the following compounds:
 - a) 2-methyl-4,4-diethylheptane;
 - b) 2-isopropyl-5-methylcyclohexanol;
 - c) trans-2,2,5,5-tetramethyl-3-hexene;
 - d) 2,4,6-trinitrophenol;
 - e) 3,4,5-trihydroxybenzoic acid;
 - f) 1,3-pentadiene.
- 3. Write the products formed in the reactions of Br₂ with following compounds:
 - a) ethane;
 - b) 2-methylpropane;
 - c) methylcyclohexane;
 - d) 3-ethylpentane;
- 4. Draw all possible monochlorination products from the radical chlorination of 2,2,4-trimethylpentane. Estimate approximately the amounts of each isomer of product that forms.
- 5. Write the structures and names of the product or products expected from the addition of HCl and H₂O to each of the following compounds:
 - a) methylpropene;
 - b) 3-methyl-1-butene;
 - c) $H_2C = C-CH_2-CH_2-CH_3$ CH_3 H_3C
 - d) (1)
 - e) $H_2C = CHBr$

f) CH₃-CH=CH-C
$$\stackrel{\bigcirc}{\sim}$$
OH
g) HOOC-CH=C-CH₂-COOH
COOH

- 6. What reaction products, if any, result from the reaction of cyclohexene with the following reagents?
 - a) H_2 (Pt);
 - b) Br₂;
 - c) KMnO₄;
 - d) HBr.
- 7. Predict the major mononitration products from each of the following aromatic compounds:
 - a) Toluene;
 - b) Benzoic acid;
 - c) 1,3-dimethylbenzene;
 - d) 4-methylphenol;
 - e) 4-ethylbenzoic acid.
- 8. Predict the major products of the monosulphonation of the following substances:
 - a) phenol;
 - b) methoxybenzene;
 - c) nitrobenzene;
 - d) bromobenzene;
 - e) 3-nitrobenzoic acid.
- 9. What product is formed in the following reaction?

10. Vitamin E is an important antioxidant that prevents the formation of hydroperoxides in unsaturated fatty acids. Vitamin E is found most abundantly in oil seeds rich in these unsaturated fatty acids. Chemists postulate that vitamin E inhibits radical degradation of cellular materials. If true, vitamin E might slow the aging process in mammals. Show how vitamin E might be a radical chain inhibitor.

$$HO$$
 CH_3
 H_3C
 CH_3
 CH_3

6. Laboratory work:

Experiment №1. Reaction of alkanes with bromine water.

Sequence of operations: Place 3 ml of cyclohexane in two test-tubes. Add 4 drops of the bromine in CCl_4 solution. Keep the test-tube N_2 1 on the light and the test-tube N_2 2 in the darkness during 1 or 2 days.

Check the result: the change of colour in test-tube N_2 1.

Write:

$$+ Br_2 \xrightarrow{hv} -Br + HBr$$
 cycloxexane

Explain the result and write conclusion.

Experiment №2. Reaction of alkenes with bromine water.

Sequence of operations: Place 3 drops of bromine water in two test-tubes. Add one by one several drops of cyclohexene in the test-tube \mathbb{N}_2 1 and several drops of cyclohexane in the test-tube \mathbb{N}_2 2.

Check the result: the change of colour in the test-tube N_2 1.

Write:

$$\left\langle \begin{array}{c} \\ \\ \end{array} \right\rangle + Br_2 \longrightarrow \left\langle \begin{array}{c} \\ \\ Br \end{array} \right\rangle$$

cyclohexene

Explain the result and write conclusion.

Experiment No.3. Oxidation of alkenes by KMnO₄.

Sequence of operations: Place 2 drops of KMnO₄ solution in two test-tubes. Add one by one several drops of cyclohexene in the test-tube N_2 1 and several drops of cyclohexane in the test-tube N_2 2.

Check the result: the change of colour and brown precipitate in the test-tube N_2 1.

Write:

$$3 \longrightarrow +2 \text{KMnO}_4 + 4 \text{H}_2 \text{O} \longrightarrow 3 \longrightarrow +2 \text{MnO}_2 + 2 \text{KOH}$$

cyclohexene

Explain the result and write conclusion.

Experiment No4. Reaction of benzene and toluene with bromine water and their oxidation by KMnO4.

a) **Sequence of operations:** Place 2 drops of benzene in the test-tube № 1 and 2 drops of toluene in the test-tube № 2. Add 3 drops of bromine water in these test-tubes.

Check the result: there is no change of colour.

b) Sequence of operations: Place 2 drops of benzene in the test-tube \mathbb{N}_2 1 and 2 drops of toluene in the test-tube \mathbb{N}_2 2. Add 2 drops of KMnO₄ solution and 1 drop of H₂SO₄ in these test-tubes. Warm the test-tubes.

Check the result: the change of colour in the test-tube N_2 . Write:

CH₃

$$+ \frac{KMnO_4 / H_2SO_4, t^o}{-H_2O}$$
Deluene

benzoic acid

Explain the result and write conclusion.

Experiment №5. Reaction of aniline with bromine water.

Sequence of operations: Place 1 drop of aniline and 6 drops of water in the test-tube. Shake the test-tube. Add 3 drops of bromine water.

Check the result: white precipitate.

Write:

Explain the result and write conclusion.

7. Approximate version of the card for the final control of the class:

Variant

1. Write the scheme and outline mechanism of the hydrobromination reaction of 2-methylpropene (reaction of 2-methylpropene with HCl).

2. Write the schemes of the following reactions. Indicate interacted reaction centers of the substrate and the reagent (if it possible). Indicate the type and mechanism of the reactions.

THEME 5 Reactivity of alcohols, phenols, thiols, amines. Acid base properties of organic compounds.

1. Training and educational goals:

- 1. To form knowledge of:
- Bronsted-Lowry and Lewis definition of acids and bases;
- quantitative and qualitative evaluation the strength of acids and bases;
- reaction centers and reactivity of alcohols, thiols, phenols and amines;
- nucleophilic substitution reactions (S_{N1} and S_{N2} reactions);
- elimination reactions (E₁-reactions) of alcohols;
- the biologically important dehydration reactions and the alkylation reactions.
- 2. To form skills in:
- predicting the strength of acidic and basic centers of the biologically important compounds;
- finding the reaction centers in alcholols, phenols, thiols and amines;
- comparing reactivity of alcohols in nucleophilic substitution and elimination reactions;
- writing the reaction mechanisms;
- carrying out the characteristic and qualitative reactions for alcohols, phenols, amines.

2. Program questions:

- 1. Reaction centers of alcohols, phenols, thiols and amines. Acidity or basicity: Bronsted-Lowry and Lewis definition of acids and bases. Qualitative and quantitative characteristics of acidic and basic properties of organic compounds.
- 2. The acidic and basic properties: the chemical nature of the atom in acidic and basic centers, electronic effects of substituents, solvatation effect. Toxicity of strong acids and bases. Amphoterism. The hydrogen bond as specific manifestation of acid and basic properties.

- 3. Nucleophilic substitution reactions at sp^3 -hybrid carbon atom. S_{N1} and the S_{N2} mechanisms. Stereochemistry of nucleophilic substitution reactions.
- 4. Nucleophilic substitution of the hydroxyl group in alcohols. The role of acid catalysis.
- 5. The alkylation reactions of alcohols, thiols, amines. The alkylation *in vi-vo*.
- 6. Elimination reactions (dehydration) of alcohols. The biologically important dehydration reactions of alcohols.
- 7. Oxidation reactions of alcohols, phenols, thiols. Reduction reactions of disulfides. NAD⁺-NADH system; hydride transfer as one of the stages of the biological oxidation–reduction reactions with participation of this system. Phenols and thiols as antioxidants.

3. Literature:

- 1. Bioorganic chemistry: учебное пособие для иностранных студентов / О.Н. Ринейская [и др.]. Минск: Новое знание, 2018. р. 46-52.
- 2. Hidranovich, L.G. Bioorganic chemistry lecture course / L.G. Hidranovich. Vitebsk, 2004. p. 75-91.
- 3. Chernykh, V.P. Organic chemistry. Basic lecture course: The study guide for students of higher schools / V.P. Chernykh, L.A. Schemchuk. Kharkiv, 2011. p. 61-138.

4. Homework:

- 1. Prepare the theoretical material according to the program questions of the theme 5.
 - 2. Prepare the laboratory work protocol.
- 3. Solve the problems N_{2} 3, N_{2} 4,6, N_{2} 11, N_{2} 13(b) presented on the pages 27-30.

5. Problems.

1. What is the conjugate base of each of the following acids?

a)
$$N^{+}H_{4}$$
 d) $C_{6}H_{5}OH$ g) F C O OH b) $H_{2}O$ e) $H_{3}O^{+}$ f) $CH_{3} - C$ O h) $CH_{3} - N^{+}H_{3}$

2. What is the conjugate acid of each of the following bases?

a) H

d) NH_2 g) OH^-

b) H_2O e) $C_2H_5 - O^-$ h) NH_3

c) CH_3NH_2 f) CH_3CO_2

3. Compare the strength of acids:

a)
$$CH_3$$
— CH — C
OH
OH

b) CH_3 - CH_2 - C
OH

b)
$$CH_3-CH_2-C < O$$

4. Compare the strength of acidic centers of each of the following acids.

$$\begin{array}{c|c} HO & \begin{array}{c} H \\ C - CH_2 \\ I & I \\ OH \ NH_2 \end{array}$$

5. Compare the strength of bases:

strength of bases:

a)
$$CH_2$$
- CH_2
 $|$ |
 NH_2 OH

b) $H_2N - CH_2 - CH$
 CH_3

6. Compare the strength of basic centers of each of the following bases.

a)
$$\stackrel{N}{\underset{H}{\bigvee}} \stackrel{H_2}{\underset{C}{\longleftarrow}} \stackrel{H_2}{\underset{C}{\longleftarrow}} \stackrel{H_2}{\underset{N}{\longleftarrow}} \stackrel{H_2}{\underset{D}{\longleftarrow}} \stackrel{H_2}{\underset{N}{\longleftarrow}} \stackrel{N}{\underset{N}{\longleftarrow}} \stackrel{N}{\underset{N}{\longrightarrow}} \stackrel{N}{\underset{N}{\longrightarrow}} \stackrel{N}{\underset{N}{\longrightarrow}} \stackrel{N}{\underset{N}{\longrightarrow}} \stackrel{N}{\underset{N}{\longrightarrow}} \stackrel{N}{\underset{N}{\longrightarrow}} \stackrel{N}{\underset{N}$$

7. Give systematic IUPAC names for each of the following:

d)
$$CH_2 - CH_2 - CH_2 - CH_2 - CH_2$$

 NH_2 NH_2
e) H_5C_2O NH_2

e)
$$H_5C_2O$$
 NH₂

- 8. Write a structural formula for each of the following compounds:
- a) 2-ethoxypentane;
- b) 2,2-dimethyl-1-propanol;
- c) 1,4-pentanediol;
- d) 5-chloro-4-methyl-2-pentanol;
- e) 1-cyclohexyl-1-butanol;
- f) N-ethyl-N-methylaniline;
- g) 4-aminophenol;
- h) ethylthioethane;
- i) 2-amino-1-(3,4-dihydroxyphenyl)-1-ethanol.
- 9. Arrange each of the following sets of compounds in decreasing order of their expected acid strength in solution:
- a) 2-chlorohexanol; 3-chlorohexanol; 4-chlorohexanol; 2,2-dichlorohexanol.
- b) 2,2-dimethyl-1-butanol: 2,2-dimethylbutanamine: 1-butanol.
- 10. Find the reaction centres in following compounds. Write the schemes and outline mechanisms of the possible reactions for these reaction centres.

a)
$$HO$$
 CH
 CH
 CH
 CH
 OH
 CH
 OH
 CH
 CH
 OH

11. Rang the following compounds in order of increasing reactivity towards S_{N1} substitution. Then rank them in order of increasing reactivity towards S_{N2} subtitution.

$$(CH_3)_2CHCH_2OH$$
 CH_3-CH_2-OH OH CH_3 $H_3C-C-OH$ CH_3

Write the schemes of reactions with HCl. Outeine the mechanisms $S_{\rm N1}$ and $S_{\rm N2}$ reactions.

12. Predict the major products of each of the following reactions. Determine whether the reaction is primarily S_{N1} or S_{N2} .

a)
$$CH_3$$
- CH_2 - CH - CH_3 $+ HCl$

OH

$$CH_3$$

c)
$$OH - CH_3I - (NaOH)$$

g)
$$C_2H_5$$
-OH + CH_3 -OH (H^+)

d)
$$NH_2$$
 + CH_3I (excess)

i) CH₃-CH-CH₂-CH₂
$$\xrightarrow{+ \text{NH}_3}$$
 large excess

13. Draw the structure for the elimination product of each of the following reactions. Justify your product with a mechanism.

a)
$$CH_3$$
- CH - CH_3 $(H_2SO_4), t^o$
OH

d)
$$CH_3$$
 CH_3 CH_3

c)
$$CH_3$$
- CH - CH_2 - OH $(H_2SO_4), t^o$
 CH_3

14. Write the schemes of the reactions that prove nucleophilic properties of following compounds.

6. Laboratory work:

Experiment №1. Reaction of alcohol with metallic Na.

Sequence of operations: Place 3 drops of absolute alcohol in the test-tube. Add the small piece of metallic sodium (Na).

Check the result: bubbles of hydrogen gas and precipitate of C₂H₅ONa.

Write:
$$C_2H_5$$
-OH + Na C_2H_5 O Na⁺ + $^1/_2$ H₂ ethanol

Explain the result and write conclusion.

Experiment №2. Formation of sodium phenoxide (C₆H₅ONa).

Sequence of operations: a) Place 3 drops of water and 2 drops of C₆H₅OH in the test-tube. Add several drops of NaOH solution.

Check the result: the formation of solution.

b) Add several drops of HCl solution.

Check the result: emulsion.

Write:

$$\begin{array}{c}
OH \\
ONa^{+} \\
+ NaOH \longrightarrow ONa^{+} \\
+ H_{2}O
\end{array}$$
phenol sodium phenoxide

$$ONa^+$$
 OH OH + NaCl sodium phenoxide phenol

Explain the result and write conclusion.

Experiment No.3. Basicity of amines.

Sequence of operations:

a) Place 1 drop of methanamine (CH₃-NH₂) on the indicator paper.

Check the result: the change of colour.

b) Place 1 drop of aniline and 3 drops of water in the test-tube.

Place 1 drop of this solution on the indicator paper strip.

Check the result: there is no change of colour.

c) Place 1 drop of aniline and 3 drops of water in two test-tubes. Add 1 drop of HCl solution in the first test-tube and 1 drop of H_2SO_4 solution in the second test-tube.

Check the result: the solution in the first test-tube and the precipitate in the second test-tube.

Write:

Explain the result and write conclusion.

Experiment №4. Oxidation reaction of alcohol.

Sequence of operations: Place 2 drops of C₂H₅OH in the first test-tube. Add 2 drops of H₂SO₄ and 2 drops of K₂Cr₂O₇ solution. Warm the mixture.

Check the result: the change of colour.

Write:

$$3CH_3-CH_2-OH+K_2Cr_2O_7+4H_2SO_4 \xrightarrow{t^0} 3CH_3-C \xrightarrow{O} + Cr_2(SO_4)_3+K_2SO_4+4H_2O$$
 ethanol ethanol

Explain the result and write conclusion.

Experiment N_25 . Reaction of glycerol with $Cu(OH)_2$. Sequence of operations:

a) Place 3 drops of CuSO₄ solution and 3 drops of NaOH solution in the first and in the second test-tubes

Check the result: blue precipitate.

b) Add 2 drops of glycerol in the second test-tube.

Check the result: blue solution.

c) Warm the mixtures.

Check the result: black precipitate of CuO in the first test-tube and blue solution in the second test-tube.

Write:

1.
$$CuSO_4 + 2NaOH \longrightarrow Cu(OH)_2 \downarrow + Na_2SO_4$$

$$Cu(OH)_2 \downarrow \xrightarrow{t^0} CuO \downarrow + H_2O$$

$$CH_2 - OH \qquad + Cu (OH)_2 \downarrow \xrightarrow{OH} CH_2 - O \xrightarrow{H} O - CH_2$$

$$CH_2 - OH \qquad + Cu (OH)_2 \downarrow \xrightarrow{OH} CH_2 - OH \qquad CH_2 - OH$$

$$CH_2 - OH \qquad CH_2 - OH \qquad CH_2 - OH$$

$$CH_2 - OH \qquad COH_2 - OH \qquad COH_2 - OH$$

$$CH_2 - OH \qquad COH_2 - OH \qquad COH_2 - OH$$

Explain the result and write conclusion.

Experiment №6. Coloured reactions of phenols with FeCl₃.

Sequence of operations: Place 1 drop of FeCl₃ in each of 5 test-tubes. Add 3 drops of one of the phenol in the test-tubes:

Check the result: the change of colour.

Test-tube	Phenols	Colour
№ 1	Catechol	Green
№ 2	Resorcinol	Violet
№ 3	Hydroquinone	Yellow-green
№ 4	Pyrogallol	Red
№ 5	Phenol	Blue-violet

Write:

$$6C_6H_5OH + FeCl_3 \xrightarrow{-3HCl} H_5C_6 \xrightarrow{O} C_6H_5 H_5 \\ H_5C_6 \xrightarrow{O} C_6H_5 \\ O \xrightarrow{C_6H_5} O \xrightarrow{O} C_6H_5$$

Explain the result and write conclusion.

7. Approximate version of the card for the final control of the class:

Variant

- **1.** Write the scheme and outline mechanism of the dehydration of methanol to the ether.
- **2.** Write the schemes of the following reactions. Indicate interacted reaction centers of the substrate and the reagent (if it possible). Indicate the type and mechanism of the reactions.

$$\begin{array}{c} +HCl \\ +H_{2}SO_{4},\,t^{o}180 \\ -CH_{2}-CH-CH_{3} \\ OH \\ -K_{2}Cr_{2}O_{7}/H_{2}SO_{4},\,t^{o} \end{array}$$

THEME 6 Reactivity of aldehydes and ketones.

1. Training and educational goals:

- 1. To form knowledge of:
- electronic structure of carbonyl group and reaction centers of aldehydes and ketones:
- reactivity of aldehydes and ketones in nucleophilic addition (A_N) reactions:
- mechanism of A_N reactions;
- mechanism of A_N-E reactions;
- reactions of oxidation.
- 2. To form skills in:
- designating of reaction centers of aldehydes and ketones;
- comparing reactivity of aldehydes and ketones in A_N and A_NE reactions;
- writing the steps of the A_N and A_N -E mechanisms;
- carrying out the characterictic and qualitative reactions for aldehydes and ketones.

2. Program questions:

- 1. Reaction centers of aldehydes and ketones. Nucleophilic addition reactions. The mechanism of nucleophilic addition reaction. Reactions of carbonyl compounds with water, alcohols, amines. Formation of cyclic hemiacetals. The biological role of acetalization reactions
- 2. Nucleophilic addition reactions. The aldol addition reactions. Reversibility of nucleophilic addition reactions. The biological role of aldol addition reactions.
- 3. Nucleophilic addition-elimination reactions of aldehydes and ketones with amines. Toxicity of aldehydes. Aldehydes as disinfectants and sterilizing agents.
- 4. Oxidation and reduction reactions of carbonyl compounds in vitro and in vivo. Qualitative reactions for aldehyde group and for acetone.

3. Literature:

- 1. Bioorganic chemistry: учебное пособие для иностранных студентов / О.Н. Ринейская [и др.]. Минск: Новое знание, 2018. p. 41-45, 53-59.
- 2. Hidranovich, L.G. Bioorganic chemistry lecture course / L.G. Hidranovich. Vitebsk, 2004. p. 75-91.
- 3. Chernykh, V.P. Organic chemistry. Basic lecture course: The study guide for students of higher schools / V.P. Chernykh, L.A. Schemchuk. Kharkiv, 2011. p. 227-248.

4. Homework:

- 1. Prepare the theoretical material according to the program questions of the theme 6.
 - 2. Prepare the laboratory work protocol.
- 3. Solve the problems N_{2} 3 (a), N_{2} 5 (b), N_{2} 6 (a), N_{2} 7 (b), N_{2} 10 (a) presented on the pages 35-37.

5. Problems.

1. Give systematic IUPAC names for each of the following:

- 2. Write the structural formula for each of the following compounds:
 - a) Trichloroethanal;
 - b) 2,3,4,5,6-pentahydroxyhexanal;
 - c) 2-methylcyclohexanone;
 - d) 2,3-butandione;
 - e) 1,2-diphenylethandione;
 - f) 3-bromo-2-isopropylpentanedial;
 - g) 3-methylcyclopentanone;
 - h) 2,5-octanedione;
 - i) 4-hydroxy-2-pentanone.

- 3. Write the structure of the hemiacetal and acetal formed by the acidcatalyzed reaction and outline mechanisms for the reactions of each of the following aldehydes or ketones with ethanol:
- a) propanal;
- b) ethyl methyl ketone;
- c) benzaldehyde.
 - 4. Write the schemes and outline mechanisms of the following reactions:

a)
$$CH_3$$
- C
 H
 $+ HO$ - CH_2 - CH_3
 (H^+)
 CH_3
 CH

5. Write the schemes and mechanisms of the forming of cyclic hemiacetals from following compounds:

- 6. Write the mechanism of the acid-catalyzed hydrolysis of the following compounds:
- a) 1,1-diethoxypropane;
- b) 1,1-dimethoxyethane.
- 7. Write the structure of the product and outline the mechanism of each of the following reactions:

- 8. For all practical purposes, the compound 2,4-cyclohexadien-1-one exists totally in its enol form. Write the structure of 2,4-cyclohexadien-1-one and of its enol form. What the special factor accounts for the stability of the enol form?
- 9. Which of the following compounds would give a positive iodoform test?

a) acetone;

d) 3-pentanone;

b) pentanal;

e) 1-phenylethanol;

c) 2-pentanone;

f) 2-butanol.

- 10. Write the mechanism for an aldol condensation (aldol-type addition) of the following compounds in base:
- a) propanal;
- b) 3-methylbutanal;
- c) acetone.

6. Laboratory work:

Experiment №1. Formation of 2,4-dinitrophenylhydrazones.

Sequence of operations: Place 1 drop of acetone in the test-tube \mathbb{N}_{2} 1 and 2 drops of formalin in the test-tube \mathbb{N}_{2} 2. Add 2 drops of 2,4-dinitrophenylhydrazine in two test-tubes.

Check the result: orange precipitate.

Write:

$$H-C \stackrel{O}{\longleftarrow} H + H_2N-NH \stackrel{NO_2}{\longleftarrow} NO_2 \xrightarrow{-H_2O} H-C \stackrel{N-NH}{\longleftarrow} NO_2 \stackrel{NO_2}{\longleftarrow} NO_2 \stackrel{NO_2}$$

formaldehyde 2,4-dinitrophenylhydrazine

formaldehyde 2,4-dinitrophenylhydrazone

O

$$H_3C-C-CH_3$$
 + H_2N-NH NO2
 $-H_2O$ NO2
 $-H_2O$ NO2
 $-H_2O$ CH₃ acetone
2,4-dinitrophenylhydrazone

Explain the result and write conclusion.

Experiment №2. Reactions of difference aldehydes from ketones. Sequence of operations:

a) Silver mirror reaction.

Take 2 test-tubes. Place 1 drop of AgNO₃ solution and 2 drops of NaOH solution in each test-tube. Add 4 drops of NH₄OH in these test-tubes. This solution is named Tollen's reagent. Add 2 drops of formalin in the test-tube N² 1 and 2 drops of acetone in the test-tube N² 2. Warm test-tubes.

Check the result: silver coating in the test-tube \mathbb{N}_{2} 1. Write:

$$\text{H-C} \stackrel{\text{O}}{\rightleftharpoons} + 2[\text{Ag}(\text{NH}_3)_2]^+ + 3\text{OH} \xrightarrow{\text{f}^{\circ}} \text{H-C} \stackrel{\text{O}}{\rightleftharpoons} + 2\text{Ag} \downarrow + 4\text{NH}_3 \uparrow + 2\text{H}_2\text{O}$$
 formaldehyde

b) Copper mirror reaction.

Sequence of operations: Place 6 drops of NaOH and 1 drop of CuSO₄ solutions in two test-tubes.

Check the result: blue precipitate.

Add 2 drops of formalin in the test-tube N_2 1 and 2 drops of acetone in the test-tube N_2 2. Warm test-tubes.

Check the result: brick-red precipitate and copper coating in the test-tube N_2 1 and black precipitate in the test-tube N_2 2.

Write:

$$CuSO_4 + 2NaOH \longrightarrow Cu(OH)_2 \downarrow + Na_2SO_4$$

$$H-C \stackrel{O}{\longleftarrow} + 2Cu(OH)_2 \downarrow \stackrel{t^o}{\longrightarrow} H-C \stackrel{O}{\bigcirc} + Cu_2O \downarrow + 2H_2O$$
formaldehyde methanoic cuprous acid oxide
$$H-C \stackrel{O}{\longleftarrow} + Cu_2O \stackrel{t^o}{\longrightarrow} H-C \stackrel{O}{\bigcirc} + 2Cu \downarrow$$
formaldehyde methanoic acid

Explain the result and write conclusion.

Experiment No.3. Formaldehyde disproportionation in water solutions.

Sequence of operations: Place 3 drops of formalin in the test-tube. Add 1 drop of methyl orange (indicator).

Check the result: the change of colour.

Write:

$$2 \text{ H-C} \stackrel{O}{\longleftarrow} + \text{HOH} \longrightarrow \text{CH}_3\text{OH} + \text{H-C} \stackrel{O}{\longleftarrow} \text{OH}$$
 formaldehyde methanol methanoic acid

Explain the result and write conclusion.

Experiment №4. Iodoform test.

Sequence of operations: Place 1 drop of I_2 (in KI solution) in the test-tube. Add 3 drops of NaOH solution and 1 drop of acetone.

Check the result: white-yellow precipitate.

Write:

$$I_2 + 2NaOH \longrightarrow NaI + NaOI + H_2O$$

$$CH_3-C-CH_3 + 3NaOI \longrightarrow CH_3-C-CI_3 + NaOH \longrightarrow CH_3-C \bigcirc_{ONa}^{O} + CHI_3 \bigvee$$
acetone iodoform

Explain the result and write conclusion.

Experiment №5. Reaction of acetone with sodium nitroprussiate.

Sequence of operations: Place 1 drop of sodium nitroprussiate solution (Na₂[Fe(CN)₅NO], 5 drops of water and 1 drop of acetone in the test-tube. Add 1 drop of NaOH solution.

Check the result: the change of colour.

Pour the part of the mixture in the other test-tube. Add 1 drop of CH₃COOH in one of the test-tubes.

Check the result: the change of colour.

Explain the result and write conclusion.

7. Approximate version of the card for the final control of the class:

Variant

- 1. Show the reaction centers of butanal. Write the scheme and mechanism of the reaction of butanal with ethanol.
- **2.** Write the schemes of the following reactions. Indicate interacted reaction centres of the substrate and the reagent (if it possible). Indicate the type and mechanism of the reactions.

$$H_2C=HC-C$$
 H
 $+C_6H_5-NH_2$
 $+HBr$
 $+LiH/H_2O$

THEME 7 Reactivity of carboxylic acids and their derivatives.

1. Training and educational goals:

- 1. To form knowledge of:
- classification and nomenclature of carboxylic acids and their derivatives;
- reaction centers of carboxylic acids and their derivatives;
- acidity of saturated, unsaturated and aromatic carboxylic acids;
- reactivity of carboxylic acids and their derivatives in substitution nucleophilic reactions;
- biologically important reactions of carboxylic acids and their derivatives.
- 2. To form skills in:
- designating reaction centers of carboxylic acids and their derivatives;
- comparing reactivity of carboxylic acids and their derivatives;
- writing the mechanism of S_N reactions;
- carryind out the characterictic and qualitative reactions for carboxylic acids and their derivatives.

2. Program questions:

- 1. Reaction centers of carboxylic acids. Acidic properties of mono- and dibasic, saturated, unsaturated and aromatic carboxylic acids.
- 2. Nucleophilic substitution reactions at the sp²-hybrid carbon atom of carboxylic acids and their derivatives. The acylation reactions such as formation of carboxylic acid anhydrides, haloanhydrides, esters, amides. Hydrolysis reactions of derivatives of carboxylic acids.

- 3. The acylating by carboxylic acid anhydrides, acid chlorides, carboxylic acids, esters, thioesters. The acylation ability of carboxylic acids derivatives. Relative reactivity of esters and thioesters. Biological importance of esters and thioesters. Acylcoenzyme A. Acylphosphates. Biologically important acylation reactions that proceed with participating of acylphosphates. Notion about phosphorilation reactions.
- 4. Amides of carboxylic acids. The structure of amide-group. Acid-base properties of amides. Hydrolysis of amides. Amide of benzoic acid.
- 5. Derivatives of carbonic acid: the urea (carbamide) as the complete amide of the carbonic acid, carbamic acid. Acid-base properties and biological importance of carbamic acid and carbamide. Biuret. Urethanes, ureides, ureidoacids in the medicine. Biological importance of creatine and phosphocreatine.

3. Literature:

- 1. Bioorganic chemistry: учебное пособие для иностранных студентов / О.Н. Ринейская [и др.]. Минск: Новое знание, 2018. р. 68-75.
- 2. Hidranovich, L.G. Bioorganic chemistry lecture course / L.G. Hidranovich. Vitebsk, 2004. p. 136-153.
- 3. Chernykh, V.P. Organic chemistry. Basic lecture course: The study guide for students of higher schools / V.P. Chernykh, L.A. Schemchuk. Kharkiv, 2011. p. 249-290.

4. Homework:

- 1. Prepare the theoretical material according to the program questions of the theme 7.
 - 2. Prepare the laboratory work protocol.
- 3. Solve the problems \mathbb{N}_{2} 2 (a,c,i,k), \mathbb{N}_{2} 3 (c,f), \mathbb{N}_{2} 4 (c,d), \mathbb{N}_{2} 6 (a), \mathbb{N}_{2} 7 (c) presented on the pages 41-44.

5. Problems.

1. Give systematic IUPAC names for each of the following:

COOH
$$(f) \qquad (COOH) \qquad$$

- 2. Write the structural formula for each of the following compounds:
- a) hexanedioic acid;
- b) N,N-diethylhexanamide;
- c) tert-butyl propanoate;
- d) 2,4-hexadiene-oic acid;
- e) 2-hydroxybenzoic acid;
- f) 3-hydroxy-3-carboxypentanedioic acid;
- g) trans-butenedioic acid;
- h) 4-hexen-oic acid;
- i) propanoyl chloride;
 - j) 2-bromopropanoyl bromide;
- k) N,N-Dimethylformamide.
- 3. Which acid of each pair shown here would you expect to be stronger?

- 4. What major organic product would you expect to obtain when acetyl chloride reacts with each of the following compounds? Outline mechanisms of these reactions.
- a) H₂O;
- b) CH₃NH₂ (excess);
- c) (CH₃)₂NH (excess);
- d) C_2H_5OH ;

f) phenol

- 5. What major organic product would you expect to obtain when acetic anhydride reacts with each of the following compounds? Outline mechanisms of these reactions.
- a) NH₃ (excess);
- c) CH₃-CH₂-CH₂-OH;

b) H₂O;

- d) C_6H_5 -NH₂ (excess).
- 6. Write the scheme and mechanism of the esterification reaction for the synthesis of the following esters:
- a) ethyl benzoate;
- b) methyl methanoate;
- c) methyl cyclopentanecarboxylate;

7. Predict the products and write mechanisms of each of the following reactions:

8. Write the mechanism for the acidic and basic hydrolysis of the following compounds:

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9. What products would you obtain from acidic and basic hydrolysis of each of the following amides?

a)) N,N-Diethylbenzamide;

b)
$$\begin{array}{c} O \\ N-H \end{array}$$
 c) $\begin{array}{c} NH_2\text{-CH-C} \\ CH_2 \\ C_6H_5 \end{array}$ OH

6. Laboratory work:

Experiment №1. Carboxylic acids dissociation reaction.

Sequence of operations: Place the small drops of CH₃COOH and HOOC-COOH solutions on the indicator paper.

Check the result: the change of the colour and values of pH. **Write:**

1.
$$CH_3$$
- C + H_2O \longrightarrow CH_3COO + H_3 + O pH<7 ethanoic OH

b)
$$\bigcirc O$$
 $\bigcirc C$ $\bigcirc C$ $\bigcirc O$ $\bigcirc C$ \bigcirc

Explain the result and write conclusion.

Experiment №2. Formation of sodium benzoate.

Sequence of operations: Place several crystals of benzoic acid and 2 drops of water in the test-tube. Add 3 drops of NaOH.

Check the result: the solution.

Add 3 drops of HCl.

Check the result: the precipitate.

Write:

2).
$$O Na^+$$
 $O OH$ + HCl OH + NaCl sodium benzoate

Explain the result and write conclusion.

Experiment №3. Formation of ethyl acetate.

Sequence of operations: Place some sodium acetate in the test-tube (to make the 2 mm high layer). Add 3 drops of C_2H_5OH and 2 drops of concentrated H_2SO_4 . Warm the test-tube (Take care!).

Check the result: the specific ethyl acetate smell (see accident prevention 2).

Write:

$$CH_{3^{-}} \ C \stackrel{O}{\underset{OH}{\longleftarrow}} + C_{2}H_{5}OH \ \stackrel{(H_{2}SO_{4}(concd))t^{o}}{\xrightarrow{\hspace{1cm}}} CH_{3^{-}} \ C \stackrel{O}{\underset{OC_{2}H_{5}}{\longleftarrow}} + H_{2}O$$
 ethanoic acid ethanol ethyl acetate

Explain the result and write conclusion.

Experiment №4. Discover of oxalic acid.

Sequence of operations: Place some oxalic acid and 3 drops of H₂O in the test-tube. Add 2 drops of CaCl₂ solution.

Check the result: white precipitate.

Pour the part of the mixture in to other test-tube. Add 3 drops of CH_3COOH in the test-tube N_2 1 and 3 drops of HCl in the test-tube N_2 2.

Check the result: the precipitate in the test-tube N_2 1 and solution in the test-tube N_2 2.

Write:

OHO C-COH + CaCl₂
$$\longrightarrow$$
 CaC₂O₄ \checkmark + 2HCl calcium oxalate

$$CaC_2O_4 + 2HCl \longrightarrow OH$$
Calcium oxalate
$$CaC_2O_4 + 2HCl \longrightarrow OH$$
calcium oxalate
$$OHO$$
oxalic acid

Explain the result and write conclusion.

Experiment №5. Decarboxylation of oxalic acid.

Sequence of operations: Place some oxalic acid in the first test-tube. Close the test-tube with the cork having the glass pipe. Lower the end of the glass pipe in the second test-tube with 3 drops of barium hydrate solution (Ba(OH)₂) in it. Warm the first test-tube.

Check the result: the precipitate in the second test-tube.

Take out the glass pipe from the second test-tube. To convince that CO is forming, set it on fire near the aperture of the glass pipe.

Check the result: blue flame.

Write:

OHO C-COH
$$\xrightarrow{t^o}$$
 $CO_2 + H-COH$ methanoic acid

H-COH $\xrightarrow{t^o}$ $CO + H_2O$

methanoic acid

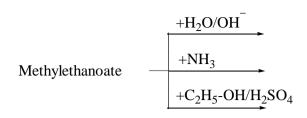
 $2CO + O_2 \longrightarrow 2CO_2$
 $CO_2 + Ba(OH)_2 \longrightarrow BaCO_3 \downarrow + H_2O$

Explain the result and write conclusion.

7. Approximate version of the card for the final control of the class:

Variant

- **1.** Show the reaction centers of propanoyl chloride. Write the scheme and mechanism of the reaction of propanoyl chloride with methanol.
- **2.** Write the schemes of the following reactions. Indicate interacted reaction centers of the substrate and the reagent (if it possible). Indicate the type and mechanism of the reactions.



THEME 8

Poly- and heterofunctional compounds, which are origin of the most important medicament groups and which participate in the processes of ability to live.

1. Training and educational goals:

- 1. To form knowledge of:
- structures of biologically important amino alcohols, hydroxy- acids, oxo-acids;
- specific features of chemical behavior of poly- and heterofunctional compounds;
- biologically important reactions of heterofunctional compounds;
- the heterofunctional benzene derivatives as medicians.
 - 2. To form skills in:
- designating reaction centers in heterofunctional compounds;
- writing characterictic and specific reactions of heterofunctional compounds;
- carrying out characterictic and qualitative reactions of heterofunctional compounds.

2. Program questions:

- 1. Classification of poly- and heterofunctional compounds. Acid-base properties. Typical reactivity of poly- and heterofunctional compounds.
- 2. Specific features of chemical hydroxyl of poly- and heterofunctional compounds: features of acid and base properties, cyclization and chelates formation. Chelate complex formation as the qualitative test for a diol fragment.
- 3. Intramolecular cyclization (γ and δ -hydroxyaldehydes, γ and δ -hydroxy- and aminoacids, dicarboxylic acids with 4 or 5 carbon atoms) intermolecular cyclization (α hydroxyl- and aminoacids). Cyclic hemiacetals, cyclic anhydrides, lactides, diketopiperasines, lactones, lactames.
- 4. Decarboxylation reactions. The elimination reactions of β -hydroxy- and β -amino acids. Tautomerization: keto–enol tautomerization and lactam–lactim tautomerization.

- 5. Polyalcohols. Their examples: ethylene glycol, glycerol, inositol, xylitol, sorbitol. Esters of polyhydric alcohols with inorganic acids (nitro-glycerol, glycerol and inositol phosphates) and with fatty acids.
- 6. Dihydric phenols. Their examples: hydroquinone, resorcinol, catechol. Oxidation of dihydric phenols. Hydroquinone-quinone system. Phenols as antioxidants. Tocopherols.
- 7. Dicarboxylic acids. Their examples: oxalic acid, malonic acid, succinic acid, glutaric acid, fumaric acid. The transformation of succinic acid to fumaric acid as an example of a biologically important dehydrogenation reaction.
- 8. Amino alcohols. Their examples: 2-aminoethanol, choline, acetylcholine. Forming of choline from L-serine. Amino phenols. Their examples: dopamine, noradrenaline (norepinephrine), adrenaline (epinephrine).
- 9. Hydroxy-acids. Lactic acid, malic acid, tartaric acid, citric acid. Oxidation reactions of lactic acid and malic acid with participating of NAD⁺. Citric acid. Citrates: preservation of donor blood. Dehydration of citric acid in vivo.
- 10. Oxo-acids (aldehyde and keto acids). Their examples: pyruvic acid, acetoacetic acid, oxaloacetic acid, α -ketoglutaric acid. Acid properties and reactivity. The decarboxylation reaction of β -ketobutyric acid and the oxidizing decarboxylation reactions of pyruvic acid. Keto-enol tautomerization. β -hydroxybutyric acid, β -ketobutyric acid, acetone as representatives of "ketone bodies", their biological and diagnostic importance.
- 11. The heterofunctional benzene derivatives as medicaments. Salicylic acid and its derivatives (acetylsalicylic acid, methyl-salicylate, phenyl-salicylate).
- 12. *p*-Aminobenzoic acid and its derivatives (benzocain, novocaine). Biological role of *p*-aminobenzoic acid (folic acid as the growth factor). Modern anesthetics.
 - 13. Sulfanilic acid and its amide. Sulfanamides. Notion of antimetabolites.

3. Literature:

- 1. Bioorganic chemistry: учебное пособие для иностранных студентов / О.Н. Ринейская [и др.]. Минск: Новое знание, 2018. р. 76-86.
- 2. Hidranovich, L.G. Bioorganic chemistry lecture course / L.G. Hidranovich. Vitebsk, 2004. p. 154-170.
- 3. Chernykh, V.P. Organic chemistry. Basic lecture course: The study guide for students of higher schools / V.P. Chernykh, L.A. Schemchuk. Kharkiv, 2011. p. 296-320.

4. Homework:

- 1. Prepare the theoretical material according to the program questions of the theme 8.
 - 2. Prepare the laboratory work protocol.

3. Solve the problems N_{2} 1 (c,f), N_{2} 3, N_{2} 5, N_{2} 7, N_{2} 8, N_{2} 10 presented on the pages 49-50.

5. Problems.

1. Give systematic IUPAC names for each of the following compounds:

- 2. Write the structural formula for each of the following compounds:
- a) 2-amino-3-(4-hydroxyphenyl)-propanoic acid;
- b) N-butyl propanamide;
- c) N-4-ethoxyphenyl ethanamide;
- d) trans-2-nitrocyclohexanecarboxylic acid;
- e) 4-aminobenzenesulfonic acid;
- f) 1,2,3,4,5-pentanepentaol.
- 3. Show the reaction centres of 2-aminoethanol. Compare nucleophilic properties of amino and hydroxyl groups. Outline the synthesis of choline by the methylation reaction of 2-aminoethanol.
- 4. Show the reaction centres of lactic acid (2-hydroxypropanoic acid). Compare the strength of it's OH acidic centres and electrophilic centres. Write the scheme of reaction of lactic acid with NaOH and outline mechanism for acid-catalyzed esterification reaction of lactic acid with C_2H_5OH .
- 5. Show the reaction centres of 2-oxopropanoic acid. Write the scheme and outline mechanism of the acid-catalyzed esterification reaction of 2-oxopropanoic acid with C_2H_5OH .
- 6. Write the scheme and mechanism of acid-catalyzed hydrolysis of acetylcholine in living systems.

7. The base-catalyzed hydrolysis reaction is used for identification of anesthesine. Write the scheme and outline the mechanism of this reaction.

8. 4-Aminobenzoic acid is prepared from toluene. Write the scheme of preparing 4-aminobenzoic acid from toluene.

$$\begin{array}{c} \text{COOH} \\ \hline \\ \text{HNO}_3(\text{H}_2\text{SO}_{4(\text{coned})}) \\ \hline \\ \text{?} \end{array} \begin{array}{c} \text{KMnO}_4(\text{H}^+) \\ \hline \\ \text{?} \end{array} \begin{array}{c} \text{Zn/HCl} \\ \hline \\ \text{NH}_2 \end{array}$$

9. Esters of 4-aminobenzoic acid are used as anesthetics. They are prepared from 4-nitrobenzoic acid. Write the schemes of reactions.

- 10. a) Write tautomeric forms of acetoacetic ester and outline schemes of reactions that prove existence of two tautomeric forms.
- b) What tautomeric form do you expect to be a stronger acid? Write scheme of reaction that proves acidic properties of acetoacetic ester.
- 11. Write the scheme of the decarboxylation reaction of acetoacetic acid. Name the product of this reaction.
 - 12. What products do you expect to get after the heating of:
 - 2-aminobutanedioic acid;
 - 4-aminopentanoic acid.
 - 13. What product do you expect to get after the heating:
 - 2- hydroxybutanoic acid;
 - 4-hydroxybutanoic acid?

6. Laboratory work:

Experiment №1. Reactions of lactic acid.

A.Discovery of formic acid.

Sequence of operations: Place 1 drop of lactic acid and 1 drop of concentrated H_2SO_4 (Take care!) Warm the mixture.

Check the result: black foam.

To convince that CO is forming, set it on fire near the aperture of the testtube. Check the result: the blue flame.

Write:

CH₃-CH-C
$$\stackrel{O}{OH}$$
 OH OH lactic acid $CO \stackrel{t^o}{\longrightarrow} CO + CH_3$ $CO \stackrel{O}{\longrightarrow} CO + CH_3$ methanoic acid $CO \stackrel{O}{\longrightarrow} CO + CO + CH_3$ methanoic acid

B.Discovery of ethanal.

Sequence of operations: Place 2 drops of H_2O , 1 drop of concentrated H_2SO_4 and 1 drop of lactic acid in the test-tube N_2O 1.

Close it with the cork with the glass pipe. Lower the end of the glass pipe in the test-tube N_2 2 with 1 drop of I_2 (in KI solution) and 2 drops of NaOH in it. Warm the test-tube N_2 1.

Check the result: white-yellow precipitate in the test-tube N_{2} .

$$I_2 + 2NaOI \longrightarrow NaI + NaOI + H_2O$$

$$CH_3 - C \leqslant_{H}^{O} + 3NaOI \longrightarrow I_3C - C \leqslant_{H}^{O} + NaOH \longrightarrow CHI_3 \downarrow + H - C \leqslant_{O^-Na^+}^{O}$$
ethanal iodoform

Explain the result and write conclusion.

Experiment №2. Tartaric acid has 2 carboxy groups.

Sequence of operations: Place 1 drop of tartaric acid solution in the test-tube. Add 2 drops of KOH. Shake the test-tube.

Check the result: white precipitate.

Add several drops of NaOH. **Check the result:** the solution.

Attention: you need this solution for the next experiment.

Write:

Explain the result and write conclusion.

Experiment №3. Tartaric acid has 2 hydroxyl groups.

Sequence of operations: Place 2 drops of CuSO₄ in the test-tube. Add 2 drops of NaOH.

Check the result: blue precipitate.

Add the potassium sodium tartrate (you received it in the experiment N_2 2).

Check the result: blue solution (it is named Fehling's solution).

Write:

$$CuSO_{4} + 2NaOH \longrightarrow Cu(OH)_{2} + H_{2}O$$

$$COO^{-}K^{+}$$

$$2 CHOH + Cu(OH)_{2} \longrightarrow 2H_{2}O$$

$$CHOH$$

$$COO^{-}Na^{+}$$

$$COO^{-}Na^{+}$$

$$Cu^{2+}$$

$$CH - O \longrightarrow H$$

$$COO^{-}Na^{+}$$

$$2$$

potassium sodium tartrate

Explain the result and write conclusion.

Experiment №4. Discovering two tautomeric forms of acetoacetic ester.

Sequence of operations: Place 1 drop of acetoacetic ester and 1 drop of FeCl₃ solution.

Check the result: violet-red solution.

Add 1 drop of bromine water.

Check the result: violet colour disappeas, but it appeas again in several seconds.

Add one more drop of bromine water.

Check the result: the same change.

Write:

$$CH_{3}\text{-}C\text{-}CH_{2}\text{-}C \xrightarrow{O} CH_{5}$$

$$CH_{3}\text{-}C\text{-}CH_{2}\text{-}C \xrightarrow{O} CH_{5}$$

$$CH_{3}\text{-}C\text{-}CH_{2}\text{-}C \xrightarrow{O} CH_{5}$$

$$3CH_{3}\text{-}C\text{-}CH\text{-}C \xrightarrow{O} CH_{5}$$

$$OC_{2}H_{5}$$

Explain the result and write conclusion.

Experiment №5. Hydrolysis of acetylsalicylic acid.

Sequence of operations: Place some acetylsalicylic acid and 6 drops of H_2O in the test-tube N_21 . Shake the test-tube. Pour the part of the mixture in the test-tube N_22 . Add 1 drop of FeCl₃ solution in the test-tube N_22 .

Check the result: violet colour is not appearing.

Warm the test-tube N_2 1 during 30 seconds. Add 1 drop of FeCl₃ solution.

Check the result: violet colour.

Write:

COOH

O-C-CH₃ +
$$H_2O$$

acetylsalicylic acid

Fe³⁺

Salicylic acid

 Fe^{3+}

Salicylic acid

 Fe^{3+}

Explain the result and write conclusion.

7. Approximate version of the card for the final control of the class:

Variant

- **1.** Write the scheme and mechanism of the reaction of 2-aminopropanoic acid with butanoyl chloride.
- **2.** Write the schemes of the following reactions. Indicate interacted reaction centers of the substrate and the reagent (if it possible). Indicate the type and mechanism of the reactions.

$$\begin{array}{c} O \\ O \\ O \\ O \\ O \\ \end{array} \begin{array}{c} +CH_3OH/H_2SO_4 \\ +H_2C-C \\ \hline \\ CO \\ \end{array} \\ \begin{array}{c} +CH_3OH/H_2SO_4 \\ \hline \\ +H_2C-C \\ \hline \\ CO \\ \end{array}$$

THEME 9 Control-test № 1.

Theoretical foundations of structure and reactivity of the main families of organic compounds

- 1. Training and educational goals:
- 1. To control knowledge of:

- the main principles of classification and nomenclature of organic compounds;
- electronic structures of carbon atoms and heteroatoms, σ and π -bonds, conjugated and aromatic systems;
- mutual influence of atoms;
- spatial structure of organic compounds, configurational and conformational stereoisomerisms:
- reactivity of monofunctional, polyfunctional and heterofunctional compounds;
- biologically important reactions.
 - 2. To control skills in:
- classifying organic compounds according to the structure of function groups;
- using principal rules of IUPAC nomenclature of organic compounds for naming of biologically important compounds;
- using criteria of aromaticity to prove thermodynamic stability of biologically important compounds;
- indicating types and signes of electronic effects, ED and EW substituents;
- drawing conformations of biologically important compounds;
- designating chirality of biologically important compounds;
- drawing Fischer projection formulas of enantiomers and diastereomers;
- carring out quantitative and qualitative evaluation of acids and bases properties;
- designating reaction centers in alcohols, phenols, thiols, amines, aldehydes, ketones, carboxylic acids and their derivatives, polyfunctional and heterofunctional compounds;
- writing mechanisms of the reactions S_R , A_E , S_E , S_{N1} , S_{N2} , E, A_N , S_N .

II. Program questions:

2. Theoretical base of the structure and reactivity of organic compounds.

2.1 Introduction. Classification and nomenclature of organic compounds.

- 1. Classification of organic compounds according to the structure of carbon skeleton and according to the functional groups.
- 2. Principal rules of IUPAC nomenclature of organic compounds; substitutive and radicofunctional nomenclature.

2.2 Chemical bond and mutual influence of atoms in organic compounds.

- 3. Electronic structure of carbon atom and heteroatoms (N, O). Hybridization.
- 4. Chemical bonding in organic compounds. Main characteristics of the σ -and π -bonds in organic compounds. Hydrogen bonds.
- 5. Conjugation (π , π and p, π -conjugation). Conjugated systems with an open chain: 1, 3 diens, polyenes, allylic radical).

- 6. Conjugated systems with a closed chain. Aromaticity: criterions (conditions) of aromaticity, Huckel's rule of aromaticity. Aromaticity of benzenoid (benzene, naphthalene, phenanthrene), nonbenzenoid compounds. Conjugation (delocalization) energy. Thermodynamic stability of biologically important molecules with opened and closed conjugated systems.
- 7. Mutual influence of atoms in organic compounds: inductive effect and mesomeric effect. Electron–withdrawing and electron–releasing substituents. Electron density delocalization in the molecule. Reaction centres.

2.3 Stereochemistry of organic compounds. Configuration and conformation of organic compounds.

- 8. Configuration and conformation of organic compounds. The relationship between steric structure of organic compounds and the hybridization type of a carbon atom: sp^3 , sp^2 , sp hybridization. Molecular models (ball-and-stick models, space-filling models); three-dimensional (stereo-chemical) formulas. Newman and Fischer projection formulas.
- 9. Chirality. Chiral molecules. The chiral carbon atom. A stereocenter. Enantiomerism. Optical activity. Relative configuration. The D-, L-system of a stereochemical designation. Glyceraldehyde as a configurational standard. Absolute configuration of stereoisomers. Notion of the R-, S –system of a stereochemical designation.
- 10. Stereoisomerism of molecules with one stereocenter. Stereoisomerism of molecules with more than one stereocenter: enantiomers and diastereomers. Meso compounds. Racemate, racemic mixtures. Notion of methods of racemic mixtures separation. π -Diastereomers.
- 11. Conformations of open chain compounds. Newman projection formulas. Torsional and Van Der Waals strains in the molecules. Energy characteristics of alkanes` conformations.
- 12. The primary formation of five- and six-membered cycles. Stability of conformations. Axial and equatorial bonds. 1,3-diaxial interaction. Conformational inversion of cyclohexane.

2.4 Reactivity of hydrocarbons.

- 13. Chemical reaction as a process. Terms: reactants (a substrate, a reagent), products (the product of interest, the by- product), a reaction center, an activation energy, the rate of the reaction, the mechanism of the reaction. Classification of organic reactions according to the result (substitution, addition, elimination reactions; rearrangements; oxidation-reduction reactions) and mechanisms such as radical reactions, ionic reactions (electrophilic, nucleophilic).
- 14. Types of reagents: radical, nucleophilic, electrophilic, acidic, basic. Types of bond cleavage in organic compounds and forming species: free radicals as the result of homolysis, carbocations and carbonions as the result of heterolysis). Electronic and steric structures of these intermediates. Factors of their relative stability.

- 15. Reactivity of saturated hydrocarbons. Free–radical substitution reactions as homolytical reactions with participation of C–H bonds at a sp³ hybridized carbon atom. The mechanism of free radicals substitution reactions on the example of the halogenation of alkanes. Free-radical substitution reactions as regionselective reactions. Ways of free radicals formation. Notion of chain processes. The role of free radical oxidation reactions in biological processes. Active forms of oxygen, peroxides.
- 16. Electrophilic addition reactions to alkenes as heterolycal reactions with participation of π -bond between two sp² hybrid carbon atoms. The mechanism of the hydration reaction. The acidic catalysis. The effect of static and kinetic factors on regionselectivity of addition reactions. Markovnikov's rule.
- 17. Electrophilic addition to conjugated systems: hydration of α , β unsaturated carboxylic acids. Qualitative reactions for the unsaturated hydrocarbons (for the double bond).
- 18. Electrophilic aromatic substitution reactions as heterolytical reactions with participation of the π -electron cloud of an aromatic system. The mechanism of the reaction. The role of catalysts in the electrophile formation.
- 19. Electrophilic aromatic substitution reactions. Effect of substituents in an aromatic ring on its reactivity in electrophilic (aromatic) substitution. Orienting effect of substituents. Halogenation and alkylation reactions in vivo.

2.5 Reactivity of alcohols, phenols, thiols and amines. Acid-base properties of organic compounds.

- 20. The acidic and basic properties: the chemical nature of the atom in acidic and basic centers, electronic effects of substituents, solvatation effect. Toxicity of strong acids and bases. Amphoterism. The hydrogen bond as specific manifestation of acid and basic properties.
- 21. Reaction centers of alcohols, phenols, thiols and amines. Acidity or basicity: Bronsted-Lowry and Lewis theories. Qualitative and quantitative characteristics of acidic and basic properties of organic compounds.
- 22. Nucleophilic substitution reactions at sp^3 -hybrid carbon atom. S_{N1} and the S_{N2} mechanisms. Stereochemistry of nucleophilic substitution reactions.
- 23. Nucleophilic substitution of the hydroxyl group in alcohols. The role of acid catalysis.
- 24. The alkylation reactions of alcohols, thiols, amines. The alkylation in vivo.
- 25. Elimination reactions (dehydration) of alcohols. The biologically important dehydration reactions of alcohols.
- 26. Oxidation reactions of alcohols, phenols, thiols. Reduction reactions of disulfides. NAD⁺-NADH system; hydride transfer as one of the stages of the biological oxidation–reduction reactions with participation of this system. Phenols and thiols as antioxidants.

2.6 Reactivity of aldehydes and ketones.

- 27. Reaction centers of aldehydes and ketones. Nucleophilic addition reactions. The mechanism of nucleophilic addition reaction. Reactions of carbonyl compounds with water, alcohols, amines. Formation of cyclic hemiacetals. The biological role of acetalization reactions
- 28. Nucleophilic addition reactions. The aldol addition reactions. Reversibility of nucleophilic addition reactions. The biological role of aldol addition reactions.
- 29. Nucleophilic addition-elimination reactions of aldehydes and ketones with amines. Toxicity of aldehydes. Aldehydes as disinfectants and sterilizing agents.
- 30. Oxidation and reduction reactions of carbonyl compounds in vitro and in vivo. Qualitative reactions for aldehyde group and for acetone.

2.7 Reactivity of carboxylic acids and their derivatives.

- 31. Reaction centers of carboxylic acids. Acidic properties of mono- and dibasic, saturated, unsaturated and aromatic carboxylic acids.
- 32. Nucleophilic substitution reactions at the sp²-hybrid carbon atom of carboxylic acids and their derivatives. The acylation reactions such as formation of carboxylic acid anhydrides, haloanhydrides, esters, amides. Hydrolysis reactions of derivatives of carboxylic acids.
- 33. The acylating by carboxylic acid anhydrides, acid chlorides, carboxylic acids, esters, thioesters. The acylation ability of carboxylic acids derivatives. Relative reactivity of esters and thioesters. Biological importance of esters and thioesters. Acylcoenzyme A. Acylphosphates. Biologically important acylation reactions that proceed with participating of acylphosphates. Notion about phosphorilation reactions.
- 34. Amides of carboxylic acids. The structure of amide-group. Acid-base properties of amides. Hydrolysis of amides. Amide of benzoic acid.
- 35. Derivatives of carbonic acid: the urea (carbamide) as the complete amide of the carbonic acid, carbamic acid. Acid-base properties and biological importance of carbamic acid and carbamide. Biuret. Urethanes, ureides, ureidoacids in the medicine. Biological importance of creatine and phosphocreatine.

3. Biologically important heterofunctional compounds.

- 3.1 Poly- and heterofunctional compounds: participating in biological processes and using in medicine (compounds, which are origin of the most important medicament groups).
- 36. Classification of poly- and heterofunctional compounds. Acid-base properties. Typical reactivity of poly- and heterofunctional compounds.
- 37. Specific features of chemical behaviour of poly- and heterofunctional compounds: features of acid and base properties, cyclization and chelates formation. Chelate complex formation as the qualitative test for a diol fragment.

- 38. Intramolecular cyclization (γ and δ -hydroxyaldehydes, γ and δ -hydroxy- and aminoacids, dicarboxylic acids with 4 or 5 carbon atoms) intermolecular cyclization (α hydroxy- and aminoacids). Cyclic hemiacetals, cyclic anhydrides, lactides, diketopiperasines, lactones, lactames.
- 39. Decarboxylation reactions. The elimination reactions of β -hydroxy- and β -amino acids. Tautomerization: keto–enol tautomerization and lactam–lactim tautomerization.
- 40. Polyalcohols. Their examples: ethylene glycol, glycerol, inositol, xylitol, sorbitol. Esters of polyhydric alcohols with inorganic acids (nitro-glycerol, glycerol and inositol phosphates) and with fatty acids.
- 41. Dihydric phenols. Their examples: hydroquinone, resorcinol, catechol. Oxidation of dihydric phenols. Hydroquinone-quinone system. Phenols as antioxidants. Tocopherols.
- 42. Dicarboxylic acids. Their examples: oxalic acid, malonic acid, succinic acid, glutaric acid, fumaric acid. The transformation of succinic acid to fumaric acid as an example of a biologically important dehydrogenation reaction.
- 43. Amino alcohols. Their examples: 2-aminoethanol, choline, acetylcholine. Forming of choline from L-serine. Amino phenols. Their examples: dopamine, noradrenaline (norepinephrine), adrenaline (epinephrine).
- 44. Hydroxy-acids. Lactic acid, malic acid, tartaric acid, citric acid. Oxidation reactions of lactic acid and malic acid with participating of NAD⁺. Citric acid. Citrates: preservation of donor blood. Dehydration of citric acid in vivo.
- 45. Oxo-acids (aldehyde and keto acids). Their examples: pyruvic acid, acetoacetic acid, oxaloacetic acid, α -ketoglutaric acid. Acid properties and reactivity. The decarboxylation reaction of β -ketobutyric acid and the oxidizing decarboxylation reactions of pyruvic acid. Keto-enol tautomerization. β -hydroxybutyric acid, β -ketobutyric acid, acetone as representatives of "ketone bodies", their biological and diagnostic importance.
- 46. The heterofunctional benzene derivatives as medicaments. Salicylic acid and its derivatives (acetylsalicylic acid, methyl-salicylate, phenyl-salicylate).
- 47. p-Aminobenzoic acid and its derivatives (benzocain, novocaine). Biological role of p-aminobenzoic acid (folic acid as the growth factor). Modern anesthetics.
 - 48. Sulfanilic acid and its amide. Sulfanamides. Notion of antimetabolites.

3.2 Biologically important heterocyclic compounds. Alkaloids.

- 49. Heterocycles with one heteroatome. Pyrrole, indole, pyridine, quinoline. Heterocycles with several heteroatoms. Pyrazole, imidazole, pyrimidine, purine. Electronic and spacial structure of pyrrolic and pyridinic heteroatoms. Aromaticity of heterocycles. Influens of heteroatoms on reactivity of pyrrole and pyridine in S_E reactions.
- 50. Heterocycles with several heteroatoms. Acid-base properties of heterocyclic compounds. The tautomerisation on the example of imidazole. Biologi-

cally important pyridine derivatives: nicotinic amide, pyridoxal, isonicotinic acid and its derivatives.

51. Barbituric acid and its derivatives (phenobarbital). The hydroxypurines: hypoxanthine, xanthine, uric acid. Notion about alkaloids.

Literature:

Study the literature from the themes $N_2 1 - N_2 8$.

4.Questions for the control-test № 1:

«Theoretic bases of main organic compounds families structure and reactivity»

Theoretical part.

Question N_2 1:

Define in the following compounds - nicotinamide (3-pyridine-caboxamide); noradrenaline (2-amino-1-(3,4-dihydroxyphenyl) ethanol); benzo-cain (4-aminoethyl benzoate); acetylsalicylic acid (2-acetyloxybenzoic acid); adrenaline(2-methylamino-1-(3,4-dihydroxyphenyl)ethanol); serine (2-amino-3-hydroxypropanoic acid); alanine (2-aminopropanoic acid); tyrosine (2-amino-3-(4-hydroxyphenyl)-propanoic acid):

- 1. a) The hybridization type of carbon atoms and heteroatoms (pyridine and pyrrole type).
- b) The type of conjugation and show the electronic structure of the conjugated systems. Designate electron's movement with curved arrows.
 - 2. a) The sign (negative or positive) of inductive and resonance effects of functional groups and heteroatoms. Show these effects with arrows. Indicate ED or EW effect of functional groups.

Question N_2 2:

Write the Newman projection formulas of all staggered and eclipsed conformations and indicate the most stable for the following compounds: 2-aminobutanoic acid (along C_2 - C_3 bond); 2-amino-3-hydroxypropanoic acid (along C_2 - C_3 bond).

Draw the standard Fischer projection formulas of stereoisomers that correspond to the following compounds. Indicate diastereoisomers and enantiomers: 2-amino-3-hydroxybutanoic acid; 2-amino-3-methylpentanoic acid; 2,3-dihydroxybutanedioic acid; 2,3,4-trihydroxybutanal.

Write two chair conformations for cis-1,4-dimethylcyclohexane; transcyclohexanediol-1,3. Show the most stable conformation.

Ouestion N_2 3:

Reactivity of saturated hydrocarbons. Free–radical substitution reactions as homolytical reactions with participation of C–H bonds at a sp³ hybridized carbon atom. The mechanism of free-radicals substitution reactions on the example of the halogenation of alkanes.

Electrophilic addition reactions to alkenes as heterolycal reactions with participation of π -bond between two sp² hybrid carbon atoms. The mechanism of the hydration reaction. The acidic catalysis. The effect of static and kinetic factors on the regioselectivity of addition reactions. Markovnikov's rule. The features of electrophilic addition to the conjugated systems: hydration of α , β – unsaturated carboxylic acids.

Electrophilic aromatic substitution reactions as heterolytical reactions with participation of the π -electron cloud of an aromatic system. The mechanism of the reaction. The role of catalysts in the electrophile formation. Effect of substituents in an aromatic ring on its reactivity in electrophilic (aromatic) substitution. Orienting effect of substituents.

Reaction centers of alcohols, phenols, thiols and amines. Acidity or basicity: Bronsted-Lowry and Lewis theories. Nucleophilic substitution reactions at $\rm sp^3$ -hybrid carbon atom. $\rm S_{N1}$ and the $\rm S_{N2}$ – mechanisms. Stereochemistry of nucleophilic substitution reactions. Nucleophilic substitution of the hydroxyl group in alcohols. The role of acid catalysis. The alkylation reactions of alcohols, thiols, amines. Elimination reactions (dehydration) of alcohols. The biologically important dehydration reactions of alcohols. Nucleophilic properties of alcohols. Oxidation reactions of alcohols, phenols, thiols.

Reaction centers of aldehydes and ketones. Nucleophilic addition reactions. The mechanism of nucleophilic addition reaction. The reactions of carbonyl compounds with water, alcohols, amines. Formation of cyclic hemiacetals. The aldol addition reactions. Reversibility of nucleophilic addition reactions. Oxidation and reduction reactions of carbonyl compounds.

Reaction centers of carboxylic acids. Acidic properties of mono- and dibasic, saturated, unsaturated and aromatic carboxylic acids. Nucleophilic substitution reactions at the sp²-hybrid carbon atom of carboxylic acids and their derivatives. The acylation reactions such as formation of carboxylic acid anhydrides, haloanhydrides, esters, amides. Hydrolysis reaction of derivatives of carboxylic acids. The acylating reagents: carboxylic acid anhydride, acid chlorides, carboxylic acids, esters, thioesters.

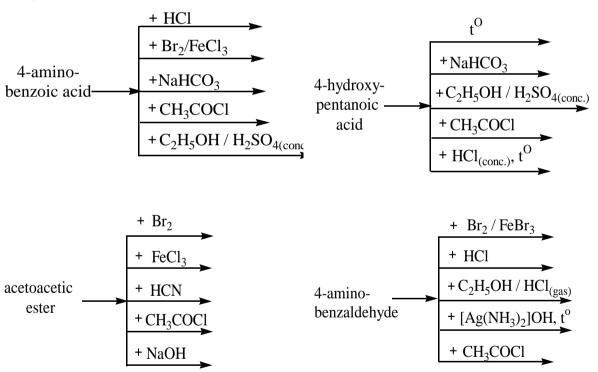
Classification of poly- and heterofunctional compounds. Polyalcohols, dihydric phenols, dicarboxylic acids, amino alcohols, amino phenols, hydroxyacids, oxo-acids (aldehyde and keto acids). Examples. Acid-base properties. Typical reactivity of poly- and heterofunctional compounds. Specific features of chemical behaviour of poly- and heterofunctional compounds: the features of acid and base properties manifestation, cyclization and chelates formation and the features conditioned by interference of functional groups in dependence of their arrangement. Intramolecular cyclization (γ - and δ -hydroxyaldehydes, γ - and δ -hydroxy- and aminoacids, dicarboxylic acids with 4 or 5 carbon atoms) intermolecular cyclization (α - hydroxy- and aminoacids). Cyclic hemiacetals, cyclic anhydrides, lactides, diketopiperasines, lactones, lactames. Decarboxylation reactions. The elimination reactions of β -hydroxy- and β -amino acids. Tautomerization: keto-enol tautomerization and lactam-lactim tautomerization.

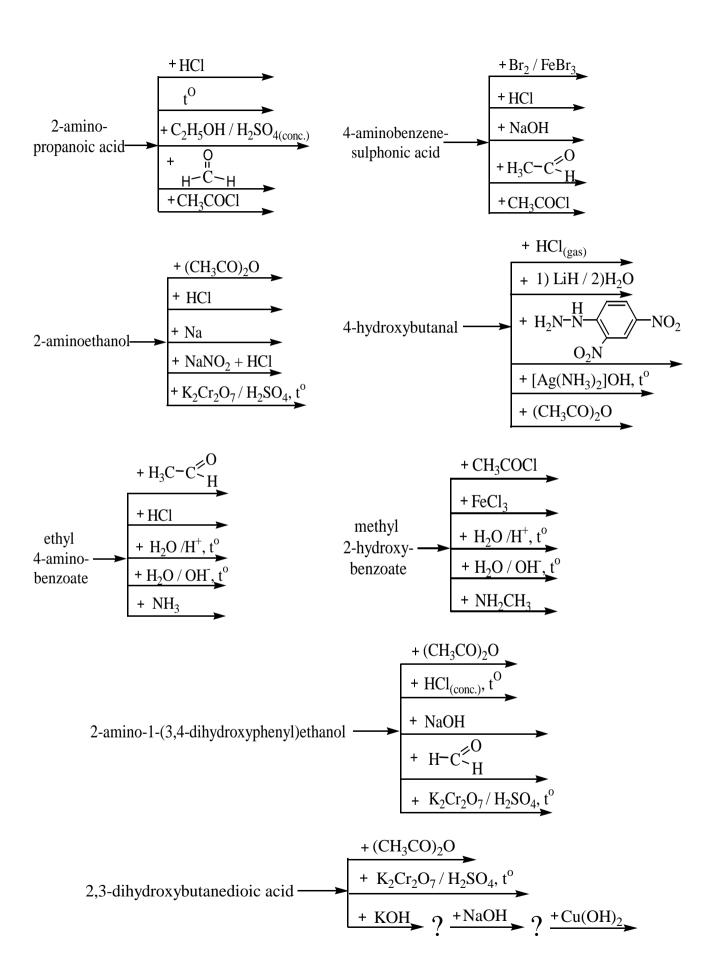
Question N_2 4:

Compare reactivity of several compounds in characteristic reactions (S_E aromatic, S_N at sp^3 carbon atom, S_N at sp^2 carbon atom, A_N , E); write the schemes and outline the mechanisms for the most reactive compounds.

Ouestion N_2 5:

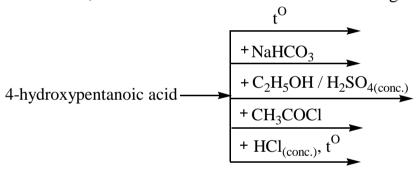
Write the schemes of reactions, represent and name reaction centers, taking part in each reaction, indicate the mechanism of the following reactions:





An example of the variant: TEST . No 1

- 1. Define the sign (negative or positive) of inductive and resonance (mesomeric) effects of functional groups and heteroatoms in the structure of benzocain (ethyl 4–aminobenzoate). Show these effects with arrows. Indicate ED or EW effect of functional groups.
- 2. Draw the standard Fischer projection formulas of stereoisomers that correspond to the structure of 2,3,4-trihydroxybutanal. Indicate diastereoisomers and enantiomers.
- 3. Carboxylic acids: acidic properties of mono- and dicarboxylic, saturated, unsaturated and aromatic carboxylic acids.
- 4. Show the reaction centers of butanethiol-1 and butanol-1. Write the scheme and outline mechanism of the S_N reaction with HCl for the most active compound.
- 5. Write the schemes of reactions, represent and name reaction centers, taking part in each reaction, indicate the mechanism of the following reactions:



THEME 10 Biologically important heterocyclic compounds. Alkaloids.

1. Training and educational goals:

- 1. To form knowledge of:
- classification and electronic structure of heterocyclic compounds;
- reactivity of the heterocyclic compounds;
- the types of tautomerisation of heterocyclic compounds and their derivatives;
- biologically important derivatives of heterocyclic compounds;
- classification and physiological influences of alkaloids.
- 2. To form skills in:
- finding the reaction centers and comparing the reactivity these reaction centers in different heterocyclic compounds;

- writing tautomeric forms of the most important derivatives of pyrimidine and pyrine;
- writing acid-base reactions, S_E and S_N reactions;
- carrying out characteristic and qualitative reactions of heterocyclic compounds.

2. Program questions:

- 1. Classification of heterocyclic compounds.
- 2. Five-membered heterocycles that contain one heteroatom (pyrrole, furan, thiophene, indole). Electronic structure of pyrrole-type nitrogen. Aromaticity of heterocycles. Reactivity of heterocycles in S_E reactions. Acid-base properties electron-rich systems. Biologically important derivatives of pyrrole and indole.
- 3. Five-membered heterocycles with two heteroatoms (imidazole, pyrazole). Electronic structure of pyridine-type nitrogen. Aromaticity. Acid-base properties. Biologically important derivatives of imidazole.
- 4. Six-membered heterocyclic compounds with one heteroatom. Pyridine as base and nucleophilic reagent. Reactivity of pyridine in electrophilic substitution (S_E) and nucleophilic substitution (S_N) reactions. Pyridine as π -deficient system. Biologically important derivatives of pyridine (nicotinamide, pyridoxal). Isonicotinic acid as the base for the syntesys of antituberculosis medicines.
- 5. Six-membered heterocycles with two heteroatoms. Pyrimidine. The basic properties of pyrimidine. Pyrimidine nucleic bases (cytosine, thymine, uracil). Barbitulic acid and its derivatives. Lactim-lactam and keto-enol tautomerism. Vitamin B_1 .
- 6. Fused heterocycles. Purine. Aromaticity. Purine nucleic bases (adenine, guanine). The hydroxypurines: hypoxanthine, xanthine, uric acid.
 - 7. Notion about alkaloids.

3. Literature:

- 1. Bioorganic chemistry: учебное пособие для иностранных студентов / О.Н. Ринейская [и др.]. Минск: Новое знание, 2018. р.
- 2. Hidranovich, L.G. Bioorganic chemistry lecture course / L.G. Hidranovich. Vitebsk, 2004. p.
- 3. Chernykh, V.P. Organic chemistry. Basic lecture course: The study guide for students of higher schools / V.P. Chernykh, L.A. Schemchuk. Kharkiv, 2011. p.

4. Homework:

- 1. Prepare the theoretical material according to the program questions of the theme 10.
 - 2. Prepare the laboratory work protocol.

3. Solve the problems $N_0 1$, $N_0 2$, $N_0 3$, $N_0 6$ presented on the pages 65-66.

5. Problems.

- 1. Compare basicity of pyridine, purine and imidazole. Wright the salt formation reaction with the strongest base.
- 2. Confirm the aromaticity of pyrrole, pyridine and pyrimidine Show the electronic structure of the pyrrole-type and pyridine-type of nitrogen atoms.
- 3. Write the structure of the product formed in each of the following reactions.

a) pyrrole +
$$H_2SO_4(conc.)$$
 \longrightarrow
b) pyridine + HNO_3 $\xrightarrow{H_2SO_4(conc.)t^o}$
c) furan + H_3C-C \xrightarrow{O} $\xrightarrow{O-NO_2}$
d) thiophene + $H_2SO_4(conc.)$ \longrightarrow
e) imidazole + CH_3 -I \longrightarrow

- 4. The amino acid histidine is a part of the active centers of many enzymes that carry out acid-base catalysis. Designate acid and base centers in the imidazole ring of histidine. Write the reactions that confirm the presence of the acid and base properties of imidazole.
- 5. Pyrimidine and purine nucleic bases are important part of nucleic acids. Write the structure of the two tautomeric forms of guanine, cytosine, uracil thymine. What kind of tautomeric form predominantes in equilibrium?
- 6. Derivatives of barbituric acid are used as sedatives and hypnotics. What types of tautomerism are characteristic of barbituric acid and phenobarbital? Write the scheme of tautomeric transformations and indicate the most active acidic centre of phenobarbital. Wright the sodium salt formation with the strongest acidic centre.
- 7. Uric acid is the final product of the metabolism of purine compounds in the human body. It is poorly soluble in water whereas disodium salts of uric acid are soluble. Write the schemes of the formation of sodium salts of uric acid.
- 8. Write the scheme and outline the mechanism of pyrrole nitration reaction by the specific agent (acetyl nitrate). Explain why it is not possible to do with nitric acid.
- 9. Acid hydrolysis is carried out to identify cocaine. Determine the reaction centers for which hydrolysis takes place and write the scheme of the reaction. Indicate the mechanism of the reaction.

10. Nicotinic acid and its amide are known as the two forms of coenzyme NAD⁺. Suggest the schemes of the reactions for the synthesis of nicotinamide from nicotinic acid. Indicate the mechanisms of the reactions.

6. Laboratory work.

Experiment № 1. Analgin oxidation reaction.

Place 5 drops of analgin in a test-tube. Add 1 drop KIO₃. Shake the mixture. Add another drop of analgin.

Check the result: colored solution.

Write:

Explain the result and write conclusion.

Experiment № 2. Solubility of uric acid and its sodium salt in water.

Place a small amount of uric acid in the test-tube. Add 4 drops of water. Uric acid is insoluble in cold water. Add 5 drops of 2н NaOH. Shake the mixture.

Check the result: the solution. Attention: you need this solution for the next experiment.

Write:

Explain the result and write conclusion.

Experiment N_2 3. The formation of poorly soluble salt of ammonium urate.

Take the solution you received in the experiment N_2 1. Add 1 drop of saturated ammonium chloride solution.

Check the result: white precipitate.

Write:

Explain the result and write conclusion.

Experiment № 4. Common reactions for alkaloids.

Place three drops of quinine hydrochloride solution on a glass slide. Add 1 drop of iodine to the first drop of quinine, 1 drop 0,5% of tannin solution to the second drop of quinine, 1 drop of saturated solution of picric acid to the third drop of quinine.

Check the result: colored precipitates.

Write:

$$\begin{array}{c|c} & \text{OH} & \text{CH=CH}_2 \\ \text{OCH}_3 & \text{CH} & \text{NO}_2 \\ \text{quinine hydrochloride} & \text{picric acid} \\ \\ & & \text{OCH}_3 & \text{OH} & \text{NO}_2 \\ & & \text{OCH}_3 & \text{OH} & \text{OH} & \text{OH} \\ & & \text{OCH}_3 & \text{OH} & \text{OH} & \text{OH} \\ & & \text{OCH}_3 & \text{OH} \\ & & \text{OCH}_3 & \text{OH} & \text{OH} \\ & & \text{OCH}_3 & \text{OH} \\ & & \text$$

Explain the result and write conclusion.

7. Approximate version of the card for the final control of the class:

Variant

- 1. Schow the order of basicity increase for the following compounds: a) pyrimidine, b) pyridine, c) imidazole. Explain the reasons for your choice. Write the salt formation reaction using the most basic compound.
- 2. Write the schemes of the following reactions. Indicate the reaction centers of the substrate and the reagent (if it is possible). Indicate the type and mechanism of the reactions:

$$\begin{array}{c} O \\ HN \\ H_2N \\ N \\ H \end{array}$$

THEME 11

Carbohydrates. Monosaccharides.

1. Training and educational goals:

- 1. To form knowledge of:
- classification of monosaccharides;
- stereochemistry of monosaccharides;
- the structures of the most biologically important pentoses, hexoses and their derivatives;
- ring-chain tautomerism of monosaccharides;
- conformations of pyranose forms of monosaccharides;
- chemical properties of different tautomeric forms of monosaccharides;
- oxidation and reduction reactins of monosaccharides.
- 2. To form skills in:
- drawing the enantiomers and the diastereomers of monosaccharides;
- writing the biologically important monosaccharides in Fischer projection formulas and Haworth formulas:
- drawing the chair conformations of pyranose forms of monosaccharides;
- designating the reaction centers of different tautomeric forms;
- writing schemes of the formation and hydrolysis of O- and N- glycosides, alkylation and acylation reactions;
- drawing the structures of biologically important phosphates of monosaccharides;
- carrying out characteristic and qualitative reactions of monosaccharides.

2. Program questions:

- 1. Monosaccharides. Classification of monosaccharides. Aldoses, ketoses; trioses, tetroses, pentoses, hexoses. Stereoisomerism of monosaccharides. Dand L-families. Biological importance of monosaccharides and their derivatives.
- 2. Structures of the most important pentoses (D-ribose, D-xylose, 2-deoxy-D-ribose) and hexoses (D-glucose, D-mannose, D-galactose, D-fructose). Amino sugars (D-glucosamine, D-mannosamine, D-galactosamine) and their properties. Neuraminic acid, sialic acids.
- 3. Open-chain structures and cyclic forms. Furanoses and pyranoses; α and β -anomers. Fischer projection formulas and Haworth formulas. A cyclo-oxo tautomerization. Mutarotation. Conformations of pyranose forms of monosaccharides. Physical properties of monosaccharides.
- 4. Chemical properties of monosaccharides. Nucleophilic substitution at an anomeric atom in cyclic forms of monosaccharides. O- and N-glycosides. Hydrolysis of glycosides. Biologically important phosphorylation reactions of monosaccharides. Phosphates of monosaccharides.

- 5. Oxidation of monosaccharides. Reducing properties of aldoses. Aldonic, aldaric, uronic acids. Reduction of monosaccharides to alditols (xylitol, glucitol (sorbitol), mannitol); application of alditols in medicine. Epimerization reaction of monosaccharides, the reversible transformation of aldoses to ketoses.
- 6. Nucleophilic addition reaction with participation of oxo-group of openchain form of glucose (glycylation reactions of peptides). Ascorbic acid. Its structure, properties, and biological importance.

3. Literature:

- 1. Bioorganic chemistry: учебное пособие для иностранных студентов / О.Н. Ринейская [и др.]. Минск: Новое знание, 2018. р. 116-126.
- 2. Hidranovich, L.G. Bioorganic chemistry lecture course / L.G. Hidranovich. Vitebsk, 2004. p. 170-186.
- 3. Chernykh, V.P. Organic chemistry. Basic lecture course: The study guide for students of higher schools / V.P. Chernykh, L.A. Schemchuk. Kharkiv, 2011. p. 401-418.

4. Homework:

- 1. Prepare the theoretical material according to the program questions of the theme 11.
 - 2. Prepare the laboratory work protocol.
- 3. Solve the problems $N_{\underline{0}}$ 1, $N_{\underline{0}}$ 3, $N_{\underline{0}}$ 6 (a,b,c), $N_{\underline{0}}$ 7 presented on the pages 69-71.

5. Problems.

1. Classify each of the following monosaccharides according to the number of carbon atoms and the type of carbonyl group it contains.

2. Label the stereocenters in each of the monosaccharides in Exercise 1 by an asterisk and determine the maximum number of stereoisomers of each. Assign each of the monosaccharides in Exercise 1 to either the D- or L- family.

- 3. Write the cyclic forms for each of the monosaccharides in Exercise 1. Indicate which is the α -anomer and which is the β -anomer. Draw conformational formulas for each of the pyranose forms.
- 4. Write a chair representation of the pyranose form of each of the following monosaccharides in Exrcise 1.
- 5. Write the Fisher projection formula for each of the following cyclic monosaccharides

- 6. Write the structure of the products, if any, of the reaction of α -D-galactopyranose with each of the following reagents.
 - (a) CH₃OH/HCl; (b) (CH₃O)₂SO₂/NaOH; (c)(RCO)₂O/CH₃COONa
 - (d) Fehling's solution; (e) Br₂/H₂O; (f) HNO₃
- 7. Write the structure of the aldonic acids and aldaric acids obtained by oxidation of each of the following monosaccharides. Write the structure of alditols obtained by reduction of each of the following monosaccharides:

Which of the products are optically active?

CHO
$$_{\rm HOH_2C}$$
 $_{\rm OH}$ $_{\rm OH$

- 8. Write the reaction of the acid-catalyzed hydrolysis of methyl α -D-glucopyranoside and pentamethyl derivative.
- 9. Write the reaction of the acid-catalyzed and base-catalyzed hydrolysis of esters of β -D-mannopyranose.

10. Salicin is naturally occurring compound, find in the bark of willow trees.

Salicin can be converted to salicylic acid which, in turn, can be converted into the most widely used modern analgetic, aspirin. Write the scheme of this reaction, show the condition, name the products.

6. Laboratory work.

Experiment № 1. Glucose has hydroxyl groups.

Sequence of operations: Place 1 drop of glucose solution in the test-tube. Add 6 drops of NaOH and 1 drop of CuSO₄.

Check the result: blue solution.

Attention: you need this solution for the next experiment.

Write:

$$CuSO_4 + 2NaOH \rightarrow Cu(OH)_2 + Na_2SO_4$$

Explain the result and write conclusion.

Experiment № 2. Oxidation of glucose by Cu(OH)₂.

Sequence of operations: Take the solution you received in the experiment N_2 1. Add 8 drops of H_2O . Warm the test-tube.

Check the result: brick-red precipitate.

Write:

$$\begin{bmatrix} CH_2OH \\ OH \\ HO \\ Cu \end{bmatrix} \xrightarrow{t^0 (OH)} Cu_2OV + oxidation products \\ (brick-red reduction product) \\ 2 & product)$$

Explain the result and write conclusion.

Experiment \mathbb{N}_2 3. Oxidation of glucose and fructose by Tollen's reagent $[Ag(NH_3)_2]OH$.

Sequence of operations: Take 2 test-tubes. Place 1 drop of AgNO₃ solution and 2 drops of NaOH solution in each test-tube. Add 4 drops of NH₄OH in these test-tubes. This solution is named Tollen's reagent.

Add 1 drop of glucose solution in the test-tube \mathbb{N}_{2} 1 and 1 drop of fructose solution in the test-tube \mathbb{N}_{2} 2. Warm the test-tubes.

Check the result: silver coating in the test-tubes.

Write:

HO
$$HO$$
 + [Ag(NH₃)₂]OH OH + OH + OH + OH + OH CH₂OH glucose

$$\rightarrow$$
 Ag \downarrow + H₂O + 2NH₃ + oxidation products

Explain the result and write conclusion.

Experiment № 4. Reaction of fructose with resorcinol.

Sequence of operations: Place 1 crystal of resorcinol and 2 drops of concentrated HCl (Take care!) in the test-tube. Add 2 drops of fructose solution. Warm the test-tube.

Check the result: the change of colour.

Explain the result and write conclusion.

Experiment No. 5. Qualitative test for pentoses.

Sequence of operations: Place some arabinose in the test-tube \mathbb{N}_2 1. Make the mixture of 3 drops of concentrated HCl (Take care!) and 3 drops of H₂O in the test-tube \mathbb{N}_2 2. Add this mixture in the test-tube \mathbb{N}_2 1. Place 1 drop of aniline and 1 drop of CH₃COOH on the filter paper. Place this filter paper on the inner border of the test-tube \mathbb{N}_2 1. Warm the test-tube.

Check the result: the filter paper becomes red coloured. **Write:**

HO

OH

$$C \stackrel{O}{=} H$$
 $C \stackrel{O}{=} H$
 $C \stackrel{O}{=} H$

Explain the result and write conclusion.

7. Approximate version of the card for the final control of the class:

Variant

1. Draw structure for pyranose forms of the D-mannose and name them.

2. Write the schemes of the following reactions. Indicate interacted reaction centers of the substrate and the reagent (if it possible). Indicate the type and mechanism of the reactions.

$$\alpha\text{-D-ribofuranose} \begin{picture}(20,0) \put(0,0){\line(1,0){100}} \put$$

THEME 12 Carbohydrates. Oligosaccharides and polysaccharides.

1. Training and educational goals:

- 1.To form knowledge of:
- classification and structures of the biologically important oligosaccharides and polysaccharides;
- principles of the structure of reducing and non- reducing disaccharides;
- primary and secondary structures of homopolysaccharides;
- structure and biological role of heteropolysaccharides;
- the reaction centers and reactivity of disaccharides.
- 2. To form skills in:
- drawing structural formulas of reducing and non-reducing disaccharides;
- indicating the configuration of glycoside linkage;
- designating the reaction centers;
- writing schemes of the formation and hydrolysis of glycosides, alkylation and acylation reactions of disaccharides, oxidation of reducing disaccharides;
- drawing the primary and secondary structures of homopolysaccharides;
- drawing the disaccharide units of the heteropolysaccharides;
- carrying out characteristic and qualitative reactions of disaccharides and polysaccharides.

2. Program questions:

1. Oligo- and polysaccharides. Common characteristic and classification of polysaccharides. Oligosaccharides. Disaccharides: maltose, cellobiose, lactose, sucrose. Structures, the cyclo-oxo tautomerization. Reducing properties. Hydrolysis.

- 2. Maltose, cellobiose, lactose. The conformational structure. The role of lactose oligosaccharides in formation of not pathogenic microflora in the intestines, which is necessary for normal digestion.
- 3. Polysaccharides. Homo- and heteropolysaccharides. Homopolysaccharides: starch (amylose, amylopectine), glycogen, dextran, cellulose. Primary structure, hydrolysis. Notion about secondary structure (amylose, cellulose). Pectins (polygalacturonic acid). Plasma replacing solutions on the basis of dextran and starch.
- 4. Heteropolysaccharides: hyaluronic acid, chondroitin sulfates. Primary structure. Notion of mixed biopolymers: proteoglycans, glycoproteins, glycolipids.

3. Literature:

- 1. Bioorganic chemistry: учебное пособие для иностранных студентов / О.Н. Ринейская [и др.]. Минск: Новое знание, 2018. р. 127-135.
- 2. Hidranovich, L.G. Bioorganic chemistry lecture course / L.G. Hidranovich. Vitebsk, 2004. p. 187-204
- 3. Chernykh, V.P. Organic chemistry. Basic lecture course: The study guide for students of higher schools / V.P. Chernykh, L.A. Schemchuk. Kharkiv, 2011

4. Homework:

- 1. Prepare the theoretical material according to the program questions of the theme 12.
 - 2. Prepare the laboratory work protocol.
- 3. Solve the problems \mathbb{N}_2 1, \mathbb{N}_2 3, \mathbb{N}_2 4, \mathbb{N}_2 10 presented on the pages 75-78.

5. Problems.

- 1. Write the structure of the product of the reaction of β -maltose with each of the following reagents:
- a) HOH/H⁺

- c) Tollen's reagent
- b) Br₂/HOH
- d) (CH₃O)₂SO₂/NaOH
- 2. Write the structure of the product of the reaction of α -cellobiose with each of the following reagents:
- a) HOH/H⁺
- c) (CH₃CO)₂O/CH₃COO⁻Na⁺
- b) Br_2/H_2O
- d) NaBH₄

- e) Fehling's solution
- 3. Direct oxidation of an aldose affects the aldehyde group first, converting in to a carboxylic acid, and most oxidazing agents that will attack 2° alcohol groups. Cleary, then, a laboratory synthesis of a uronic acid from an aldose

requires protecting these groups from oxidation. Keeping this in mind, suggest a method for carrying out a specific oxidation that would convert D-galactose to D-galacturonic acid.

- 4. Show how the following experimental evidence can be used to deduce the structure of lactose.
- a) Acid hydrolysis of lactose ($C_{12}H_{22}O_{11}$) gives equimolar quantities of D-glucose and D-galactose. Lactose undergoes a similar hydrolysis in the presence of a β -galactosidase,
- b) Lactose is a reducing sugar.
- c) Oxidation of lactose with bromine water followed by hydrolysis with dilute acid gives D-galactose and D-gluconic acid.
- d) Bromine water oxidation of lactose followed by methylation and hydrolysis gives 2,3,6-tri-0-methylgluconolactone and 2,3,4,6-tetra-O-methyl-D-galactose.
- e) Methylation and hydrolysis of lactose gives 2,3,6-tri-O-methyl-D-glucose and 2,3,4,6-tetra-O-methyl-D-galactose.
- 5. Deduce the structure of the disaccharide melibiose from the following data:
 - a) Melibiose is a reducing sugar.
 - b) Hydrolysis of melibiose with acid or with an α -galactosidase gives D-galactose and D-glucose.
 - c) Bromine water oxidation of melibiose gives *melibionic acid*. Hydrolysis of melibionic acid gives D-galactose and D-gluconic acid. Methylation of melibionic acid followed by hydrolysis gives 2,3,4,6-tetra-O-methyl-D-galactose and 2,3,4,5-tetra-O-methyl-D-gluconic acid.
 - d) Methylation and hydrolysis of melibiose gives 2,3,4,6-tetra-O-methyl-D-galactose and 2,3,4-tri-O-methyl-D-glucose.
- 6. Trehalose is a disaccharide that can be obtained from yeasts, fungi, sea urchins, algae, and insects. Deduce the structure of trehalose from the following information:
 - a). Acid hydrolysis of trehalose yields only α -glucose.
 - b). Trehalose is hydrolyzed by α -glucosidases but not by β -glucosidases.
 - c). Trehalose is a nonreducing sugar;
 - d). Methylation of trehalose followed by hydrolysis yields two molar equivalents of 2,3,4,6-tetra-O-methyl-D-glucose.
- 7. Outline chemical tests that will distinguish between each of the following:
- (a) D-Glucose and D-glucitol
- (b) D-Glucitol and D-glucaric acid

- (c) D-Glucose and D-fructose
- (d) Sucrose and maltose
- (e) Maltose and maltonic acid
- (f) Methyl β-D-glucopyranoside and 2,3,4,6-tetra-O-methyl-β-D-glucopyranose
- 8. A group of oligosaccharides called *Schardinger dextrins* can be isolated from *Bacillus macerans* when the bacillus is grown on a medium rich in amylose. These oligosaccharides are all *nonreducing*. A typical *Schardinger dextrin* undergoes hydrolysis when treated with an acid or an a-glucosidase to yield six, seven, or eight molecules of D-glucose. Complete methylation of a *Schardinger dextrin* followed by acid hydrolysis yields only 2,3,6-tri-O-methyl-D-glucose. Propose a general structure for *a Schardinger dextrin*.
- 9. Isomaltose is a disaccharide that can be obtained by enzymatic hydrolysis of amylopectin. Deduce the structure of isomaltose from the following data:
- a). Hydrolysis of 1 mol of isomaltose by acid or by an α -glucosidase gives 2 mol of D-glucose.
- b) Isomaltose is a reducing sugar.
- c) Isomaltose is oxidized by bromine water to isomaltonic acid. Methylation of isomaltonic acid and subsequent hydrolysis yields 2,3,4,6-tetra-O-methyl-D-glucose and 2,3,4,5-tetra-O-methyl-D-gluconic acid.
- d). Methylation of isomaltose itself followed by hydrolysis gives 2,3,4,6-tetra-O-methyl-D-glucose and 2,3,4-tri-O-methyl-D-glucose.
- 10. The synovial flulid of the joint contains heteropolysaccharide hyaluronic acid, it is largely responsible for the viscosity of the fluid. Hyaluronic acid is formed by joining together alternately two different sugars: D-glucuronic acid and N-acetyl-2-D-glucosamine bonded by β -(1 \rightarrow 3) glycoside linkage. Disaccharide subunits is joined by β -(1 \rightarrow 4) glycoside linkages. Write structure of hyaluronic acid segment containing two disaccharide subunits, explain its biological role.
- 11. Glycoproteins of connective tissue are chondroitin sulfates joined through the tetrasaccharide segment with polypeptide serine residues by β -glycoside linkage. The tetrasaccharide contains D-glucuronic acid (1), two D-galactopyranoses (2,3) and D-xylopyranose (4) units joined together according next scheme:

$$\begin{array}{c} \text{CO} \\ \text{Chondoroitin}_{\beta 1 \rightarrow 4} & \begin{array}{c} \text{CO} \\ \text{2} \\ \text{3} \\ \text{\beta 1} \rightarrow 3 \end{array} & \begin{array}{c} \text{OH} \\ \text{4} \\ \text{4} \end{array} + \text{HOCH}_2\text{-CH} \longrightarrow \begin{array}{c} \text{CO} \\ \text{NH} \\ \text{serine} \\ \text{residue} \end{array}$$

4- Chondroitin sulfate is composed of repeating disaccharide subunits joined together by β -(1 \rightarrow 4) glycoside linkages. Each disaccharide subunit is formed of D-glucuronic acid and N-acetyl-2-D-galactosamine-4-sulfate joined by β -(1 \rightarrow 3) glycoside linkage.

Write:

- 1) structure of 4-chondroitin sulfate segment containing two disaccharide subunits.
- 2) structure of tetrasaccharide segment and show its joining with polypeptide.

6. Laboratory work.

Experiment № 1. Lactose and sucrose have hydroxyl groups.

Sequence of operations: Place 1 drop of lactose solution in the test-tube \mathbb{N}_2 1 and 1 drop of sucrose solution in the test-tube \mathbb{N}_2 2. Add 6 drops of NaOH and 1 drop of CuSO₄ solutions in two test-tubes.

Check the result: blue solution.

Attention: you need these solutions for the next experiment.

Write:

$$CuSO_4 + 2NaOH \rightarrow Cu(OH)_2 + Na_2SO_4$$

$$\begin{array}{c} \text{CH}_2\text{OH} \\ \text{OH} \\ \text{OH} \\ \text{OH} \\ \text{OH} \\ \text{CH}_2\text{OH} \\ \text{OH} \\ \text{CH}_2\text{OH} \\ \text{Sucrose} \\ \end{array} \rightarrow \begin{array}{c} \text{CH}_2\text{OH} \\ \text{OH} \\ \text{OH} \\ \text{OH} \\ \text{CH}_2\text{OH} \\ \text{OH} \\ \text{CH}_2\text{OH} \\ \text{OH} \\ \text{CH}_2\text{OH} \\ \text{OH} \\ \text{OH} \\ \text{CH}_2\text{OH} \\ \text{OH} \\ \text{Sucrose} \\ \end{array}$$

Explain the result and write conclusion.

Experiment № 2. Reducing power of lactose and sucrose.

Sequence of operations: Warm the test-tubes with solutions you received in the experiment N_2 1.

Check the result: brick-red precipitate in the test-tube №1. **Write:**

$$\begin{bmatrix} CH_2OH & CH_2OH \\ OH & OH \\ OH & 2_{+} & O \end{bmatrix}_2 \qquad \begin{bmatrix} CH_2OH & CH_2OH \\ HO & OH \\ OH & 2_{+} & O \end{bmatrix}_2 \xrightarrow{CH_2OH} \begin{bmatrix} CH_2OH & CH_2OH \\ OH & 2_{+} & O \end{bmatrix}_2$$

$$\longrightarrow$$
 Cu₂O \downarrow + oxidation products of lactose

Explain the result and write conclusion.

Experiment № 3. Proof of sucrose hydrolysis.

Sequence of operations: Take 2 test-tubes. Place 1 drop of sucrose solution in the test-tube \mathbb{N}_2 1. Add 1 drop of HCl and 6 drops of H₂O. Warm the test-tube \mathbb{N}_2 1 during 0,5-1 minute. Pour half of the solution, received in the test-tube \mathbb{N}_2 1 in the test-tube \mathbb{N}_2 2. Add 6 drops of NaOH, 4 drops of H₂O and 1 drop of CuSO₄ in the test-tube \mathbb{N}_2 2. Warm the test-tube \mathbb{N}_2 2.

Check the result: brick-red precipitate.

Add 1 crystal of resorcinol and 2 drops of concentrated HCl (Take care!) in the test-tube N_2 1.

Check the result: the change of colour.

Write:

HOH₂C OH CH₂OH
$$t^{\circ}$$
, HCl(concd) HOH₂C OH CH₂OH t° compound red colour

Explain the result and write conclusion.

Experiment № 4. Discovery of the starch.

Sequence of operations: Place 5 drops of the starch paste solution in the test-tube. Add 1 drop of very diluted I_2 solution.

Check the result: blue solution.

Warm the test-tube.

Check the result: colourless solution.

In getting cold the solution become blue again.

Write:

Explain the result and write conclusion.

Experiment № 5. Starch has no reducing power.

Sequence of operations: Place 10 drops of the starch paste in the test-tube. Add 3 drops of NaOH and 1 drop of CuSO₄ solution. Shake the test-tube.

Check the result: blue precipitate of Cu(OH)₂

Warm the test-tube.

Check the result: black precipitate of CuO.

Write:

$$CuSO_4 + 2NaOH \longrightarrow Cu(OH)_2 + Na_2SO_4$$

 $Cu(OH)_2 \xrightarrow{t^o} CuO \downarrow + H_2O$

Explain the result and write conclusion.

Experiment № 6. Acidic hydrolysis of the starch.

Sequence of operations: Place 1 drop of the starch paste solution in the test-tube. Add 2 drops of H_2SO_4 . Warm the test-tube on the water bath during 20 minutes. Place 1 drop of this solution on the glass. Add 1 drop of very diluted I_2 (with KI) solution.

Check the result: solution has no blue colour.

Add 8 drops of NaOH and 1 drop of CuSO₄ solutions in the test-tube. Warm the test-tube.

Check the result: brick-red precipitate.

Write:

2). $CuSO_4 + 2NaOH \rightarrow Cu(OH) + Na_2SO_4$

$$\begin{array}{c} CH_2OH \\ OH \\ OH \\ OH \end{array} \longrightarrow \begin{array}{c} CH_2OH \\ OH \\ OH \end{array} \longrightarrow \begin{array}{c} CH_2OH \\ OH \\ OH \end{array} \longrightarrow \begin{array}{c} CU_2OV + H_2O + \text{oxidation products} \end{array}$$

Check the result and write conclusion.

7. Approximate version of the card for the final control of the class:

Variant

- **1.** Draw the primary structure of amylose. Indicate type of glycosidic linkages between structural units. Show secondary structure for amylose.
- **2.** Write the schemes of the following reactions. Indicate interacted reaction centres of the substrate and the reagent (if it possible). Indicate the type and mechanism of the reactions.

$$\alpha\text{-cellobiose} \xrightarrow{\begin{array}{c} C_2H_5OH/H^+ \\ \\ H_3C-C \\ \\ O \\ \\ \hline \\ Br_2/H_2O \end{array}} ? \xrightarrow{\begin{array}{c} H_2O/OH^- \\ \\ ? \\ \\ \hline \end{array}} ?$$

THEME 13 Natural amino acids.

1. Training and educational goals:

- 1.To form knowledge of:
- classification, structure and stereochemistry of naturally occurring amino acids;
- reaction centers and chemical properties of α -amino acids as heterofunctional compounds;
- some α -amino acids biosynthesis and methabolism pathways.
 - 2. To form skills in:
- drawing D- and L-stereoisomers of α -amino acids;
- writing ionic forms of α -amino acids at different pH values;
- characterizing reactivity of α -amino acids by the presence of certain reaction centers;
- writing deamination reactions, transamination reactions and decarboxylation reactions;
- carrying out characteristic and qualitative reactions of $\alpha\mbox{-amino}$ acids.

2. Program questions:

- 1. Amino acids that can be obtained from proteins. Classification of naturally occurring amino acids taking into account different signs: acid and base properties, chemical nature of a side chain and its substituents. Structure, nomenclature. Stereoisomerism.
 - 2. Acid and base properties, dipolar ions. Essential amino acids.

- 3. The formation of α -amino acids: hydrolysis of proteins, synthesis from α -halo acids. Reducing amination reactions and transamination reactions. Pyridox-al catalysis.
- 4. Chemical properties of α -amino acids as heterofunctional compounds. Formation of intracomplex salts. Esterification, acylation, alkylation, deamination reactions, formation of amines. Qualitative tests for α -amino acids.
- 5. Biologically important reactions of α -amino acids. Decarboxylation of α -amino acids the way of formation of biogenic amines and biological regulators (2-aminoethanol, histamine, tryptamine, serotonin, dopamine, γ -amino butyric acid), their biological importance. Notion about neuromediators.
- 6. Oxidative and non-oxidative deamination reactions. Hydroxylation reactions: phenylalanine \rightarrow tyrosine, tyrosine \rightarrow 3, 4-dihydroxyphenylalanine, tryptophan \rightarrow 5-hydroxytryptophan, proline \rightarrow 4-hydroxyproline. Cysteine oxidation. Disulfide bond.

3. Literature:

- 1. Bioorganic chemistry: учебное пособие для иностранных студентов / О.Н. Ринейская [и др.]. Минск: Новое знание, 2018. р. 136-144.
- 2. Hidranovich, L.G. Bioorganic chemistry lecture course / L.G. Hidranovich. Vitebsk, 2004. p. 205-217.
- 3. Chernykh, V.P. Organic chemistry. Basic lecture course: The study guide for students of higher schools / V.P. Chernykh, L.A. Schemchuk. Kharkiv, 2011. p. 312-315.

4. Homework:

- 1. Prepare the theoretical material according to the program questions of the theme 13.
 - 2. Prepare the laboratory work protocol.
- 3. Solve the problems N_{2} 2 (c,d), N_{2} 3 (b,c), N_{2} 7, N_{2} 8 presented on the pages 83-84.

5. Problems.

- 1. Write Fischer projection formulas for each of the following amino acids:
- (a) L-Valine, (b) D-Cysteine (c) L-Glutamine (d) L-Phenylalanine
- 2. Write the structure of each of the following amino acids in solution at pH=3, pH=8, pH=11
 - (a) Leu, (b) Met, (c) Asp, (d) Lys
 - 3. Write the structure of the predominant form of each of the following amino acids at the pH of blood 7,4

- (a) Ser (b) Glu (c) His (d) Gly
- 4. Write the structure of the predominant form of threonine in each solution of the following pH:
- (a) pH=0,2
- (b) pH=9,8
- (c) pH=13
- (d) pH=5,0
- 5. Which of the side chains of the 20 amino acids are charged at pH=7?
- 6. Write the structure of the product of the reaction of isoleucine with each of the following reagents:
 - a. CH₃OH/HCI
 - b. Basic aqueous solution of bensoyl chloride
 - c. acetic anhydride
- 7. Write the structure of the product formed in each of the following reactions:
- (a) Asn + NaOH/HOH(t^{o}) \rightarrow
- (b) Lys + HCI \rightarrow
- (c) $Asp + NaOH \rightarrow$
- (d) Trp + NaNO₂/HCI \rightarrow
- (e) Phe + $H_2C=O \rightarrow$
 - 8. Write the structure of the product of each of the following reactions:
 - (a) 2-oxopropanoic acid + Glutamic acid aminotransferase
 - **(b)** 2-oxobutandioic acid + alanine aminotransferase
 - (c) Histidine decarboxylase
 - (d) Write the scheme of the deamination reaction of Glu.
- 9. Arginine is the most basic of the 20 common α -amino acids. A molecula of Arg has a total of four nitrogen atoms. Which of the four is the most basic? Explain your choice and find most basic centre in the side chain of Arg. Write the structure of the predominant form of arginine at pH of blood 7,4.

6. Laboratory work.

Experiment 1. Glycine solution has neutral pH value.

Sequence of operations: Place 3 drops of glycine solution in the test-tube. Add 1 drop of 0,2% methyl red (indicator) solution.

Check the result: change of colour.

Remember that indicator methyl red colour change zone is at pH 4,4-6,2.

Write:

$$H_2N-CH_2-COOH \longrightarrow H_3N-CH_2-C < \bigcirc \bigcirc$$
 glycine

Explain the result and write conclusion.

Experiment 2. Glycine reacts with formaldehyde.

Sequence of operations: Place 3 drops of 40% formadehyde solution in the test-tube. Add 1 drop of 0,2% methyl red (indicator) solution. Note the red colour of solution. Use the thin glass capillary to add only a small amount of 2 M NaOH solution to achieve neutral pH value (the solution will become yellow). Add this solution to glycine solution (obtained in previous experiment).

Check the result: the red colour of solution, that indicated the low pH value of the solution.

Write:

Explain the result (why the solution became acidic?) and write conclusion.

Experiment 3. Formation of copper and glycine complex compound.

Sequense of operations: Place CuO on tip spade in the test-tube. Add 3 drops of 0,2 M glycine solution and warm the test-tube

Check the result: dark-blue copper salt glycine solution.

Write:

Explain the result and write conclusion.

Experiment 4. Glycine reacts with nitrous acid.

Seguence of operations: Place 5 drops of 0,2 M glycine solution in the test-tube. Add 5 drops of 5% sodium nitrite (NaNO₂) solution and 2 drops of concentrated acetic acid. Shake mixture carefully.

Check the result: bubbles of gas.

Write:

$$NaNO_2 + CH_3COOH \longrightarrow HNO_2 + CH_3COON^{\dagger}a$$
 $H_2N-CH_2-COOH + HNO_2 \longrightarrow HO-CH_2-COOH + N_2 + H_2O$
glycine

Explain the result and write conclusion.

Experiment 5. Glycine reacts with ningidrin.

Sequence of operations: Place 4 drops of 0,2 M glycine solution in the test-tube. Add 2 drops of ningidrin solution. Warm the test-tube carefully.

Check the result: blue-red colour.

Write:

Explain the result and write conclusion.

7. Approximate version of the card for the final control of the class:

Variant

- 1. Write the structure of the predominant form of cysteine at the pH of blood 7,4 and pH 12.
- 2. Write the schemes of the following reactions. Indicate interacted reaction centers of the substrate and the reagent (if it possible). Indicate the type and mechanism of the reactions.

Tyrosine
$$\frac{H_3C-C \stackrel{O}{\longleftarrow} H}{HNO_3/H_2SO_4(conc)}$$

THEME 14 Peptides and proteins.

1. Training and educational goals:

- 1. To form knowledge of:
- principles of the structures of peptides and proteins;
- electronic structure of peptide bond;
- acid-base properties of peptides and hydrolysis of the peptide bond;
- primary structure of peptides and proteins;
- strategy of peptide synthesis;
- spatial structure of polypeptide chain;
- secondary, tertiary and quaternary structures of proteins.
- 2. To form skills in:
- writing structures of di- and tripeptides;
- writing ionic forms of peptides at different pH values;

- finding isoelectric points of peptides
- explaning the strategy of peptide synthesis;
- explaning spatial structure of polypeptide chains;
- drawing interactions that form secondary and tertiary structures of polypeptides;
- carrying out characteristic and qualitative reactions of peptides and proteins.

2. Program questions:

- 1. Peptides. Electronic and steric structure of a peptide bond. Hydrolysis of polypeptides. Individual representatives of polypeptides: aspartame, glutathione, neuropeptides, insulin.
- 2. Determination of primary structure of polypeptides. Amino acid sequence of polypeptides and proteins.
 - 3. Notion about the strategy of peptide synthesis.
- 4. Primary structure of proteins. Notion of secondary, tertiary (domains) and quaternary structures. Hemoglobin, heme group structure.
- 5. Notion of complex proteins: glycoproteins, phosphoproteins, metalloproteins, hemoproteins, nucleoproteins.

3. Literature:

- 1. Bioorganic chemistry: учебное пособие для иностранных студентов / О.Н. Ринейская [и др.]. Минск: Новое знание, 2018. р. 145-149.
- 2. Hidranovich, L.G. Bioorganic chemistry lecture course / L.G. Hidranovich. Vitebsk, 2004. p. 217-237.

4. Homework:

- 1. Prepare the theoretical material according to the program questions of the theme 14.
 - 2. Prepare the laboratory work protocol.
 - 3. Solve the problems $N_0 1$, $N_0 2$, $N_0 5$, $N_0 9$ presented on the pages 88-90.

5. Problems.

1. Write the sructure of tripeptide Ala-Met-Glu in solution at:

(a)
$$pH=1$$
; (b) $pH=3$; (c) $pH=11$

- 2. Aspartame, a widely used nonnutritive sweetener, is the methyl ester of the dipeptide Asp-Phe. Draw the full structure of aspartame. The isoelectric point of aspartame is 5.9. Draw the structure present in aqueous solution at this Ph.
- 3. Write a reaction showing how 2,4-dinitrofluorobenzene could be used to identify the N-terminal amino acid of Val-Ala-Gly.

- 4. What products would you expect (after hydrolysis) when Val-Lys-Gly is treated whith 2,4-dinitrofluorobenzene?
- 5. Write the reaction involved in a sequential Edman degradation of Met-Ile-Arg.
- 6. Indicate where N≡CBr, trypsin and chymotrypsin will cleave the following polypeptide chain:

Ala-Val-Lyz-Met-Ile-Pro-Tyr-Thr-Arg-Ser-Met-Leu-His-Gln.

- 7. The following peptide was subjected to:
 - 1) Edman degradation;
 - 2) trypsin hydrolysis;
 - 3) chymotrypsin hydrolysis.

What result would you find from each of these three experiments:

- 8. Give the amino acid sequence of the following polypeptides using only the data given by partial acidic hydrolysis
 - (a) Ser, Hys, Pro, Thr \rightarrow Ser-Thr + Thr-Hys + Pro-Ser
 - (b) Ala, Arg, Cys, Val, Leu → Ala-Cys + Cys-Arg + Arg-Val + Leu-Ala
- 9. Show all steps in the synthesis of Gly-Met-Ser using the benzyloxycarbonyl group as a protecting group.
- 10. The synthesis of polypeptide containing lysine requires the protection of both amino groups. Show how you might do this in synthesis of Lys-Ile using the benzyloxycarbonyl group as a protecting group.
- 11. Bradykinin is a nonapeptide released by blood plasma globulins in response to a wasp—sting. It is a very potent pain-causing agent. Its molecular formula is Arg₂, Gly, Phe₂, Pro₃, Ser. The use of 2,4-dinitrofluorobenzene and carboxypeptidase show that both terminal residues are arginine. Partial acid hydrolysis of bradykinin gives the following di- and tripeptides:

$$Phe \cdot Ser + Pro \cdot Gly \cdot Phe + Pro \cdot Pro + Ser \cdot Pro \cdot Phe + Phe \cdot Arg + Arg \cdot Pro$$

What is the amino acid sequence of bradykinin?

12. Complete hydrolysis of a heptapeptide showed that it had the following molecular formula:

Deduce the amino acid sequence of this heptapeptide from the following data. Treatment of the heptapeptide with 2,4-dinitrofluorobenzene followed by in-

complete hydrolysis gave, among other products: valine labeled at the α -amino group, lysine labeled at the ϵ -amino group, and a dipeptide, DNP — Val Leu (DNP = 2,4- dinitrophenyl-). Hydrolysis of the heptapeptide with carboxypeptidase gives an initial high concentration of alanine, followed by a rising concentration of glutamic acid. Partial enzymatic hydrolysis of the heptapeptide gave a dipeptide (A) and a tripeptide (B).

- a. Treatment of **A** with 2,4-dinitrofluorobenzene followed by hydrolysis gave DNP-la beled leucine and lysine labeled only at the ε -amino group.
- b. Complete hydrolysis of B gave phenylalanine, glutamic acid, and alanine. When **B** was allowed to react with carboxypeptidase, the solution showed an initial high concentration of glutamic acid. Treatment of **B** with 2,4-dinitrofluorobenzene followed by hydrolysis gave labeled phenylalanine.

6. Laboratory work.

Experiment 1. Biuret test on peptide linkage.

Sequence of operations: Place 5-6 drops of white egg solution (the white protein) in the test-tube. Add 5-6 drops of 2 M NaOH solution and add 1-2 drops of copper (II)-sulphate (CuSO₄) solution alongside the test-tube.

Check the result: red-violet colour.

Write:

Explain the result and write conclusion.

Experiment 2. Xanthoproteinic test.

Sequence of operations: Place 5 drops of white egg (the white protein) solution in a test-tube. Add 2 drops of concentrated nitric acid. Warm the test-tube carefully, shaking it all the time. Solution and precipitate take in yellow colour. Cool the test-tube. Carefully add 1-3 drops of 2 M NaOH solution.

Check the result: brightly – orange colour.

Write:

$$H_2N$$
- CH_2 - $COOH$
 CH_2
 $+ HNO_3$
 $-H_2O$
 OH
 $Tyrosine$
 H_2N - CH - $COON_a$
 CH_2
 OH
 OH

Explain the result and write conclusion.

Experiment 3. Reaction on presence of sulfurous α-amino acids.

Sequence of operations: Place 5 drops of white egg (the white protein) solution in test-tube. Add 10 drops of 2 M NaOH solution. Mix contents of the test-tube, warm it until boiling (1-2 minutes). Add 5 drops of 10% lead-(II)-acetate (Pb(CH₃COO)₂) solution and boil it once again.

Check the result: grey-black precipitate.

Write:

$$\begin{array}{ccc}
SH & + (CH_3COO)_2Pb & & & & \\
SH & + (CH_3COO)_2Pb & & & & & \\
\end{array}$$

Explain the result and write conclusion.

Experiment 4. Three-chlorineacetic acid and sulfosalicylic acid concrets protein.

Sequense of operations: Place 5 drops of white egg (the white protein) solution in test-tube. Add 5 drops of sulfosalicylic acid solution. Repeat this test with three-chlorineacetic acid solution.

Check the result: precipitate of protein.

Explain the result and write conclusion.

Experiment 5. Dehydrating agents concrets protein.

Sequence of operations: Place 5 drops of white egg (the white protein) solution in two test-tubes. Add 10-15 drops of alcohol in the first test-tube, add 10-15 drops of acetone in the second test-tube.

Check the result: precipitate of protein.

Explain the phenomenon, which takes place with protein under the influence of organic solvents **and write conclusions**.

7. Approximate version of the card for the final control of the class:

Variant

- 1. Write the structure of Arg-Val-Phe. Show the C-and N-terminal residues. Show the structure of the predominant form of tripeptide at the pH of saliva 7.0.
- **2.** Write the schemes of the following reactions. Indicate interacted reaction centers of the substrate and the reagent (if it possible). Indicate the type and mechanism of the reactions.

Tyr-Lys
$$O_2N$$
— F
 O_2N — F
 $O_2H_5OH/H_2SO_4 c.$ O_2N — O_2

THEME 15 Nucleic acids.

1. Training and educational goals:

- 1. To form knowledge of:
- nomenclature, structures and tautomeric forms of pyrimidine and purine nucleic bases;
- nomenclature and structures of nucleosides and nucleotides:
- primary structure of RNA and DNA;
- secondary structure of RNA and DNA;
- biological roles of RNA and DNA;
- structure and biological roles of ATP, c-AMP, NAD⁺ and NADP⁺.
- 2. To form skills in:
- drawing tautomeric form of nucleic bases;
- writing the structures of nucleosides and nucleotides according to their systematic names;
- finding reaction centers of nucleosides and nucleotides;
- writing the schemes of the reactions for different reaction centers;
- drawing the primary structure of RNA and DNA;
- carrying out characterictic and qualitative reactions of nucleotides.

2. Program questions:

1. Nucleic (heterocyclic) bases that can be obtained from nucleic acids. Pyrimidine (uracil, thymine, cytosine) and purine (adenine, guanine) heterocyclic bases derived from RNA and DNA. Aromatic properties. A lactim–lactam tautomerization. Deamination reactions.

- 2. Nucleosides. Nucleotides. Structure of mononucleotides that can be obtained from nucleic acids. Nomenclature. Nucleotides hydrolysis.
- 3. Primary structure of nucleic acids. The phosphate diester linkage. Ribonucleic and deoxyribonucleic acids. Nucleotides found in RNA, nucleotides found in DNA. Hydrolysis of nucleic acids. Structure and properties of m-RNA, t-RNA, r-RNA.
- 4. Notion of the secondary structure of DNA. The role of hydrogen bonds in formation of the DNA secondary structure. Complementarity of heterocyclic bases. Hydrogen bonds in complementary pairs of heterocyclic bases.
- 5. Medications derived from modified heterocyclic bases. Change of heterocyclic base structures caused with chemical mutagens, UV irradiation and radiation.
- 6. Nucleoside mono- and polyphosphates. AMP, ADP, ATP. The role of ATP as the impotant energy source in cell. Nucleoside cyclophosphates (cyclic AMP, cyclic GMP) as secondary mediators in the regulation of cell metabolism.
- 7. Notion of coenzymes. Structures of NAD⁺ and its phosphate (NADPh⁺). NAD⁺-NADH system; hydride transfer as one of the stages of the biological oxidation–reduction reactions with participation of this system.

3. Literature:

- 1. Bioorganic chemistry: учебное пособие для иностранных студентов / О.Н. Ринейская [и др.]. Минск: Новое знание, 2018. р. 150-156.
- 2. Hidranovich, L.G. Bioorganic chemistry lecture course / L.G. Hidranovich. Vitebsk, 2004. p. 237-256.
- 3. Chernykh, V.P. Organic chemistry. Basic lecture course: The study guide for students of higher schools / V.P. Chernykh, L.A. Schemchuk. Kharkiv, 2011. p. 394-399.

4. Homework:

- 1. Prepare the theoretical material according to the program questions of the theme 15.
 - 2. Prepare the laboratory work protocol.
- 3. Solve the problems $N_0 1$, $N_0 2$, $N_0 4$, $N_0 6$, $N_0 7$, $N_0 10(a)$, $N_0 11(a)$ presented on the pages 93-95.

5. Problems.

- 1. Write the sructure of the two tautomeric forms of guanine, cytosine, uracil, and thymine.
- 2. Write structural formulas showing the hydrogen bonds in complementary base pairs of DNA and RNA.

- 3. The most stable tautomeric form of guanine is the lactam form. This form is normally present in DNA and it pairs specifically with cytosine. Guanine can tautomeraze to the abnormal lactim form and make the pair with thymine. Write structural formulas showing the hydrogen bonds in these base pairs.
- 4. Nitrous acid (HNO₂) is a potent chemical mutagen. Propose the reaction of adenine's amino group with HNO₂ and show the taumerization of the product.
- 5. Write the structure and give the name of the nucleoside formed by combining each of the following pairs of heterocyclic bases and pentoses.

a) Ribose and guanine

c) Cytosine and ribose

b) Thymine and 2-deoxyribose

- d) Adenine and 2-deoxyribose
- 6. Uridine and 2-deoxyguanosine are stable in dilute base. In dilute acid, however, they undergo rapid hydrolysis yilding a sugar and heterocyclic base. Write the reaction of nucleosides hydrolysis.
- 7. Write the structures of 5'-guanilic acid, cytidine -5'-phosphate, 2'-deoxyadenosine-5'-phosphate, uridilic acid. Write the reaction of acid and base-catalyzed hydrolylis of nucleotides.
- 8. ATP is the abbreviation of adenosine triphoshate. Based on the structure of adenosine 5'-monophoshate, propose a structure for ATP.
- 9. In some cells, biochemists found a cyclic form of AMP in which the phosphate form a cyclic ester between C3' and C5'. Propose structure for cyclic AMP.
- 10. Write the structure of mRNA portion with following nucleotides sequences:
 - (a) 5'-end U-A-C 3'-end
 - (b) 5'-end G-U-A 3'-end
- 11. Write the structure of DNA portion with following nucleotides sequences:
 - a) 5'-end A-T-G 3'-end
 - b) 5'-end T-G-C 3'-end
- 12. The portion of one chain of DNA molecule has the following nucleotides sequence:

5'-end AGGCTATTCGT 3'-end. Write the sequence of nucleotides in the complementary chain of the DNA molecule.

6. Laboratory work.

Experiment 1. Discovering of purine bases ("silver test").

Sequence of operations: Place 5 drops of yeast hydrolysate in a test-tube. Add one by one some drops of concentrated ammonia solution (unti the universal indicator paper will show basic reaction). Then add 5 drops of 2% ammoniacal silver-nitrate solution. Don't mix contents of the test-tube. Leave the test-tube for 3-5 minutes.

Check the result: bright-brown precipitate.

Write:

Explain the result and write conclusion.

Experiment 2. Discovering five-carbon monosaccacharide in products of nucleotides hydrolysis.

a) Quantitative reaction for aldopentoses (Molish test).

Seguence of operations: Place 5 drops of yeast hydrolyzate in a test-tube. Add 3 drops of 1% thymol alcohol solution. Mix and pour concentrated sulphuric acid along the side the test-tube. Shake the test-tube.

Check the result: there is the test-tube the red coloured product of condensation furfural with thymol on the bottom.

b) Discovering of ribose and deoxyribose.

Seguence of operations: Place 5 drops of yeast hydrolyzate in a test-tube. Add 2 drops of 1% diphenylamine solution. Warm the test-tube on water bath during 15 minutes.

Check the result: blue-green colour.

Remember: 1) concentrated sulphuric acid with five carbon monosaccacharide lead to their dehydration and formation of furfural, which gives red coloured product of condensation with thymol; 2) diphenylamine gives blue colour with deoxyribose, but green colour with ribose.

Write:

$$C \rightleftharpoons H$$
 $C \rightleftharpoons H$
 $C \to H$
 $C \rightleftharpoons H$
 $C \to H$
 C

Explain the result and write conclusion.

Experiment 3. Discovering phosphoric acid in product of nucleotides hydrolysis.

Sequence of operations: Place 5 drops of yeast hydrolyzate in the test-tube. Add 10 drops of molibdenic reagent. Warm the test-tube. The liquid bacomes lemon-yellow. Cool the test-tube.

Check the result: lemon-yellow precipitate.

Write:

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3$$

$$\xrightarrow{t^o} (NH_4)_3PO_4 \bullet 12MoO_3 \downarrow + 21NH_4NO_3 + 12H_2O$$
ammonium phoshomolibdic

Explain the result and write conclusion.

7. Approximate version of the card for the final control of the class:

Variant

- 1. Write the structure of the purines and show it's tautomeric forms. Give the names and write the structure of the complementary base pairs in.
- 2. Write the scheme of acid-catalyzed hydrolysis of 2'-deoxycytidine 5'-monophosphate. Indicate mechanism of this reaction.
- 3. Write the structure the portion of one chain of DNA molecule with following nucleotides sequence: 5'end C-G-T 3'end.

THEME 16

Control-test № 2. «Biopolimers and their structural units».

1. Training and educational goals:

1. To control knowledge of:

- structures, properties and biological roles of monosaccharides, oligosaccharides, polysaccharides, α -amino acids, peptides and proteins, nucleic acids and their structural units.

2. Program questions:

Carbohydrates.

- 1. Monosaccharides. Classification of monosaccharides. Aldoses, ketoses; trioses, tetroses, pentoses, hexoses. Stereoisomerism of monosaccharides. Dand L-families. Biological importance of monosaccharides and their derivatives.
- 2. Structures of the most important pentoses (D-ribose, D-xylose, 2-deoxy-D-ribose) and hexoses (D-glucose, D-mannose, D-galactose, D-fructose). Amino sugars (D-glucosamine, D-mannosamine, D-galactosamine) and their properties. Neuraminic acid, sialic acids.
- 3. Open-chain structures and cyclic forms. Furanoses and pyranoses; α and β -anomers. Fischer projection formulas and Haworth formulas. A cyclo-oxo tautomerization. Mutarotation. Conformations of pyranose forms of monosaccharides. Physical properties of monosaccharides.
- 4. Chemical properties of monosaccharides. Nucleophilic substitution at an anomeric atom in cyclic forms of monosaccharides. O- and N-glycosides. Hydrolysis of glycosides. Biologically important phosphorylation reactions of monosaccharides. Phosphates of monosaccharides.
- 5. Oxidation of monosaccharides. Reducing properties of aldoses. Aldonic, aldaric, uronic acids. Reduction of monosaccharides to alditols (xylitol, glucitol (sorbitol), mannitol); application of alditols in medicine. Epimerization reaction of monosaccharides, the reversible transformation of aldoses to ketoses.
- 6. Nucleophilic addition reaction with participation of oxo-group of openchain form of glucose (glycylation reactions of peptides). Ascorbic acid. Its structure, properties, and biological importance.
- 7. Oligo- and polysaccharides. Common characteristic and classification of polysaccharides. Oligosaccharides. Disaccharides: maltose, cellobiose, lactose, sucrose. Structures, the cyclo-oxo tautomerization. Reducing properties. Hydrolysis.
- 8. Maltose, cellobiose, lactose. The conformational structure. The role of lactose oligosaccharides in formation of not pathogenic microflora in the intestines, which is necessary for normal digestion.
- 9. Polysaccharides. Homo- and heteropolysaccharides. Homopolysaccharides: starch (amylose, amylopectine), glycogen, dextran, cellulose. Primary structure, hydrolysis. Notion about secondary structure (amylose, cellulose). Pectins (polygalacturonic acid). Plasma replacing solutions on the basis of dextran and starch.
 - 10. Heteropolysaccharides: hyaluronic acid, chondroitin sulfates.

Primary structure. Notion of mixed biopolymers: proteoglycans, glycoproteins, glycolipids.

Amino acids. Peptides and proteins.

- 11. Amino acids that can be obtained from proteins. Classification of naturally occurring amino acids taking into account different signs: acid and base properties, chemical nature of a side chain and its substituents. Structure, nomenclature. Stereoisomerism.
 - 12. Acid and base properties, dipolar ions. Essential amino acids.
- 13. The formation of α -amino acids: hydrolysis of proteins, synthesis from α -halo acids. Reducing amination reactions and transamination reactions. Pyridoxal catalysis.
- 14. Chemical properties of α -amino acids as heterofunctional compounds. Formation of intracomplex salts. Esterification, acylation, alkylation, deamination reactions, formation of amines. Qualitative tests for α -amino acids.
- 15. Biologically important reactions of α -amino acids. Decarboxylation of α -amino acids the way of formation of biogenic amines and biological regulators (2-aminoethanol, histamine, tryptamine, serotonin, dopamine, γ -amino butyric acid), their biological importance. Notion about neuromediators.
- 16. Oxidative and not oxidizing deamination reactions. Hydroxylation reactions: phenylalanine \rightarrow tyrosine, tyrosine \rightarrow 3, 4-dihydroxyphenylalanine, tryptophan \rightarrow 5-hydroxytryptophan, proline \rightarrow 4-hydroxyproline. Cysteine oxidation. Disulfide bond.
- 17. Peptides. Electronic and steric structure of a peptide bond. Hydrolysis of polypeptides. Individual representatives of polypeptides: aspartame, glutathione, neuropeptides, insulin.
- 18. Determination of primary structure of polypeptides. Amino acid sequence of polypeptides and proteins. Notion about the strategy of peptide synthesis.
- 19. Primary structure of proteins. Notion of secondary, tertiary (domains) and quaternary structures. Hemoglobin, heme group structure. Notion of complex proteins: glycoproteins, phosphoproteins, metalloproteins, hemoproteins, nucleoproteins.

Nucleic acids.

- 20. Nucleic (heterocyclic) base that can be obtained from nucleic acids. Pyrimidines (uracil, thymine, cytosine) and purines (adenine, guanine) heterocyclic bases derived brom RNA and DNA. Aromatic properties. A lactim–lactam tautomerization. Deamination reactions.
- 21. Nucleosides. Nucleotides. Structure of mononucleotides that can be obtained from nucleic acids. Nomenclature. Nucleotides hydrolysis.
- 22. Primary structure of nucleic acids. The phosphate diester linkage. Ribonucleic and deoxyribonucleic acids. Nucleotides found in RNA, nucleotides

found in DNA. Hydrolysis of nucleic acids. Structure and properties of m-RNA, t-RNA, r-RNA.

- 23. Notion of the secondary structure of DNA. The role of hydrogen bonds in formation of the DNA secondary structure. Complementarity of heterocyclic bases. Hydrogen bonds in complementary pairs of heterocyclic bases.
- 24. Medications derived from modified heterocyclic bases. Change of heterocyclic base structures caused with chemical mutagens, UV irradiation and radiation.
- 25. Nucleoside mono- and polyphosphates. AMP, ADP, ATP. The role of ATP as the important energy source in cell. Nucleoside cyclophosphates (cyclic AMP, cyclic GMP) as secondary mediators in the regulation of cell metabolism.
- 26. Notion of coenzymes. Structures of NAD⁺ and its phosphate (NADPh⁺). NAD⁺-NADH system; hydride transfer as one of the stages of the biological oxidation–reduction reactions with participation of this system.

2. Literature:

Study the literature from the themes N_2 11 - N_2 15.

3. Questions for the control-test N_2 2:

Question № 1. Program questions of the following topics:

Monosaccharides. Classification of monosaccharides. Stereoisomerism. D- and L-families. The structures of the most important pentoses and hexoses. Amino sugars and their properties. Open-chain structures and cyclic forms. Furanoses and pyranoses; α - and β -anomers. Fischer projection formulas and Haworth formulas. A cyclo-oxo tautomerization. Mutarotation. The conformations of pyranose forms of monosaccharides. Chemical properties of monosaccharides. Nucleophilic substitution at an anomeric atom in cyclic forms of monosaccharides. O- and N-glycosides. Hydrolysis of glycosides. Phosphates of monosaccharides. Oxidation of monosaccharides. Reducing properties of aldoses. Aldonic, aldaric, uronic acids. Reduction of monosaccharides to alditols. Epimerization reaction of monosaccharides, the reversible transformation of aldoses to ketoses.

Oligosaccharides and polysaccharides. Classification of polysaccharides. Oligosaccharides. The disaccharides: maltose, cellobiose, lactose, sucrose. The conformational structure. The cyclo-oxo tautomerization. The reducing properties. Hydrolysis. Polysaccharides. Homo- and heteropolysaccharides. Homopolysaccharides: starch (amylose, amylopectine), glycogen, dextran, cellulose. Primary structure, hydrolysis. Notion about secondary structure (amylose, cellulose). Pectins. Heteropolysaccharides: hyaluronic acid, chondroitin sulfates. Primary structure.

Natural amino acids. Amino acids that can be obtained from proteins. Classification of naturally occurring amino acids taking into account different signs: acid and base properties, chemical nature of a side chain and its substitu-

ents. Structure, nomenclature. Stereoisomerism. Acid and base properties, dipolar ions. Essential amino acids. The formation of α -amino acids: hydrolysis of proteins, synthesis from α -halo acids. Reducing amination reactions and transamination reactions. Chemical properties of α -amino acids as heterofunctional compounds. Formation of intracomplex salts. Esterification, acylation, alkylation, deamination reactions, formation of imines. Biologically important reactions of α -amino acids.

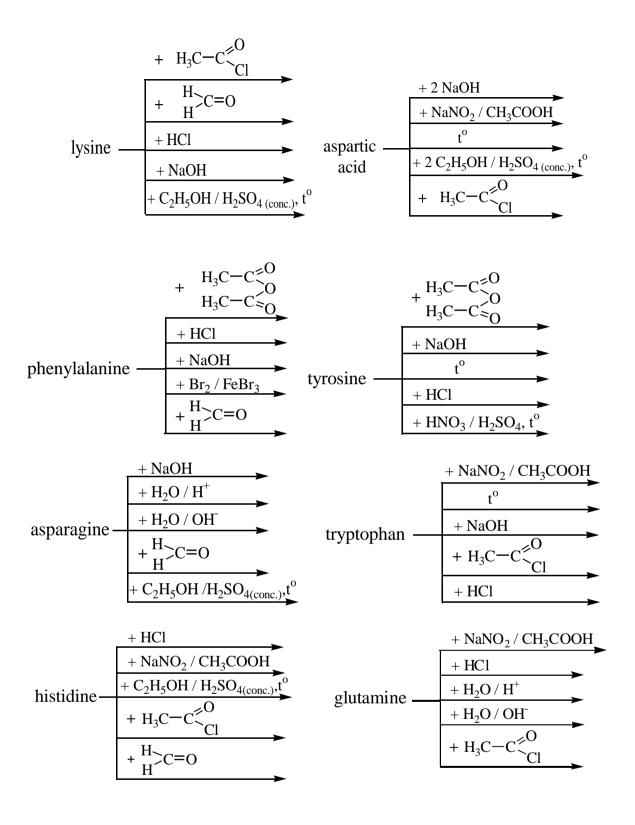
Peptides and proteins. Electronic and steric structure of a peptide bond. Hydrolysis of polypeptides. The establishment of primary structure of polypeptides. The strategy of peptide synthesis. Secondary, tertiary (domains) and quaternary structures.

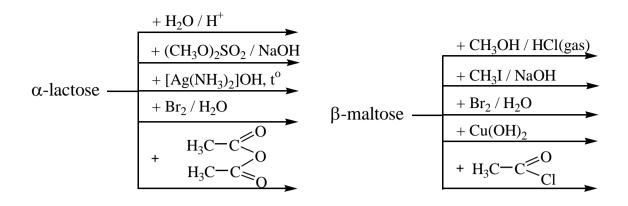
Nucleosides. Nucleotides. Nucleic acids. Nucleic (heterocyclic) base that can be obtained from nucleic acids. A lactim–lactam tautomerization. Deamination reactions. Structure of nucleosides and mononucleotides that can be obtained from nucleic acids. Nomenclature. Hydrolysis. Primary structure of nucleic acids. Ribonucleic and deoxyribonucleic acids. The nucleotides found in RNA, the nucleotides found in DNA. Hydrolysis of nucleic acids. Secondary structure of DNA. The role of hydrogen bonds in formation of the DNA secondary structure. Complementarity of heterocyclic bases. The hydrogen bonds in the complementary pairs of heterocyclic bases. Nucleoside mono- and polyphosphates. AMP, ADP, ATP. The role of ATP as the accumulator and the carrier of free energy in cell. Coenzymes. Structures of NAD⁺ and its phosphate (NADPh⁺). NAD⁺-NADH system; hydride transfer as one of the stages of the biological oxidation–reduction reactions with participation of this system.

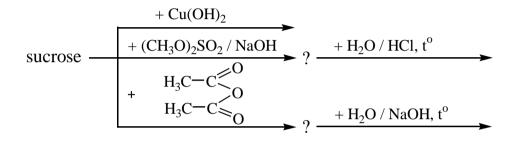
Question \mathcal{N}_{2} **2.** Write the formulas of:

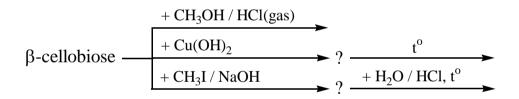
- Oxo- and cyclic forms of biologically important monosaccharides;
- Disaccharides;
- Ionic forms of natural α -amino acids at given pH;
- Dipeptides;
- Nucleosides, nucleotides and dinucleotides.

Question \mathcal{M} 3. Write the schemes of reactions, represent and name reaction centers, taking part in each reaction, indicate the mechanism of the following reactions:

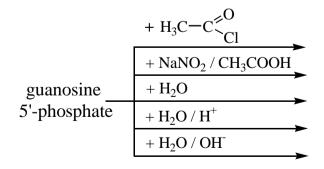


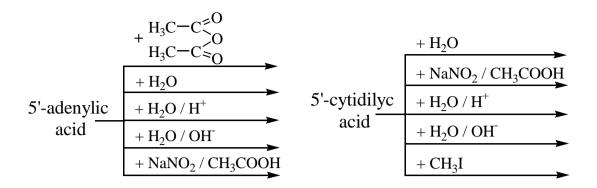






$$\alpha\text{-maltose} \xrightarrow{+ \text{H}_{3}\text{C}-\text{C} < \bigcirc \text{Cl}} + \text{H}_{2}\text{O} / \text{NaOH, } t^{\circ} \\ + [\text{Ag(NH}_{3})_{2}]\text{OH, } t^{\circ} \\ + (\text{CH}_{3}\text{O})_{2}\text{SO}_{2} / \text{NaOH} ? \xrightarrow{+ \text{H}_{2}\text{O} / \text{HCl, } t^{\circ}} ?$$





THEME 17 Lipids.

1. Training and educational goals:

- 1. To form knowledge of:
- classification and biological role of lipids;
- structures and properties of simple and complex lipids;
- relationship of structure of complex lipids and their biological functions;
- the peroxidation of polyunsaturated fatty acids in the cell membranes, its mechanism and biological role;
- antioxidant protection systems.

2. To form skills in:

- writing the structural formulas of simple and complex lipids;
- finding reaction centers according to structure of functional groups;
- writing schemes of the reactions for different reaction centers;
- finding hydrophobic and hydrophilic parts in the structure of complex lipids;
- writing the schemes of reactions of peroxide lipid oxidation;
- carrying out characteristic and qualitative reactions of lipids and fatty acids.

2. Program questions:

- 1. Classification. Biological importance. Neutral fats. Notion of the structure of waxes.
- 2. Common natural fatty acids that can be obtained from lipids: palmitic, stearic, oleic, linoleic, linilenic, arachidonic acids. Features of unsaturated fatty acids, ω -nomenclature. The role of free fatty acids in the energy reservation and thermoregulation
- 3. Phospholipids. Phosphatidic acids. Phosphatidylethanolamines (cephalins), phosphatidylserines, phosphatidylcholines (lecithines), phosphatidylinositols as structural components of cellular membranes. Notion about composition and the role of surfactant.

- 4. Sphingolipids and glycolipids, the role in myelinization of nerve fibers.
- 5. Rancidness of fats that is free radical chain process as the model of the peroxidation of polyunsaturated fatty acids in the cell membranes, its mechanism and its biological role. The role of the peroxide lipid oxidation in realization of damage by environment factors. Notion about antioxidant protection systems.

3. Literature:

- 1. Bioorganic chemistry: учебное пособие для иностранных студентов / О.Н. Ринейская [и др.]. Минск: Новое знание, 2018. р. 157-166.
- 2. Hidranovich, L.G. Bioorganic chemistry lecture course / L.G. Hidranovich. Vitebsk, 2004. p. 256-268.
- 3. Chernykh, V.P. Organic chemistry. Basic lecture course: The study guide for students of higher schools / V.P. Chernykh, L.A. Schemchuk. Kharkiv, 2011. p. 291-295.

4. Homework for the class:

- 1. Prepare the theoretical material according to the program questions of the theme 17.
 - 2. Prepare the laboratory work protocol.
- 3. Solve the problems \cancel{N}_{2} 2, \cancel{N}_{2} 5 (b), \cancel{N}_{2} 6, \cancel{N}_{2} 8 presented on the pages 104-105.

5. Problems.

- 1. How would you convert stearic acid into each of the following?
 - (a) Ethyl stearate
 - (b) Sodium stearate
 - (c) Stearyl chloride
 - (d) Stearamide
 - (e) N,N-Dimethylstearamide
- 2.Using oleic acid as an example illustrate the following reactions of the double bond.
 - (a) Addition of bromine
 - (b) Addition of hydrogen
 - (c) Hydroxylation
 - (f) Addition of HCI
- 3. When oleic acid is heated to 180-200°C (in the presence of a small amount of selenium), an equilibrium is established between oleic acid (33%) and an isomeric compound called elaidic acid (67%). Suggest a possible structure for elaidic acid.

- 4. The formation of glycerides raises the question of steochemistry. Glycerol is achiral. It's molecule has a plane of symmetry but many glyceride lipids are chiral due to the loss of molecular symmetry on acylation. Draw the general structures of all possible monoacylglycerols, diacylglycerols and triacylglycerols formed from glycerol and an achiral fatty acid, and specify whether each will be chiral or achiral.
- 5. Write the structure and name triacylglycerols formed by combining of the following fatty acids with glycerol:
 - (a) Palmitic acid, oleic acid, stearic acid
 - (b) Linoleic acid, stearic acid, linolenic acid
 - (c) Oleic acid, linoleic acid, stearic acid.
- 6. Both triacylglycerols and phospholipids have fatty acid ester components, but only one group can be considered amphipathic. Indicate wich is amphipathic and explain why. Using 1-0-stearoyl-2-0-oleioyl-3-0-palmitoyl-glycerol and lecithin ullustrate yours answer.
- 7. Write the structure of phosphatidyl serine and show it's the hydrophilic and hydrophobic portions.
- 8. Under suitable conditions all of the ester linkages of phosphatide can be hydrolyzed. What organic compounds would you expect to obtain from the complete hydrolysis of (a) lecithin, (b) cephalin, c) choline containing plasmalogen.
- 9. Castor oil react with sulfuric acid to give a sulfated castor oil known as "Turkey-red oil" due to its use as a surfactant or wefting agent in "Turkey-red" dyeing using madder root (the active due is alizarin). Turkey-red oil soaps, obtained by hydrolysis of the oil, are not particularly good detergents (i.e. they form micelles not so well). The structure of a typical Turkey-red oil soap is given below. Suggest why these amphipathic compound might not form micelles very well.

Show the hydrophilic and hydrophobic portion of "Turkey-red oil".

6. Laboratory work. Experiment 1. Oleic acid reacts with bromine water.

Sequense of operations: Place 3-4 drops of oleic acid in a test-tube. Add 4-5 drops of bromine water.

Check the result: bleaching of solution.

Write:

Explain the result and write conclusion.

Experiment 2. Oleic acid reacts with KMnO₄ solution.

Sequence of operations: Place 2 drops of oleic acid in a test-tube. Add 2 drops of 5% Na₂CO₃ solution and 2 drops KMnO₄ solution. Shake the test-tube.

Check the result: bleaching of solution.

Write:

Explain the result and write conclusion.

Experiment 3. Saponification of fats.

Sequense of operations: Place 0,5 ml of castor oil in a test-tube. Add 0,5 ml of alcohol and 0,5 ml of 35% NaOH solution. Mix and warm contents of the test-tube on water bath during 5-7 minutes. Place some drops of solution in a new test-tube, add 2-3 ml of distilled water and warm it. Complete dissolving of the substens in water shows its complete saponification. Add 3-4 ml of saturated hot NaCl solution. (Salting-out soap).

Check the result: layer of soap lift up.

Write:

$$\begin{array}{c} \text{CH}_2\text{-O-C} \stackrel{O}{\underset{R_1}{\triangleleft}} \\ \text{CH-O-C} \stackrel{O}{\underset{R_2}{\triangleleft}} \\ \text{CH}_2\text{-O-C} \stackrel{O}{\underset{R_3}{\triangleleft}} \\ \text{CH}_2\text{-O-C} \stackrel{O}{\underset{R_3}{\triangleleft}} \\ \text{triacylglycerol} \\ \end{array} \\ \begin{array}{c} \text{CH}_2\text{OH} \\ \text{R}_1\text{-C} \stackrel{O}{\underset{O}{\triangleleft}} \\ \text{Na}^+ \\ \text{CH}_2\text{OH} \\ \text{R}_3\text{-C} \stackrel{O}{\underset{O}{\triangleleft}} \\ \text{ONa}^+ \\ \text{CH}_2\text{OH} \\ \text{salts of fatty acids} \\ \text{(soaps)} \\ \end{array}$$

Explain the result and write conclusion.

Experiment 4. Extraction of free fat acids from soap.

Sequence of operations: Place 5 drops of concentrated soap solution in a test-tube. Add 1 drop of 2 M H₂SO₄ solution.

Check the result: white flaky oily precipitate.

$$2 C_{17}H_{35}C \stackrel{O}{\underset{O}{\bigcirc}Na^{+}} + H_{2}SO_{4} \rightarrow 2 C_{17}H_{35}C \stackrel{O}{\underset{OH}{\bigcirc}V} + Na_{2}SO_{4}$$
salt of acid stearic acid (soap)

Explain the result and write conclusion.

7. Approximate version of the card for the final control of the class:

Variant

1. Write the structure of the following fatty acid and lecithin, illustrate the conformation of alkyl (alkenyl) chains and the configuration of double bonds and a stereocenter.

Write the shemes of the following reactions. Indicate interacted reaction centers of the substrate and the reagent (if it possible). Indicate the type and mechanism of the reactions.

a) linoleic acid
$$(-1) \frac{\text{KMnO}_4/\text{H}_2\text{O}}{2) \text{ H}_2\text{O}}$$
?

b) 1-O-stearoyl-2-O-linolenoylphosphatidyl choline $(-1) \frac{\text{H}_2\text{O}/\text{H}^+, t^o}{2}$?

NaOH, H₂O, t^o?

THEME 18 Low molecular weight bioregulators. Steroids.

1. Training and educational goals

- 1. To form knowledge of:
- classification, structure and biological role of steroids;
- stereochemical structure of steroids;
- reaction centers and reactivity of steroids.
- 2. To form skills in:
- writing structural formulas of steroids according to their systematic names;

- characterizing the configuration of chiral centers in α , β -stereochemical nomenclature, ring junctions and three-dimensional structures of 5α and 5β series of steroids;
- writing the schemes of the reactions for different reaction centers of steroids.

2. Program questions:

- 1. Steroids. Notion about their biological role. Gonan (steran, perhydrocyclopentanophenanthrene), stereochemical structure of 5α , 5β series of steroids. Physical properties of steroids. Hydrocarbons that are parent structures of steroid groups: estrane, androstane, pregnane, cholane, cholestane.
- 2. Steroid hormones. Sex hormones: estrogens, androgens; progestins; adrenocortical hormones. Structure, biological role.
- 3. Bile acids: cholic acid, conjugated bile acids (glycocholic, taurocholic acids), their structure, their biological role.
- 4. Cholesterol as one of sterols, its conformational structure. Its properties, its role in metabolism and structure of cell membranes, in development of cardiac pathology. 7-Dehydrocholesterol, its transformation to vitamin D_3 (cholecalciferol). Ergosterol, its transformation to vitamin D_2 (ergocalciferol). The role of vitamin D in regulation of calcium-phosphorus metabolism.

3. Literature:

- 1. Bioorganic chemistry: учебное пособие для иностранных студентов / О.Н. Ринейская [и др.]. Минск: Новое знание, 2018. р. 167-173.
- 2. Hidranovich, L.G. Bioorganic chemistry lecture course / L.G. Hidranovich. Vitebsk, 2004. p. 269-281.

4. Homework:

- 1. Prepare the theoretical material according to the program questions of the theme 18.
 - 2. Prepare the laboratory work protocol.
- 3. Solve the problems N_2 1, N_2 3, N_2 4, N_2 6 presented on the pages 108-109.

5. Problems.

- 1. Draw the two basic ring systems for the 5α and 5β series showing all hydrogen atoms of the cyclohexane rings. Label each hydrogen atom as to whether it is axial or equatorial (using estradiol (1,3,4(10)-estra-triene-3,17 β -diol) as an example).
- 2. Designate with the star the eight stereocencers of cholesterol.

- 3. The adrenocortical steroids are apparently involved in the regulation of a large number of biological activities including carbohydrate, protein, and lipid metabolism, water and electrolyte balance, and reactions to allergic and in flammatory phenomena. Cortisone and cortisol, two adrenocortical steroids, have the systematic name 17α , 21-dihydroxy-4-pregnene-3,11,20-dione and 11β , 17α , 21-trihydroxy-4-pregnene-3,20-dione. Draw a three-dmensional formula for cortisone and cortisol.
- 4. Androsterone, a secondary male sex hormone, has the systematic name 3α -hydroxy- 5α -androstan-17-one. Give a three-dimensional formula for androsterone.
- 5. Norethynodrel, a synthetic steroid that has been widely used in oral contraceptives, has the systematic name 17α -ethynyl- 17β -hydroxy-5(10)-estren-3-one. Give a three dimentional formula for norethynodrel.
- 6. Show how you might convert cholesterol into each of the following compounds:
 - (a)5α,6β-Dibromocholestan-3β-ol
 - (b)Cholestane 3β , 5α , 6β -triol
 - (d) 5α -Cholestan-3-one
- 7. The estrogens (estrone and estradiol) are easily separated from the androgens (androsterone and testosterone) on the basis of one of their chemical properties. What is the property and how could such separation be accomplished?
- 8. Write the photochemical reaction of convertion of ergosterol to vitamin D.

7. Approximate version of the card for the final control of the class:

Variant

1. Write the structure of ergosterol (24-methyl-5,7,22-cholestatriene-3 β -ol). Give a three-dimensional formula for it. Find and name the functional groups and corresponding families. Write the scheme of reaction of ergosterol with Br₂/H₂O. Indicate type and the mechanism of this reaction. Indicate interacted reaction centers.

Biopolymers and their structural units

1. TRAINING AND EDUCATIONAL GOALS:

- 1. To form knowledge:
 - primary structures and biological roles of heteropolysaccharides: hyaluronic acid, chondroitin sulfates, heparin; glycolipids and glycoproteins;
 - secondary, tertiary and quaternary structures of proteins;
 - RNA and protein synthesis.
- 2. To form skills:
 - writing primary structures of heteropolysaccharides and its joining with proteins in glycoproteins;
 - using the RNA genetic code to write primary structure of polypeptide.
 - drawing interaction fixed secondary, tertiary and quaternary structure of protein.

2. GENERAL GUIDELINES:

To form a systematic approach of study of bio-organic chemistry it is recommended to consider the questions of program with examples of problems.

3. COURSE OF THE CLASS:

Problems:

1. The synovial flulid of the joint contains heteropolysaccharide hyaluronic acid, it is largely responsible for the viscosity of the fluid. Hyaluronic acid is formed by joining together alternately two different sugars: D-glucuronic acid and N-acetyl-2-D-glucosamine bonded by β -(1 \rightarrow 3) glycoside linkage. Disaccharide subunits is joined by β -(1 \rightarrow 4) glycoside linkages. Write structure of hyaluronic acid segment containing two disaccharide subunits, explain its biological role.

2.Glycoproteins of connective tissue are chondroitin sulfates joined through the tetrasaccharide segment with polypeptide serine residues by β -glycoside linkage. The tetrasaccharide contains D-glucuronic acid (1), two D-galactopyranoses (2,3) and D-xylopyranose (4) units joined together according next scheme:

chondoroitin
$$\beta \rightarrow 1$$
 $\beta \rightarrow 3$ $\beta \rightarrow 3$

4- Chondroitin sulfate is composed of repeating disaccharide subunits joined together by β -(1 \rightarrow 4) glycoside linkages. Each disaccharide subunit is formed of

D-glucuronic acid and N-acetyl-2-D-galactosamine-4-sulfate joined by β -(1 \rightarrow 3) glycoside linkage.

Write:

- 1) structure of 4-chondroitin sulfate segment containing two disaccharide subunits.
- 2) structure of tetrasaccharide segment and show its joining with polypeptide.
- 3. 1) Write the structure of polypeptide formed by the codons on each of the following mRNA molecules (see the table 14.3 of [1], p. 255):
 - a) 5'-end C-U-A-A-U-C-G-U-U 3'-end.
 - b) 5'-end G-A-C-A-C-A-G-C-U-A-U-U-U-A 3'-end.
- 2) Write the structure of the mRNA portion for the first of codons using in point (1).
- 4. The antiparallel β -pleated sheet is a predominant structure of silk fibroin had a repeating structural segment Gly-Ala-Gly-Ser-Gly-Ala-. Write β -pleated sheet structure for silk fibroin and indicate bonds fixed it.

Literature:

- 1. Bioorganic chemistry: учебное пособие для иностранных студентов / О.Н. Ринейская [и др.]. Минск: Новое знание, 2018. р. 127-173.
- 2. Hidranovich, L.G. Bioorganic chemistry lecture course / L.G. Hidranovich. Vitebsk, 2004. p. 199-203, 226-235, 251-256.

EXAMINATION TEST 1. CLASSIFICATION AND NOMENCLATURE OF ORGANIC COMPOUNDS.

- 1. According to the classification for functional groups 4-hydroxy-3-ethoxybenzaldehyde is:
- 1. only phenol;
- + 2. aldehyde, phenol and ether;
- 3. ester;
- 4. carboxylic acid;
- 5. alcohol.
- 2. According to the classification for the main chain structure 2-isopropyl-5-methylcyclohexanol is:
- + 1. carbocyclic compound;
- 2. heterocyclic compound;
- 3. unsaturated compound;
- 4. aromatic compound;
- 5. acyclic compound.
- 3. Pyrimidine is classified as:
- 1. carbocyclic aromatic compound;
- + 2. heterocyclic compound;
- 3. saturated compound;
- 4. aliphatic compound;
- 5. acyclic compound.
- 4. Glycerol (1,2,3-propanetriol) is:
- 1. monofunctional compound;
- + 2. polyfunctional compound;
- 3. heterofunctional compound;
- 4. cyclic compound;
- 5. aromatic compound.
- 5. According to the classification for functional groups epinephrine (2-methylamino-1-(3,4-dihydroxyphenyl)ethanol) is:
- 1. thiol;
- 2. ether and primary alcohol;
- + 3. phenol, secondary alcohol and secondary amine;
- 4. carboxylic acid and primary amine;
- 5. only phenol.

- 6. One of functional group in the structure of procaine (2-(diethylamino)ethyl 4-aminobenzoate) is:
- 1. an alkoxy group;
- + 2. an ester group;
- 3. a secondary amino group;
- 4. a hydroxyl group;
- 5. a carbonyl group.
- 7. The substitutive IUPAC name of malic acid is:
- 1. 2,3-dihydroxy-1,4-butanedioic acid;
- 2. 2-hydroxypropanoic acid;
- 3. 2-aminopropanoic acid;
- + 4. 2-hydroxy-1,4-butanedioic acid;
- 5. 1,4-butanedioic acid.
- 8. The IUPAC substitutive name of compound is:

- 1. 4-aminobenzyl ethyl ether;
- + 2. ethyl 4-aminobenzoate;
- 3. anesthesine;
- 4. 4-aminobenzoic acid;
- 5. ethyl benzoate.
- 9. The IUPAC substitutive name of compound is:

$$\begin{array}{c|c} & OH \\ H_2 & \mid & H_2 \\ -C -C -C -COOH \\ & \mid & \\ COOH \end{array}$$

- + 1. 3-carboxy-3-hydroxy-1,5-pentanedioic acid;
- 2. 2-carboxy-2-hydroxy-1,3-propenedioic acid;
- 3. 3-hydroxy-1,3,5-pentanetrioic acid;
- 4. citric acid;
- 5. 3-hydroxy-1,5-pentanedioic acid.

- 10. The IUPAC substitutive name of threonine is:
- 1. 2-aminopropanoic acid;
- 2. 2-amino-3-methylbutanoic avid;
- + 3. 2-amino-3-hydroxybutanoic acid;
- 4. 2-amino-4-methylpentanoic acid;
- 5. 2.6-diaminohexanoic acid.
- 11. The IUPAC substitutive name of glutamine is:
- + 1. 2-amino-4-carbamoylbutanoic acid;
- 2. 2-amino-3-carbamoylpropanoic acid;
- 3. 2-amino-1,5-pentanedioic acid;
- 4. 4-aminopentanoic acid;
- 5. 2-aminoethanoic acid.

2. ELECTRONIC STRUCTURE OF ORGANIC COMPOUNDS.

- 12. Covalent sigma bond:
- 1. is formed by side-by-side overlap of p-orbitals:
- 2. has less energy;
- + 3. is formed by end-on overlap of two sp³ hybrid orbitals;
- 4. is destroyed in the result of the rotation of the molecule part around the bond axis;
- 5. can be easily polarizated.
- 13. Covalent π -bond:
- + 1. is formed by side-by-side overlap of p-orbitals and can be easily polarizated;
- 2. has high energy;
- 3. is formed by end-on overlap of two sp³ hybrid orbitals;
- 4. is not destroyed in the result of the rotation of the molecule part around the bond axis;
- 5. is not polarised.
- 14. There are only sp³ hybrid oxygen atoms in the following compounds:
- + 1. ethoxyethane;
- 2. methoxybenzene;
- 3. phenol;
- 4. 4-hydroxybenzyl alcohol;
- 5. oxaloacetic acid.
- 15. There are no sp² hybrid atoms in the following compounds:
- + 1. glycerol;

- 2. propanoic acid;
- 3. Thymine (2,4-dihydroxy-5-methylpyrimidine);
- 4. phenol;
- 5. aniline.
- 16. There are only pyridinic heteroatoms in the following compounds:
- 1. 4-ethoxyaniline;
- + 2. ethanal;
- 3. benzoic acid;
- 4. 4-nitrophenol;
- 5. 3-aminopropanoic acid.
- 17. There are pyrrolic heteroatoms in functional groups of the following families of organic compounds:
- + 1. arylamines;
- 2. saturated aliphatic amines;
- 3. ketones;
- 4. alcohols;
- 5. ethers.
- 18. There are pyrrolic heteroatoms in functional groups of the following families of organic compounds:
- 1. aldehydes;
- 2. saturated aliphatic amines;
- 3. nitriles;
- 4. alcohols:
- + 5. carboxylic acids.
- 19. There is π π conjugation in the structure of the following compounds:
- 1. propanol;
- + 2. 1,3-pentadiene;
- 3. 1,4-pentadiene;
- 4. propanal;
- 5. propanoic acid.
- 20. There is π - π conjugation in the structure of the following compounds:
- + 1. benzene;
- 2. cyclohexene;
- 3. 1,4-pentadiene;
- 4. propanal;
- 5. propanoic acid.

- 21. There is p-π conjugation in the structure of the following compounds:
 1. propanol;
 + 2. 2-hydroxypropanoic acid;
 3. glycerol;
 4. pyridine;
- 22. Aromatic compoundis:
- 1. cyclohexane;

- 5. 2-propene-al.

- 2. cyclooctatetraene;
- 3.1,3-cyclopentadiene;
- 4. ethylene;
- + 5. benzene.
- 23. Aromatic compoundis:
- 1. cyclohexane;
- 2. cyclooctatetraene;
- 3. acetylene;
- + 4. pyrrole;
- 5.1,3-cyclopentadiene.
- 24. The fuctional group has only negative indictive effect in the following compounds:
- 1. phenol;
- + 2. ethylene glycol;
- 3. aniline;
- 4. ethandioic acid:
- 5. methyl phenyl ketone.
- 25. The fuctional group has negative inductive and negative mesomeric (resonance) effects simultaneously in the following compounds:
- 1. phenol;
- 2. ethylene glycol;
- 3. 2-propanamine;
- 4. 1,4-butandioic acid;
- + 5. methyl phenyl ketone.
- 26. The functional group has negative resonance (mesomeric) effect in the following compound:
- 1. ethanol;
- 2. glycerol;
- 3. acetone;

- + 4. 2-butene-al:
- 5. 4-methylaniline.
- 27. The following compound has only electron attracting functional groups:
- + 1.2-aminoethan-1-ol;
- 2. 2-hydroxybenzoic acid;
- 3. 4-aminobenzenesulfonic acid:
- 4. 4-hydroxy-3-methybenzaldehyde;
- 5. cytosine (4-amino-2-hydroxypyrimidine).
- 28. Which of the following compound has all functional groups as electron donating:
- 1. 2-isopropyl-5-methylcyclohexanol;
- + 2. 2-isopropyl-5-methylphenol;
- 3. n-aminobenzaldehyde;
- 4. succinic acid (1,4-butanedioic acid);
- 5. 2,3-dihydroxypropanal.

3. STEREOCHEMISTRY OF ORGANIC COMPOUNDS.

- 29. The Newman projection formulas are used to show the peculiarity of:
- 1. chemical structure of the compound;
- + 2. the conformation of the molecule;
- 3. the constitutional isomers;
- 4. the configuration;
- 5. the structure of E and Z π -diastereomers.
- 30. The molecule of 1,2-dimethylcyclohexane has the maximum energy in chair conformation when:
- 1. both methyl groups are placed on the equatorial bonds;
- + 2. both methyl groups are placed on the axial bonds;
- 3. one of the methyl groups is placed on the axial bond;
- 4. one of the methyl groups is placed on the equatorial bond;
- 5. one of the methyl groups is placed on the axial bond and other on the equatorial bond.
- 31. The potential energy of 1-propanamine *anti*-conformation is less than its *gauche*-conformation because the molecule in *anti*-conformation has:
- 1. less angle strain;
- 2. another configuration;
- 3. less torsional strain;
- + 4. less Van-der-Vaals strain;
- 5. ahother chemical structure.

- 32. The potential energy of 2-butanol eclipsed conformation is more than its staggered conformation because the molecule in eclipsed conformation has:
- 1. another configuration;
- + 2. more torsional strain and higher Van-der-Vaals repulsion;
- 3. more angle strain;
- 4. less torsional strain:
- 5. another electronic structure;
- 33. The conformations of 1-chloropropane with torsional angle 60^{0} and 300^{0} are degenerated because the molecule in these conformations has:
- + 1. the same torsional and Van-der-Vaals strains;
- 2. the same configurations;
- 3. the same chemical structure;
- 4. the different configurations;
- 5. the same electronic structure.
- 34. The chiral molecule is:
- 1. glycine (2-aminoethanoic acid);
- + 2. proline;
- 3. xylitol;
- 4. 1-butanol;
- 5. 3-pentanol.
- 35. The chiral molecules are:
- + 1. D-glucose andalanine;
- 2. citric acid and acetoacetic acid:
- 3. 2-aminoethanol-1;
- 4. adenine:
- 5. furol (2-furancarbaldehyde).
- 36. 2-aminopropanoic acid has the following number of stereoisomers:
- 1. 1:
- + 2. 2:
- 3.3;
- 4.4;
- 5. 5.
- 37. 2,3,4-trihydroxybutanal has the following number of stereoisomers:
- 1.1;
- 2. 2:
- 3. 3;

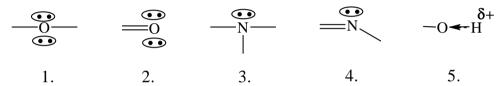
1	4.	۵٠
+	4.	4,

38. 2,3-dihydroxy-1,4-butanedioic acid has the following number of stereoisomers:

- 1. 1;
- 2. 2:
- +3.3;
- 4. 4;
- 5. 5.

4. ACID-BASE PROPERTIES OF ORGANIC COMPOUNDS.

39. The acidic reaction centre is:



- 1.
- 2.
- 3.
- 4.
- + 5.

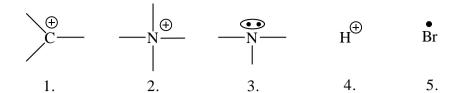
40. The functional group of the following family of organic compounds has the OH-acidic reaction centre:

- 1. esters;
- 2. ketones;
- + 3. sulfonic acids;
- 4. acyl chlorides;
- 5. ethers.

41. The functional group of the following family of organic compounds has the NH-acidic reaction centre:

- 1. esters;
- 2. ketones;
- 3. acid anhydride;
- + 4. amides;
- 5. ethers.

42. The basic reaction centre is:



- 1.
- 2.
- + 3.
- 4.
- 5.
- 43. The functional group of the following family of organic compounds has the basic reaction centre on the nitrogen atom:
- 1. esters;
- 2. ketones;
- + 3. amines;
- 4. amides;
- 5. ethers.
- 44. The strongest acidic reaction centre of 3,4-dihydroxyphenylalanine (DOPA) (2-amino-3-(3,4-dihydroxyphenyl)propanoic acid) molecule is:
- 1. CH-acidic centre;
- 2. NH-acidic centre;
- 3. phenol OH group;
- + 4. carboxylic acid OH group;
- 5. amino group.
- 45. The organic compound with the strongest OH-acidic reaction centre is:
- 1. ethanoic acid;
- 2. propanoic acid;
- 3. 2-methylpropanoic acid;
- + 4. 2,2,2-trichloroethanoic acid;
- 5. 2-aminopropanoic acid.
- 46. The weakest acid is:
- + 1. ethanamine;
- 2. ethanol;
- 3. phenol;
- 4. ethanoic acid;
- 5. ethanethiol.
- 47. The strongest basic reaction centre of histamine moleculeis:

$$CH_2 - CH_2 - NH_2$$

- + 1. sp³ hybridized nitrogen atom;
- 2. sp² hybridized pyrrole nitrogen atom;
- 3. sp² hybridized pyridine nitrogen atom;
- 4. conjugated system with closed chain;
- 5. reactivity of all basic centres are equal.
- 48. The strongest base is:
- 1. 2-aminoethanol;
- 2. ethanamine;
- 3. methylamine;
- + 4. dimethylamine;
- 5. pyridine.
- 49. Which of the following compounds have acidic properties and form salts in reaction with strong base:
- 1. pyridine;
- 2. thiophene;
- 3. pyridine;
- + 4. barbituric acid (2,4,6-thrihydroxypyrimidine);
- 5. oxazole (1-aza-3-oxocyclopenta-2,4-diene);

5. CLASSIFICATION AND THE MECHANISMS OF THE REACTIONS IN ORGANIC CHEMISTRY. HYDROCARBONS. S_R , S_E , A_E REACTIONS.

- 50. According to the product the organic reactions types are:
- 1. bimolecular;
- + 2. addition, substitution and elimination;
- 3. unimolecular;
- 4. nucleophilic;
- 5. synchronic.
- 51. According to the type of the reagent organic reactions types are:
- 1. bimolecular;
- 2. substitution and elimination;
- 3. unimolecular;
- + 4. nucleophilic and electrophilic;

- 5. synchronic.
- 52. The bonds are broken by homolysis in the molecules of the following compound:
- 1. HCl;
- 2. CH₃Cl;
- $+ 3. CH_3 CH_3;$
- 4. HCN;
- 5. H₂SO₄.
- 53. The bonds are broken by heterolysis in the molecules of the following compound:
- $-1.Br_2;$
- $-2.CH_3 CH_3$;
- 3. Cl₂;
- $+ \ 4.CH_3 CH_2 Cl;$
- $-5.CH_3 CH_2 CH_3$.
- 54. The electrophilic reagent is the next of the following:
- 1. OH;
- + 2. Br +;
- 3. Br -;
- 4. CH₃-NH₂;
- 5. CH₃-O⁻.
- 55. The nucleophilic reagent is the next of the following:
- $+ 1. C_2H_5-NH_2;$
- $-2. Br^{+};$
- -3. NO₂⁺;
- 4. H⁺;
- 5. CH₄.
- 56. The most stable is the following carbocation:

57. The most stable is the following carbon radical:

- 58. The alkanes react according to the following mechanisms:
- $-1. A_{N}-E;$
- 2. A_R ;
- 3. S_E ;
- $+4. S_R;$
- 5. A_E .
- 59. The product of the reaction of 2-methylpentane and bromine is:
- 1. 1-bromo-4-methylpentane;
- 2. 2-bromo-4-methylpentane;
- 3. 3-bromo-4-methylpentane;
- + 4. 2-bromo-2-methylpentane;
- 5. 1-bromo-2-methylpentane.

- 60. The reaction of butane bromation occurs in the following conditions:
- 1. the room temperature;
- + 2. ultraviolet irradiation;
- 3. cooling;
- 4. AlCl₃ as catalist;
- 5. the acidic solution.
- 61. The chlorination reaction occurs as the radical substitution reaction for the following compound:
- 1. cyclohexene;
- 2. benzene;
- + 3. 2-methylbutane;
- 4. acetylene;
- 5. 2-methyl-1,3-butadiene.
- 62. Alkenes and alkadienes participate in the following reactions:
- $+ 1. A_{E};$
- $-2. A_{N};$
- $-3. S_{E}$;
- $-4. S_R;$
- $-5. S_N.$
- 63. The reaction of cyclohexene bromation occurs in the following conditions:
- + 1. the room temperature and neutral solution;
- 2. the high temperature;
- 3. ultraviolet irradiation;
- 4. AlCl₃ as catalist;
- 5. the acidic solution.
- 64. The product of 1-pentene hydrobromation is:
- 1.1-bromopentane;
- + 2. 2-bromopentane;
- 3. 3-bromopentane;
- 4. 1,2-dibromopentane;
- 5.pentane.
- 65. The reaction of 2-butene hydration occurs in the following conditions:
- 1. the room temperature and the neutral solution;
- 2. the excess of NaOH;
- 3. ultraviolet irradiation;
- 4. FeCl₃ as catalyst;

- + 5. the acidic catalyst.
- 66. The product of the 2-methyl-2-butene hydration reaction is:
- 1. 2-methylbutane;
- 2. 2-methyl-1,2-butanediol;
- 3. 2-methyl-2,3-butanediol;
- + 4.2-methyl-2-butanol;
- 5. 3-methyl-2-butanol.
- 67. The product of the 2-methyl-2-butenoic acid hydration reaction is:
- 1. 2-methylbutane;
- 2. 2-methylbutanal;
- 3. 2-methylbutanoic acid;
- 4. 2-methyl-2-hydroxybutanoic acid;
- + 5. 2-methyl-3-hydroxybutanoic acid.
- 68. The product of the fumaric acid (*trans*-2-butenedioic acid) hydration reaction is:
- 1. 2-hydroxybutanoic acid;
- 2. 2,3-dihydroxybutanoic acid;
- + 3. 2-hydroxybutanedioic acid;
- 4. 2,3-dihydroxybutanedioic acid;
- 5. citric acid.
- 69. The product of the aconitic acid (3-carboxy-2-pentenedioic acid) hydration reaction according to the Markovnikov's rule is:
- 1. malic acid;
- 2. lactic acid;
- 3. acetoacetic acid;
- 4. isocitric acid;
- + 5. citric acid.
- 70. Conjugated alkadienes unlike simple alkenes participate in the following reactions:
- 1. only 1,2-elctrophilic addition;
- +2. 1,2- and 1,4-electrophilic addition;
- 3. electrophilic substitution;
- 4. nucleophilic substitution;
- 5. elimination.
- 71. The reaction of equimolecular 1,3-butadiene bromation results:
- 1. 3-bromo-1-butene;

- 2. 4-bromo-1-butene;
- 3. only 3,4-dibromo-1-butene;
- + 4. 3,4-dibromo-1-butene and 1,4-dibromo-2-butene;
- 5. 1,3-dibromobutane.
- 72. The product of oxidation of 2-methyl-2-butene with KMnO₄ solution (without heating) is:
- 1. 2-methyl-2-butanol;
- 2. acetone and ethanoic acid;
- 3. 2-methylbutane;
- 4. 2-methyl-2,3-epoxybytane;
- + 5. 2-methyl-2,3-butanediol.
- 73. Qualitative test on unsaturated hydrocarbons can be carried out with following compounds:
- 1. H₂SO₄;
- $2. O_3/H_2O;$
- $+ 3. Br_2, H_2O;$
- 4. HBr;
- 5. KCr₂O₇, H₂SO₄ / t^0 .
- 74. Using the reaction with bromine water at the room temperature the following compound can be identified:
- 1. pentane;
- + 2. 2-pentene;
- 3. cyclopentane;
- 4. benzene;
- 5. toluene.
- 75. Qualitative test on unsaturated hydrocarbons can be carried out with following compounds:
- 1. H₂SO₄;
- 2. O₃/H₂O;
- 3. FeCl₃;
- 4. HBr;
- + 5. KMnO₄, H₂O.
- 76. The aromatic ring of toluene is characterized by following:
- 1. the acyclic structure;
- 2. sp²and sp³hybridization types of carbon atoms are present simultaneously;
- 3. absence of the planar structure;

- + 4. cyclic conjugated system with the number of π -electrons according to the Huckel's rule: N=4n+2;
- 5. the number of π -electrons corresponds to the equilibrium: N=2ⁿ.
- 77. Benzene is characterized by the following reactions:
- 1. S_N ;
- $+ 2. S_{E}$;
- $-3. S_{R};$
- 4. oxidation;
- $-5. A_{E}.$
- 78. The reaction of benzene bromation occurs in the following conditions:
- 1. the room temperature;
- 2. ultraviolet irradiation;
- 3. cooling;
- + 4. AlCl₃ as catalyst and relatively high temperature;
- -5. pH < 7.
- 79. The product of phenol bromation with bromine water is:
- 1. 2-bromophenol;
- 2. 3-bromophenol;
- 3. 4-bromophenol;
- 4. 3,5-dibromophenol;
- + 5. 2,4,6-tribromophenol.
- 80. The reaction of methoxybenzene mononitration results:
- +1. 1-methoxy-2-nitrobenzene and 1-methoxy-4-nitrobenzene;
- 2. 1-methoxy-3-nitrobenzene;
- 3. 1-methoxy-2,3-dinitrobenzene;
- 4. 1-methoxy-3,5-dinitrobenzene;
- 5. 1-methoxy-2,3,5-trinitrobenzene.
- 81. The reaction of benzoic acid with concentrated sulfuric acid in heating results:
- 1. 2-sulfobenzoic acid;
- +2. 3-sulfobenzioc acid;
- 3. 4-sulfobenzoic acid;
- 4.3,4-disulfobenzoic acid;
- 5. benzenesulfonic acid.
- 82. The product of benzaldehyde monomethylation reaction is:
- 1. 2-methylbenzaldehyde;

- +2. 3-methylbenzaldehyde;
- 3. 4-methylbenzaldehyde;
- 4. 2,3-dimethylbenzaldehyde;
- 5. methyl phenyl ketone.
- 83. The reaction of toluene with acetyl chloride in presence of FeCl₃ results:
- 1. benzyl methyl ketone;
- +2. 2-acetyltoluene and 4-acetyltoluene;
- 3. 3-acetyltoluene;
- 4. 2,3-diacetyltoluene;
- 5. 3,4-diacetyltoluene.
- 84. The general practical result of toluine oxidation by KMnO₄/H₂SO₄in heating is:
- 1. the brown precipitate forming;
- + 2. bleaching of the solution;
- 3. bubbles of the gas;
- 4. no changes;
- 5. change of pH meaning.

6. ALCOHOLS, PHENOLS, THIOLS, AMINES. S_N AND E REACTIONS.

- 85. Ethanol is:
- 1. secondary alcohol;
- + 2. monohydric primary alcohol;
- 3. polyhydric alcohol;
- 4. aromatic alcohol;
- 5. unsaturated alcohol.
- 86. Glycerol is:
- -1. monohydric primary alcohol;
- 2. dihydric phenol;
- + 3. polyhydric vicinal alcohol;
- 4. tertiary alcohol;
- 5. geminal alcohol.
- 87. Tert.-butyl alcohol is:
- 1. monohydric primary;
- 2. monohydric secondary;
- + 3. monohydric tertiary;
- 4. polyhydric vicinal;
- 5. polyhydric geminal.

- 88. Propargyl alcohol is:
- 1. primary saturated;
- 2. secondary saturated;
- 3. tertiary saturated;
- + 4. primary unsaturated;
- 5. secondary unsaturated.
- 89. Primary aromatic alcohol is:
- 1. methanol;
- + 2. benzyl alcohol;
- 3. isobutul alcohol;
- 4. isopropyl alcohol;
- 5. cyclohexyl alcohol.
- 90. Primary saturated alcohol is:
- 1. methanol;
- 2. benzyl alcohol;
- + 3. isobutyl alcohol;
- 4. isopropyl alcohol;
- 5. cyclohexyl alcohol.
- 91. Secondary alcohols are:
- + 1. pentanol-3 andisopropyl alcohol;
- 2. propene-2-ol and propyne-2-ol;
- 3. 2-methylbutanol-2;
- 4. allyl alcohol and benzyl alcohol;
- 5. ethyl alcohol and tert.-butyl alcohol.
- 92. Tertiary alcohol is:
- 1. 1,2,3-Trihydroxybenzen;
- 2. 2-methylpentanol-3;
- + 3. 2-methylpropanol-2;
- 4. cyclohexanol;
- 5. butanol-2.
- 93. According to the IUPAC substitutive nomenclature the name of hydroquinone is:
- 1. phenylmethanol;
- 2. cyclohexanol;
- 3. 2-isopropyl-5-methycyclohexan-1ol;
- 4. 1,2-dihydroxybenzene;

- + 5. 1,4-dihydroxybenzene.
- 94. According to the IUPAC substitutive nomenclature the name of ethyl methyl ether is:
- 1. methylthioethane;
- + 2. methoxyethane;
- 3. methoxybenzene;
- 4. 1,2-dimethoxyethane;
- 5. 2-methoxyetanol.
- 95. The tertiary amine is:
- 1. *tert*.-butylamine;
- 2. isobutylamine;
- + 3. trimethylamine;
- 4. dimethylamine;
- 5. aniline.
- 96. There are only sp³ hybrid oxygen atoms in the following compound:
- + 1. glycerol;
- 2. phenol;
- 3. hydroquinone;
- 4. catechol;
- 5. Anisole (methoxybenzene).
- 97. There are only sp² hybrid oxygen atoms in the following compound:
- 1. glycerol;
- 2. 1-propanol;
- 3. diethyl ether;
- + 4. catechol;
- 5. tetrahydrofuran.
- 98. There are only pyrrole oxygen atoms in the molecules of the following compound:
- 1. glycerol;
- + 2. resorcinol;
- 3. ethanol;
- 4. picric acid (2,4,6-trinitrophenol);
- 5. ethoxyethane.
- 99. Propanol-1 has following reaction centres:
- 1. NH-acidic and ammonium basic;
- 2. SH-acidic;

- 3. only electrophilic, but not nucleophilic;
- + 4. OH-acidic, basic, electrophilic and nucleophilic;
- 5. it doesn't have any reaction centres.

100. Phenol has following reaction centers:

- + 1. OH-acidic and nucleophilic;
- 2. SH-acidic;
- 3. electrophilic;
- 4. strong basic;
- 5. CH-acidic.
- 101. One of reaction center of ethanethiol is:
- 1. OH-acidic;
- 2. CH-acidic;
- + 3. SH-acidic;
- 4. NH-acidic;
- 5. electrophilic.
- 102. The strength of OH-acidic centers increases from left to right in the following order:
- 1. glycerol \rightarrow ethanol \rightarrow phenol;
- 2. glycerol \rightarrow catechol \rightarrow methanol;
- + 3. isopropyl alcohol \rightarrow glycerol \rightarrow resorcinol;
- 4. hydroquinone → glycerol → propanol;
- 5. \underline{o} -cresol \rightarrow sec-butyl alcohol \rightarrow 1,2,3-propanetriol.
- 103. Which of the following compounds will react with sodium hydroxide:
- 1. CH₃CH₂OH;
- 2. C₆H₅CH₂OH;
- $+ 3. C_6H_5OH;$
- 4. (CH₃)₂CHOH;
- 5. CH₃CH₂CH₂OH.
- 104. Phenol is dissolved in:
- 1. the water:
- + 2. the alkaline solution;
- 3. acids;
- 4. the NaHCO₃ saturated solution;
- 5. the NaCl saturated solution.
- 105. The chelate complex formation with $Cu(OH)_2$ is qualitative test for discovery of:

- 1. monohydric alcohols;
- 2. primary and secondary alcohols;
- 3. ethers;
- + 4. polyhydric vicinal alcohols;
- 5. phenols.
- 106. Using the reaction of chelate formation with Cu(OH)₂the following compound can be identified:
- 1. phenol;
- + 2. glycerol;
- 3. catechol;
- 4. ethyl alcohol;
- 5. cyclohexene.
- 107. The general practical result of polyhydric vicinal alcohol complex formation reaction with Cu(OH)₂is:
- + 1. dissolving of the Cu(OH)₂ light-blue precipitate to give dark-blue solution;
- 2. blue-greene solution;
- 3. bleaching solution;
- 4. violet colour;
- 5. bubbles of gas.
- 108. The violet coloured complex product is the result of the reaction of FeCl₃ and:
- 1. 2-propanol;
- 2. glycerol;
- + 3. phenol;
- 4. formaldehyde;
- 5. tartaric acid.
- 109. The strongest base is:
- 1. isobutyl alcohol;
- 2. butanethiol;
- 3. resorcinol;
- 4. isobutylamine;
- + 5. isobutylmethylamine.
- 110. The basic reaction centre of ethers on the oxygen atom provides their reactions:
- + 1. with strong acids;
- 2. with strong bases;
- 3. oxidation;

- 4. reduction:
- 5. with electrophiles.
- 111. Nucleophilic properties of heteroatoms are increasing in range:
- + 1. 2-methylphenol \rightarrow 2-methyl-1-propanol \rightarrow 2-methyl-1-propanamine;
- 2. 2-ethoxypropane \rightarrow 2-isopropyl-5 methylphenol \rightarrow thiophenol;
- 3. methylthiobenzen \rightarrow methylthioethane \rightarrow 1,4-benzenediol;
- 4. 1,4-dioxane → cyclohexanol → Ethoxybenzen;
- 5. propanthiol \rightarrow 2-propanol \rightarrow ethylthioethane.
- 112. Alcohols as nucleophilic reagents react with the following family of organic compounds:
- 1. thios;
- + 2. carboxylic acids;
- 3. amines:
- 4. phenols;
- 5. alkenes.
- 113. The tertiary alcohol undergoes the following reactions with the electrophilic centre:
- $-1. A_{\rm N};$
- $-2. A_{\rm E};$
- $-3. A_{N-E}$;
- $+4. S_{N}1;$
- $-5. S_{N}2.$
- 114. In nucleophilic substitution reactions (S_N) alcohol molecule can be:
- 1. a radical reagent;
- + 2. a nucleophilic reagent and a substrate with electrophilic centre;
- 3. an electrophilic reagent and a substrate with nucleophilic centre;
- 4. only a substrate with electrophilic centre;
- 5. only a substrate with nucleophilic centre.
- 115. Which of the following compound is most reactive in S_N1 reactions as substrate?
- 1. ethanol;
- 2. isobutyl alcohol;
- 3. 2-butanol;
- + 4. 2-methyl-2-propanol;
- 5. cyclohexanol.

- 116. Which of the following compound is most reactive in S_N 2 reactions as substrate?
- + 1. ethanol;
- 2. isobutyl alcohol;
- 3. 2-butanol;
- 4. 2-methyl-2-propanol;
- 5. cyclohexanol.
- 117. Inversion of configuration takes place at the stereocentre of chiral alcohols molecules in reactions according to the mechanism:
- $-1. S_N 1;$
- $+ 2. S_N 2;$
- $-3. A_{E};$
- $-4. A_{\rm N};$
- 5. E1.
- 118. Which of the following can readily undergo dehydration:
- 1. ethanol;
- + 2. *tert*-butyl alcohol;
- 3. phenol;
- 4. benzyl alcohol;
- 5. acetic acid.
- 119. Hydroxyl group in phenols is:
- 1. both o,p-directing and deactivating;
- + 2. both o,p-directing and activating;
- 3. both m-directing and activating;
- 4. both m-directing and deactivating;
- 5. only m-direting.
- 120. Which of the following compound is most reactive in S_E reactions?
- + 1. phenol;
- 2. benzoic acid;
- 3. benzene;
- 4. toluene;
- 5. naphthalene.
- 121. The main products of the phenol C-methylation reaction (in presence AlCl₃) are:
- + 1. 2-methylphenol and 4-methylphenol;
- 2. 3-methylphenol;
- 3. methoxybenzene;

- 4. 3,5-dimethylphenol;
- 5. phenyl acetate.
- 122. The reaction of phenol with methylchloride in alkaline solution mainly results:
- 1. 2-methylphenol and 4-methylphenol;
- 2. 3-methylphenol;
- + 3. methoxybenzene;
- 4. 3,5-dimethylphenol;
- 5. phenyl acetate.
- 123. K₂Cr₂O₇ in presence the H₂SO₄ solution in heating oxidizes:
- 1. only primary alcohols;
- 2. only secondary alcohols;
- + 3. primary and secondary alcohols;
- 4. tertiary alcohols;
- 5. ethers.

7. CARBONYL COMPOUNDS. ALDEHYDES AND KETONES. A_N REACTIONS.

- 124. The reaction centres of aldehydes are:
- + 1. electrophilic, basic, alfa-CH-acidic;
- 2. only nucleophilic and basic;
- 3. only nucleophilic, basic and OH-acidic;
- 4. only electrophilic and nucleophilic;
- 5. only basic and alfa-CH-acidic.
- 125. Aromatic hydrocarbons that have oxo-group, with straight bonding to the aromatic ring have no following reaction centres:
- 1. electrophilic;
- 2. electrophilic and basic;
- 3. basic, electrophilic, alfa-CH-acidic;
- + 4. alfa-CH-acidic;
- 5. basic.
- 126. Cyclohexanone is classified as:
- 1. aliphatic aldehyde;
- 2. aromatic aldehyde;
- 3. aromatic ketone;
- + 4. carbocyclic ketone;
- 5. heterocyclic ketone.

- 127. Aldehydes and ketones are characterized by the following reactions:
- $-1. S_{\rm E};$
- $-2.S_{N}$;
- $-3.A_{\rm E}$;
- $+4.A_{\rm N};$
- $-5.S_{R}$.
- 128. Aldehydes and ketones are not characterized by the following reactions:
- $-1.A_{N}$;
- $-2. A_{N}-E;$
- 3. reduction and oxidation;
- 4. reactions of alfa-CH-acidic centre.
- $+ 5. S_{N}.$
- 129. The most reactive in A_N reactions is:
- 1. ethanal;
- + 2. chloral (2,2,2-trichloroethanal);
- 3. acetone;
- 4. methyl phenyl ketone;
- 5. 2,2-dimethylpropanal.
- 130. The role of acid catalyst in A_N reactions of aldehydes and ketones is:
- 1. increasing of electrophilic carbon opening;
- 2. changing of configuration;
- 3. decreasing of electrophilic centre carbon positivity and reactivity;
- + 4. increasing of electrophilic centre carbon positivity and reactivity;
- 5. leaving group formation.
- 131. The product of the addition reaction of water to the aldehyde is:
- 1. ketone:
- 2. ester:
- 3. vicinal alcohol;
- + 4. geminal dihydric alcohol;
- 5. hemiacetal.
- 132. The final product of the reaction between ethanol and propanal in presence of gaseous HCl is:
- 1. ethyl propanoate;
- 2. propyl ethanoate;
- + 3. 1,1-diethoxypropane;
- 4. 1,1-dipropoxyethane;
- 5. 1-ethoxypropane.

- 133. The 1,1-dimethoxyethane acid catalyzed hydrolysis reaction results:
- 1. methanol and ethanol;
- + 2. methanol and ethanal;
- 3. methanal and ethanol;
- 4. methanol and ethanoic acid;
- 5. methane and ethanoic acid.
- 134. 1,1-dimethoxybutane can be synthesized by the reaction between following compounds:
- 1. methanol and butanoic acid;
- 2. butanol and formic acid;
- 3. methanal and butanol;
- + 4. methanol and butanal;
- 5. methanol and butanol.
- 135. The mechanism of reactions of aldehydes and ketones with amines is:
- $-1. A_{\rm N};$
- $-2. S_{N};$
- 3. E;
- $+ 4. A_{N}-E;$
- 5. A_E.
- 136. The reaction of aldehydes and ketones with primary amines gives:
- 1. hemiacetals;
- 2. acetals:
- -3. oximes:
- + 4. imines;
- 5. 2,4-dinitrophenylhydrazones.
- 137. The qualitative test for discovery of a carbonyl group in the structures of aldehydes and ketones can be realized with following compound:
- 1. Br_2/H_2O ;
- 2. Tollen's reagent / t⁰;
- 3. FeCl₃;
- 4. I₂ / NaOH;
- + 5. 2,4-dinitrophenylhydrazine;
- 138. Reactions of alfa-CH-acidic reaction centre are possible for the following compound:
- 1. benzaldehyde;
- 2. formaldehyde;

- + 3. acetone;
- 4. 2,2-dimethylbutanal;
- 5. 2-ethyl-2-phenylpentanal.
- 139. Reactions of alfa-CH-acidic reaction centre are possible for the following compound:
- 1. benzaldehyde
- + 2. ethanal;
- 3. formaldehyde;
- 4. 2,2-dimethylbutanal;
- 5. 2-ethyl-2-isopropylpentanal.
- 140. The haloform reaction is possible for the following compound:
- 1.formaldehyde;
- + 2. ethanal;
- 3. benzaldehyde;
- 4. formic acid;
- 5. diphenyl ketone.
- 141. The iodoform test is qualitative test for discovery of an alfa-methylcarbonyl group in the following compound:
- + 1. acetone;
- 2. diphenyl ketone;
- 3. benzaldehyde;
- 4. formaldehyde;
- 5. methanal.
- 142. The following compound forms the primary alcohols as the result of the reduction reaction:
- 1. acetone:
- + 2. propanal;
- 3. 2-pentanon;
- 4. methyl propyl ketone;
- 5. acetophenone.
- 143. 3-methyl-2-butanol can be product of the reduction reaction of the following compound:
- 1. 3-methylbutanal;
- 2. 3-methylpentanal;
- + 3. 3-methyl-2-butanone;
- 4. 2-methyl-3-butanone;
- 5. 2-pentanone.

- 144. Cupric hydroxide (II)-Cu(OH)₂ in the basic solution (in heating) doesn't oxidize the following carbonyl compound:
- 1. formaldehyde;
- 2. propanal;
- + 3. acetone;
- 4. 3-methylpentanal;
- 5. 2-methylbutanal.
- 145. As the result of oxidation of benzaldehyde by Tollen's reagent forms:
- 1. benzyl alcohol and brick-red precitate;
- + 2. benzoic acid (its salt) and silver mirror;
- 3. benzyl alcohol and silver mirror;
- 4. benzene and brick-red precipitate;
- 5. benzoic acid (its salt) and brick-red precipitate.
- 146. As the result of disproportionation reaction of formaldehyde the following compounds are formed;
- 1. methanol and water;
- + 2. methanol and methanoic acid;
- 3. formic acid and water;
- 4. methanol and hydrogen;
- 5. methanol, methanoic acid, water and hydrogen.

8. CARBOXYLIC ACIDS AND DERIVATIVES. S_N REACTIONS.

- 147. According to the number of carboxyl groups carboxylic acids can be classified as:
- + 1. Monocarboxylic anddicarboxylic;
- 2. unsaturated:
- 3. saturated;
- 4. aliphatic;
- 5. aromatic.
- 148. According to the carbon chain structure carboxylic acids can be classified as:
- 1. Monocarboxylic;
- 2.dicarboxylic;
- 3. tricarboxylic;
- + 4. aliphatic and aromatic;
- 5. amino acids.
- 149. Monocarboxylic aliphatic saturated carboxylic acid is:

- + 1. ethanoic:
- 2. ethanedioic:
- 3. benzoic;
- 4. 2-butenoic acid;
- 5. phthalic acid (1,2-benzene dicarboxylic acid).

150.Monocarboxylic aromatic carboxylic acid is:

- 1. ethanoic;
- 2. ethanedioic;
- + 3. benzoic;
- 4. 2-butenoic acid;
- 5. phthalic acid (1,2-benzene dicarboxylic acid).

151. Dicarboxylic aliphatic acids are:

- 1. acetic acid and butyric acid;
- + 2. oxalic acid (ethanedioic acid) and succinic acid (butanedioic acid);
- 3. acrylic acid (propenoic acid);
- 4. isophthalic acid (1,3-benzene dicarboxylic acid);
- 5. benzoic acid.

152. The derivative of carboxylic acid is:

- 1. ethanoic acid;
- 2. ethanal;
- 3. chloroethane;
- 4. ethyl alcohol;
- + 5. methyl benzoate.

153. The derivative of carboxylic acid is:

- 1. ethanoic acid:
- + 2. ethanoyl chloride;
- 3. chloroethane;
- 4. benzaldehyde;
- 5. ethanol.

154. The structure of a carboxyl group is characterized by:

- + 1. sp²-hybridized carbon and both oxygen atoms formedconjugated system;
- 2. sp²-hybridized carbon atom and one of both oxygen, and sp³-hybridized another oxygen;
- 3. the linear geometry;
- 4. the absence of conjugated system;
- 5. the tetrahedral geometry.

- 155. The electronic structure of a carboxyl group provides following reaction centres in carboxylic acid molecules:
- 1. NH-acidic and basic;
- + 2. OH-acidic, electrophilic and *alfa*-CH acidic;
- 3. SH-acidic and nucleophilic;
- 4. OH-acidic and beta-CH-acidic;
- 5. only nucleophilic.
- 156. Acidity of carboxylic acids occurs in reaction centre:
- + 1. OH-acidic;
- 2. NH-acidic:
- 3. nucleophilic;
- 4. electrophilic;
- 5. basic.
- 157. Water-soluble carboxylic acids are characterized by:
- + 1. pH < 7;
- 2. neutral aqueous solution;
- -3, pH > 7;
- 4. basic aqueous solution;
- 5. pH=7.
- 158. Water insoluble carboxylic acids are dissolved in:
- 1. HCl solution;
- + 2. the alkaline solution and the NaHCO₃ saturated solution;
- 3. strong acids;
- 4. H₂SO₄ solution;
- 5. the NaCl saturated solution.
- 159. In alkaline solution at room temperature is dissolved:
- 1. methyl benzoate;
- + 2. benzoic acid;
- 3. aniline;
- 4. butyl acetate;
- 5. methyl phenyl ether.
- 160. Relatively strong acidic properties of carboxylic acids among organic compounds are provided by:
- + 1. high polarity of OH-bond of -COOH group and high stability of carboxylate anione;
- 2. low stability of carboxylate anion;
- 3. reactivity of alfa-CH-acidic centre;

- 4. low polarity of OH-bond of –COOH group;
- 5. electrophilic centre.
- 161. High stability of carboxylate anion is provided by:
- 1. π - π -conjugation;
- +2. complete delocalization of its negative charge as result of p,π -conjugation;
- 3. conjugated system with closed chain;
- 4. localization of its negative charge on one of oxygen atom;
- 5. aromaticity.
- 162. The order of carboxylic acids: butanoic \rightarrow malonic (1,3-propanedioic) \rightarrow oxalic (1,2-ethanedioic) is characterized by the following order of pKa (pK_{a1}for dicarboxylic acids):
- $-1.1.23 \rightarrow 2.83 \rightarrow 4.81$;
- $-2.4.81 \rightarrow 1.23 \rightarrow 2.83$;
- $-3.2.83 \rightarrow 4.81 \rightarrow 1.23$;
- $+4.4.81 \rightarrow 2.83 \rightarrow 1.23$;
- $-5.2.83 \rightarrow 1.23 \rightarrow 4.81.$
- 163. Functional group carboxylic acids derivatives are formed as the result of the following reactions:
- 1. electrophilic addition (A_E);
- 2. nucleoplic addition (A_N);
- + 3. acyl transfer reaction asnucleophilic substitution (S_N).;
- 4. electrophilic substitution (S_E) ;
- 5. radical substitution.
- 164. Functional group carboxylic acids derivatives are formed with participating of the following reaction centre:
- 1. OH-acidic;
- 2. alfa-CH-acidic;
- + 3. electrophilic;
- 4. nucleophilic;
- 5. NH-acidic.
- 165. Thioester is formed as the result of acetic acid reaction with the reagent:
- 1. alcohol/H⁺, t;
- $+ 2. thiol/H^+, t;$
- 3. NH₃/t;
- 4. SOCl₂/t;
- 5. PCl₅.

- 166. Product of reaction of butanoic acid with ammonia in prolonged heating is:
- 1. ethylbutanoate;
- 2. butanamine:
- 3. butanoyl chloride;
- + 4. butanamide;
- 5. anhydride of butanoic acid.
- 167. The reaction of butanoic acid with methanol in heating and presence of acid catalyst results:
- 1. 1,1-dimethoxybutane;
- 2. ethyl propanoate;
- 3. butyl formiate;
- 4. butyl methanoate;
- + 5. methyl butanoate.
- 168. Acyl transfer reactions of carboxylic acid derivatives occurs in the main reaction centre:
- 1. nucleophilic centre;
- + 2. electrophilic centre;
- 3. NH-acidic centre;
- 4.alfa-CH-acidic centre;
- 5.basic centre.
- 169. Hydrolysis of carboxylic acid derivatives occurs in the main reaction centre:
- 1. basic centre:
- 2. alfa-CH-acidic centre;
- 3. NH-acidic centre:
- + 4. electrophilic centre;
- 5. nucleophilic centre.
- 170. The main product of the reaction of acetyl chloride with dipropylamine is:
- 1. ethyldipropylamine;
- 2. acetamide and 2 moll of 1-chloropropane;
- + 3. N,N-dipropylacetamide;
- 4. N-propylacetamide and 1-chloropropane;
- 5. 2-(N,N-dipropyl)ethanoyl chloride.
- 171. The reaction of ethyl propanoate with methanamine results:
- + 1. N-methylpropanamide and ethanol;
- 2. propanamide and ethoxymethane;
- 3. ethylmethylpropylamine;

- 4. propanoic acid and ethylmethylamine;
- 5. propanol and N-methylethanamide.
- 172. Ethyl benzoate may be synthesized by the reaction of benzoyl chloride with the following reagent:
- 1. ethane;
- 2. chloroethane;
- 3. ethanoic acid;
- + 4. ethanol;
- 5. ethylene.
- 173. The original carboxylic acid is resulted hydrolysis reaction of the following substrate in the neutral water:
- 1. ethyl ethanoate;
- 2. propanamide;
- + 3. ethanoic anhydride;
- 4. butanenitrile;
- 5. acetamide.
- 174. The original carboxylic acid is resulted acid-catalyzed hydrolysis reaction of the following substrate:
- + 1. ethyl ethanoate;
- 2. propanamine;
- 3. ethane;
- 4. butyl chloride;
- 5. diethyl ether.
- 175. The base-catalyzed hydrolysis reaction of benzamide is resulted the following products:
- 1. benzoic acid and ammonium salt;
- + 2. benzoic acid salt and ammonia;
- 3. benzene and ammonia;
- 4. phenol and ammonium salt;
- 5. aniline and formic acid salt.
- 176. In acyl transfer reactions the most reactive is the following acyl compound:
- +1. ethanoyl chloride;
- 2. ethanamide;
- 3. methyl ethanoate;
- 4. ethanoic anhydride;
- 5. ethanoic acid.

- 177. In hydrolysis reactions the most reactive is the following compound:
- 1. ethyl chloride;
- 2. ethanamide;
- 3. methyl ethanoate;
- + 4. ethanoic anhydride;
- 5. hexyl thioester of ethanoic acid.
- 178. The reaction of myristic acid (tetradecanoic acid) with bromine in presence of small amount of red phosphorus results:
- 1. myristyl chloride;
- + 2. 2-bromomyristic acid;
- 3. 3-bromotetradecanoic acid;
- 4. 12-bromotetradecanoic acid;
- 5. tetradecyl chloride.
- 179. Which of the following compounds will be easily decarboxylated in heating:
- 1. ethanoic acid;
- + 2. oxalic acid (ethandioic acid);
- 3. benzoic acid;
- 4. propanoic acid;
- 5. butanoic acid.

9. HETEROFUNCTIONAL COMPOUNDS.

- 180. The heterofunctional compound is the following:
- 1. oxalic acid:
- + 2. oxaloacetic acid:
- 3. malonic acid;
- 4. glycerol;
- 5. sorbitol.
- 181. The hydroxycarboxylic acid is the following:
- 1. oxalic acid:
- 2. oxaloacetic acid;
- 3. malonic acid;
- + 4. citric acid;
- 5. valeric acid.
- 182. The strongest acid is the following
- + 1. 2-hydroxypropanoic acid;
- 2. 3-hydroxypropanoic acid;
- 3. 3-hydroxy-3-methylbutanoic acid;

- 4. 4-hydroxybutanoic acid;
- 5. 4-hydroxy-3-methylbytanoic acid.
- 183. In the molecules of hydroxycarboxylic acids electron accepting interference of α -hydroxyl and carboxyl groups increases strength of the following reaction centers:
- 1. basic;
- 2. nucleophilic;
- 3. basic and nucleophilic;
- + 4. OH-acidic and electrophilic;
- 5. no one.
- 184. Specific reaction of α -amino acids in mild heating is:
- 1. elimination to give α , β -unsaturated carboxylic acid;
- 2. formation of lactides;
- 3. formation of lactones;
- + 4. formation of diketopiperasines;
- 5. formation of lactams.
- 185. In mild heating valine usually forms:
- 1. Lactone and H₂O;
- 2. Lactam and H₂O;
- 3. Lactide and H₂O;
- + 4. Diketopiperasine and H₂O;
- 5. 3-methyl-2-butenoic acid and NH₃.
- 186. Mild heating of lactic acid (2-hydroxypropanoic aicd) lead to formation of:
- 1. Lactone and H₂O;
- 2. Lactamand H₂O;
- + 3. Lactide and H₂O;
- 4. Diketopiperasineand H₂O;
- 5. propenoic acidand H₂O.
- 187. Heating of lactic acid in presence of concentrated H_2SO_4 lead to formation of the following products:
- 1. methanal and ethanoic acid
- + 2. methanoic acid and ethanal;
- 3. lactone:
- 4. lactide;
- 5. propenoic acid.
- 188. Gamma-lactone is formed in mild heating of the following compound:

- 1. 2-hydroxybutanoic acid;
- 2. 3-hydroxybutanoic acid;
- +3. 4-hydroxypentanoic acid;
- 4. 2-aminopropanoic acid;
- 5. 4-aminobutanoic acid.
- 189. The reaction of 3-aminobutanoic acid in heating results the following products:
- +1. 2-butenoic acid and ammonia;
- 2. 3-butenoic acid and ammonia;
- 3. lactam and the water;
- 4. diketopiperasine and the water;
- 5. lactide and the water.
- 190. Diketopiperasines are formed in heating of:
- + 1. 2-aminopropanoic acid;
- 2. beta-alanine;
- 3. 2-aminobenzoic acid;
- 4. 4-aminobutanoic acid;
- 5. 3-aminopentanoic acid.
- 191. Gamma-lactam is resulted the reaction in mild heating of the following compound:
- 1. 2-aminopropanoic acid;
- 2. beta-alanine;
- 3. 2-aminobenzoic acid:
- + 4. 4-aminobutanoic acid;
- 5. 3-aminopentanoic acid.
- 192. The oxocarboxylic acid is the following:
- 1. oxalic acid;
- + 2. pyruvic acid;
- 3. malonic acid:
- 4. citric acid:
- 5. valeric acid.
- 193. The strongest alfa-CH-acidic centre is present in the molecules of the following oxoacids:
- 1. 2-oxobutanoic acid;
- 2. 2-oxopentanoic acid;
- + 3. 3-oxobutanoic acid;
- 4. 4-oxopentanoic acid;

- 5. 2-oxo-3,3-dimethylbutanoic acid.
- 194. Decarboxylation reaction occurs in heating in presence of diluted sulfuric acid usually for the following compounds:
- 1. 2-hydroxypropanoic acid;
- 2. 3-hydroxypropanoic acid;
- + 3. 2-oxopropanoic acid;
- 4. 4-aminopentanoic acid;
- 5. 5-hydroxyhexanoic acid.
- 195. Decarboxylation reaction occurs easy at room temperature usually for the following compounds:
- 1. 2-hydroxypropanoic acid;
- 2. 3-hydroxypropanoic acid;
- 3.5-hydroxyhexanoic acid;
- 4. 2-oxopropanoic acid;
- + 5. 3-oxobutanoic acid .
- 196. The reaction of acetoacetic ester with bromine water and following reaction with FeCl₃ proves:
- 1. π , π -conjugation;
- + 2. the phenomenon of acetoacetic ester keto-enol tautomerism;
- 3. p,π-conjugation;
- 4. ester group;
- 5. carbonyl group.
- 197. The derivative of *para*-aminobenzoic acid used as pharmaceutical substance is the following compound:
- +1. procaine;
- 2. isoniazid;
- 3. sulfamethoxypyridazine;
- 4. sulfanilamide;
- 5. methyl salicylate.
- 198. The derivative of sulfanilic acid used as pharmaceutical substance is the following compound:
- 1. procaine;
- 2. isoniazid;
- + 3. sulfamethoxypyridazine;
- 4. benzocain;
- 5. methyl salicylate.

- 199. The derivative of salicylic acid used as pharmaceutical substance is the following compound:
- 1. procaine;
- 2.benzocain;
- 3. sulfamethoxypyridazine;
- + 4. acetylsalicylic acid;
- 5.sulfanilamide.
- 200. The hydroxycarboxylic acid is the following:
- 1. oxalic acid;
- 2. oxaloacetic acid;
- 3. malonic acid;
- + 4. tartaric acid;
- 5. valeric acid.
- 201. The oxocarboxylic acid is the following:
- + 1. oxalacetic acid;
- 2. malic acid:
- 3. malonic acid;
- 4. citric acid;
- 5. valeric acid.

Carbohydrates. Monosaccharides. Oligosaccharides and polysaccharides.

- 202. D-glucose is:
- 1. ketopentose;
- 2. polysaccharide;
- 3. aldopentose;
- 4. ketohexose;
- + 5. aldohexose.
- 203. D-Ribose is:
- 1. ketopentose;
- 2. polysaccharide;
- + 3. aldopentose;
- 4. ketohexose;
- -5. aldohexose.
- 204.D-Xylose is:
- 1. ketopentose;
- 2. polysaccharide;
- + 3. aldopentose;

- 4. ketohexose;
- -5. aldohexose.

205.D-mannose is:

- 1. ketopentose;
- 2. polysaccharide;
- 3. aldopentose;
- 4. ketohexose;
- + 5. aldohexose.

206.D-galactose is:

- 1. ketopentose;
- 2. polysaccharide;
- 3. aldopentose;
- 4. ketohexose;
- + 5. aldohexose.

207. D-fructose is:

- 1. disaccharide;
- + 2. ketohexose;
- 3. aldohexose;
- 4. ketopentose;
- 5. aldopentose.

208.D-Ribulose is:

- 1. disaccharide;
- -2. ketohexose:
- 3. aldohexose:
- + 4. ketopentose;
- 5. aldopentose

209.D-Xylulose is:

- 1. disaccharide;
- -2. ketohexose:
- 3. aldohexose;
- + 4. ketopentose;
- 5. Aldopentose

210. The number of chiral centers in D-glucose is:

- 1. 2;
- +2.4;
- 3. 8;

- 4. 16; - 5. 64.
211.The number of chiral centers in D-mannose is: - 1. 2; + 2. 4; - 3. 8; - 4. 16; - 5. 64.
212.The number of chiral centers in D-galactose is: - 1. 2; + 2. 4; - 3. 8; - 4. 16; - 5. 64.
213.The number of chiral centers in D-Ribose is: - 1. 2; + 2. 3; - 3. 8; - 4. 16; - 5. 64.
214.The number of chiral centers in D-Xylose is: - 1. 2; + 2. 3; - 3. 8; - 4. 16; - 5. 64.
215.The number of chiral centers in D-fructose is: - 1. 2; + 2. 3; - 3. 8; - 4. 16; - 5. 64.
216. The number of chiral centers in D-Ribulose is: + 1. 2; - 2. 3; - 3. 8;

- 4. 16;
- 5, 64,
- 217. The number of chiral centers in D-Xylulose is:
- +1.2;
- -2. 3;
- 3. 8;
- 4. 16;
- 5. 64.
- 218. The open-chain form of D-glucose contains the following functional groups:
- + 1. Hydroxyl and aldehyde;
- 2. Only hydroxyl;
- 3. Only aldehyde;
- 4. Hydroxyl and oxo-group of ketone;
- 5. Only oxo-group of ketone.
- 219. The open-chain form of D-mannose contains the following functional groups:
- + 1. Hydroxyl and aldehyde;
- 2. Only hydroxyl;
- 3. Only aldehyde;
- 4. Hydroxyl and oxo-group of ketone;
- 5. Only oxo-group of ketone.
- 220. The open-chain form of D-galactose contains the following functional groups:
- + 1. Hydroxyl and aldehyde;
- 2. Only hydroxyl;
- 3. Only aldehyde;
- 4. Hydroxyl and oxo-group of ketone;
- 5. Only oxo-group of ketone.
- 221. The open-chain form of D-Ribose contains the following functional groups:
- + 1. Hydroxyl and aldehyde;
- 2. Only hydroxyl;
- 3. Only aldehyde;
- 4. Hydroxyl and oxo-group of ketone;
- 5. Only oxo-group of ketone.
- 222. The open-chain form of D-Xylose contains the following functional groups:

- + 1. Hydroxyl and aldehyde;
- 2. Only hydroxyl;
- 3. Only aldehyde;
- 4. Hydroxyl and oxo-group of ketone;
- 5. Only oxo-group of ketone.
- 223. The open-chain form of D-fructose contains the following functional groups:
- 1. Hydroxyl and aldehyde;
- 2. Only hydroxyl;
- 3. Only aldehyde;
- +4. Hydroxyl and oxo-group of ketone;
- 5. Only oxo-group of ketone.
- 224. The open-chain form of D-Ribulose contains the following functional groups:
- 1. Hydroxyl and aldehyde;
- 2. Only hydroxyl;
- 3. Only aldehyde;
- +4. Hydroxyl and oxo-group of ketone;
- 5. Only oxo-group of ketone.
- 225. The open-chain form of D-Xylulose contains the following functional groups:
- 1. Hydroxyl and aldehyde;
- 2. Only hydroxyl;
- 3. Only aldehyde;
- + 4. Hydroxyl and oxo-group of ketone;
- 5. Only oxo-group of ketone.
- 226. Which of the following compounds are monosaccharides:
- 1. lactose;
- + 2. D-mannose;
- 3. cellobiose:
- 4. glycogen;
- 5. starch.
- 227. Which of the following compounds are monosaccharides:
- 1. lactose;
- + 2. D-xylulose;
- 3. cellobiose;
- 4. glycogen;

- 5. starch.
228. Which of the following compounds are monosaccharides: - 1. lactose; - 2. cellulose; - 3. cellobiose; - 4. glycogen; + 5. D-fructose.
229. Which of the following compounds are monosaccharides:

- 1. lactose;
- -2. cellulose;
- 3. cellobiose;
- + 4. D-Ribose;
- -5. D-starch.
- 230. Which of the following compounds are monosaccharides:
- 1. lactose;
- -2. cellulose;
- 3. cellobiose;
- + 4. D-galactose;
- -5. D-starch.
- 231. Which of the following compounds are disaccharides:
- + 1. sucrose;
- 2. D-fructose;
- 3. D-glucose;
- 4. starch;
- 5. cellulose.
- 232. Which of the following compounds are disaccharides:
- + 1. cellobiose;
- 2. D-fructose:
- 3. D-glucose;
- 4. starch:
- 5. cellulose.
- 233. Which of the following compounds are disaccharides:
- 1. cellulose;
- 2. D-fructose;
- 3. D-glucose;
- 4. starch;

- +5. lactose.
- 234. Which of the following compounds are disaccharides:
- 1. cellulose;
- +2. maltose;
- 3. D-glucose;
- 4. starch;
- 5. D-fructose.
- 235. Which of the following compounds are homopolysaccharides:
- 1. D-mannose;
- 2. heparin;
- 3. lactose;
- 4. maltose;
- + 5. cellulose.
- 236. Which of the following compounds are homopolysaccharides:
- 1. D-mannose;
- 2. heparin;
- + 3. starch;
- 4. maltose;
- 5. lactose.
- 237. Which of the following compounds are reducing disaccharides:
- 1. D-glucose;
- 2.D-glucuronic acid;
- 3. sucrose;
- 4. glycogen;
- + 5. maltose.
- 238. Which of the following compounds are reducing disaccharides:
- + 1.lactose;
- 2.D-glucuronic acid;
- 3. sucrose;
- 4. glycogen;
- 5. D-glucose.
- 239. Which of the following compounds are reducing disaccharides:
- 1.ribose;
- 2.D-glucuronic acid;
- 3. sucrose;
- + 4. cellobiose;

- 5. D-glucose.

240. D-glucose and L-glucose are:

- + 1. enantiomers;
- 2. diastereomers;
- 3. anomers;
- 4. epimers;
- 5. structural isomers.

241.D-mannose and L-mannose are:

- 1. structural isomers
- + 2. enantiomers;
- 3. diastereomers:
- 4. anomers;
- 5. epimers;

242.D-galactose and L-galactose are:

- 1. structural isomers
- 2. diastereomers;
- 3. anomers;
- + 4. enantiomers;
- 5. epimers;

243.D-ribose and L-ribose are:

- + 1. enantiomers:
- 2. structural isomers
- 3. diastereomers:
- 4. anomers;
- 5. epimers;

244.D-ribulose and L-ribulose are:

- 1. diastereomers:
- + 2. enantiomers;
- 3. anomers;
- 4. epimers;
- 5. structural isomers

245.D-fructose and L-fructose are:

- 1. diastereomers;
- 2. anomers;
- 3. epimers;
- 4. structural isomers

+ 5. enantiomers; 246.D-xylose and L-xylose are: - 1. anomers; - 2. epimers; + 3. enantiomers; - 4. structural isomers - 5. diastereomers; 247. D-mannose and D-glucose are: - 1. anomers; - 2. structural isomers; - 3. enantiomers; + 4. epimers; - $5.\pi$ -diastereomers. 248.D-galactose and D-glucose are: - 1. anomers; - 2. structural isomers; - 3. enantiomers; - $4.\pi$ -diastereomers. + 5. epimers; 249. Number of tautomeric forms of D-glucose (found in solution) is: - 1. two; - 2. three: - 3. four: + 4. five; - 5. possible only cyclic form of molecule. 250. Number of tautomeric forms of D-galactose (found in solution) is: - 1. two: - 2. three: - 3. four: + 4. five: - 5. possible only cyclic form of molecule. 251. Number of tautomeric forms of D-mannose (found in solution) is: - 1. one - 2. two:

- 3. three;- 4. four;

+ 5. five;
252.Number of tautomeric forms of D-fructose (found in solution) is: - 1. 1; - 2. 2; - 3. 3; - 4.4; + 5. 5.
253.Number of tautomeric forms of D-ribose (found in solution) is: - 1. 1; - 2. 2; - 3. 3; - 4.4; + 5. 5.
 254. Choose the carbon atom which determines the property of monosaccharide to stereochemical designation: 1. anomeric atom in beta-anomer molecule; 2. any stereocenter in monosaccharide molecule; 4. highest number stereocenter; 4. second carbon atom in monosaccharide molecule; 5. first carbon atom in monosaccharide molecule.
 255. Deoxysugars are derivatives of monosaccharides, which have molecules with: 1. oxidated oxo-group; 2. one or two hydroxyl-groups replaced by hydrogen atoms; 3. hydroxyl group (usually at the second carbon atom) replaced by aminogroup; 4. oxidated primary hydroxyl-group; 5. reducted oxo-group.
256. Aminogroup of aminosugars can easily react with: - 1. Cu(OH) ₂ ; - 2. C ₂ H ₅ OH; + 3. HCl; - 4. NaOH:

257. Aminogroup of aminosugars can easily react with:

- 5. H₂/Pt.

- 1. NaOH;

- 2. KOH;
- -3. Br₂;
- + 4.HCl:
- 5. NaBr

258. D-mannose forms in water solution the following tautomeric forms:

- 1. Only open-chain form;
- 2. open-chain form and two furanose forms;
- 3. open-chain form and two pyranose forms;
- 4. two furanose forms and two pyranose forms;
- + 5. open-chain form, two furanose forms and two pyranose forms.

259. D-glucose forms in water solution the following tautomeric forms:

- 1. Only open-chain form;
- 2. open-chain form and two furanose forms;
- 3. open-chain form and two pyranose forms;
- 4. two furanose forms and two pyranose forms;
- + 5. open-chain form, two furanose forms and two pyranose forms.

260. D-galactose forms in water solution the following tautomeric forms:

- 1. Only open-chain form;
- 2. open-chain form and two furanose forms;
- 3. open-chain form and two pyranose forms;
- 4. two furanose forms and two pyranose forms;
- + 5. open-chain form, two furanose forms and two pyranose forms.

261. D-fructose forms in water solution the following tautomeric forms:

- 1. Only open-chain form;
- 2. open-chain form and two furanose forms;
- 3. open-chain form and two pyranose forms;
- 4. two furanose forms and two pyranose forms;
- + 5. open-chain form, two furanose forms and two pyranose forms.

262. D-ribose forms in water solution the following tautomeric forms:

- + 1. open-chain form, two furanose forms and two pyranose forms;
- 2. open-chain form and two furanose forms;
- 3. open-chain form and two pyranose forms;
- 4. two furanose forms and two pyranose forms;
- 5. only open-chain form.

263. Anomers are:

- 1. D-glucose and D-galactose;
- 2. D-glucose and D-fructose;
- + 3. α -D-glucopyranose and β -D-glucopyranose;
- 4. D-glucose and L-glucose;
- 5. α -D-glucopyranose and α -D-glucofuranose.

264. Anomers are:

- 1. D-mannose and D-galactose;
- 2. D-glucose and D-fructose;
- + 3. α -D-mannopyranose and β -D-mannopyranose;
- 4. D-mannose and L-mannose;
- 5. α -D-mannopyranose and α -D-glucofuranose.

265. Anomers are:

- 1. D-galactose and D-mannose;
- 2. D-glucose and D-fructose;
- 3. D-galactose and L-mannose;
- 4. α -D-mannopyranose and α -D-galactofuranose.
- + 5. α -D-galactopyranose and β -D-galactopyranose;

266. Anomers are:

- 1. D-ribose and D-mannose;
- 2. D-glucose and D-ribose;
- 3. D-galactose and L-mannose;
- 4. α -D-ribopyranose and α -D-galactofuranose.
- + 5. α -D-ribopyranose and β -D-ribopyranose;

267. Epimers are:

- 1. D-glucose and L-glucose;
- + 2. D-glucose and D-galactose;
- 3. α -D-galactopyranose and β -D-galactopyranose;
- 4. D –glucose and D-ribose;
- 5. D-mannose and cellulose.

268. The products of acidic hydrolisys of O-methyl-α-D-galactopyranoside are:

- 1. α,β-D-galactopyranose and CH₃COOH;
- 2. α-D-galactopyranoside and CH₃COOH;
- 3. α -D-galactopyranose and β -D-galactopyranose;
- + 4. α , β -D-galactopyranose and CH₃OH;
- 5. α,β-D-galactopyranose, CH₃COOH and CH₃OH.

- 269. Aminosugars are derivatives of monosaccharides which have molecules with:
- 1. oxidated oxo-group;
- 2. one or two hydroxyl-groups replaced by hydrogen atoms;
- + 3. hydroxyl group (usually at the second carbon atom) replaced by aminogroup;
- 4. oxidated primary hydroxyl-group;
- 5. reducted oxo-group.
- 270. Glucosides are formed in reaction of monosaccharides with:
- 1. bromine water;
- 2. acetic anhydride;
- + 3. alcohol/HCl;
- $-4. H_2/Pt;$
- 5. nitric acid.
- 271.Glucosides are formed in reaction of monosaccharides with:
- $-1. Br_2;$
- 2. NaOH;
- + 3. alcohol/HCl;
- 4. KOH;
- 5. HNO₃.
- 272.Glucosides are formed in reaction of monosaccharides with:
- 1. Br₂;
- 2. NaOH:
- 3. LiOH:
- 4. HNO₃.
- + 5. C₂H₅OH/HCl;
- 273. The conditions of Trommer's test for D-glycose are following:
- 1. $[Ag(NH_3)_2]OH$, t;
- 2. Br_2/H_2O ;
- + 3. Cu(OH)₂, NaOH, t;
- 4. HNO₃ (dilut.);
- 5. C₂H₅OH/HCl.
- 274. Which of the following structural fragments participates in oxidation of D-glucose to form D-glucuronic acid:
- + 1. primary hydroxyl-group with preliminary protection of oxo-group;
- 2. hydroxyl-group at the second carbon atom;
- 3. this is a reduction reaction;

- 4. oxo- and primary hydroxyl-groups;
- 5. oxo-group.

275. Which of the following structural fragments participates in oxidation of D-galactose to form D-galacturonic acid:

- + 1. primary hydroxyl-group with preliminary protection oxo-group;
- 2. hydroxyl-group at the second carbon atom;
- -3. this is a reduction reaction;
- 4. oxo- and primary hydroxyl-groups;
- 5. oxo-group.

276. What information is true for glycosides:

- 1. can be oxidated Br2/H2O;
- 2. has open-chain and cyclic hemiacetal forms;
- 3. can be oxidated by Tollen's reagent and in conditions of Trommer's test;
- + 4. can be hydrolyzed at acidic solution and stable at basic solution;
- 5. can be hydrolyzed at basic solution.

277. What information is true for glycosides:

- + 1. can be hydrolyzed in acidic solution;
- 2. not stable at basic solution;
- 3. has open-chain and cyclic hemiacetal forms;
- 4. can be oxidated by Tollen's reagent and in conditions of Trommer's test;
- 5. can be hydrolyzed at basic solution.

278. Which of the following compounds are oxidated by Tollen's reagent and in conditions of Trommer's test:

- 1. glycosides;
- + 2. reducing disaccharides;
- 3. nonreducing disaccharides;
- 4. cellulose;
- 5. starch.

279. Maltose is:

- 1. monosaccharide:
- 2. nonreducing disaccharide;
- 3. oligopeptide;
- + 4. reducing disaccharide;
- 5. polysaccharide.

280. Lactose is:

- 1. monosaccharide;

- 2. nonreducing disaccharide;
- 3. oligopeptide;
- + 4. reducing disaccharide;
- 5. polysaccharide.

281. Cellobiose is:

- 1. monosaccharide;
- 2. nonreducing disaccharide;
- 3. oligopeptide;
- + 4. reducing disaccharide;
- 5. polysaccharide.

282. Sucrose is:

- 1. monosaccharide;
- 2. dipeptide;
- 3. reducing disaccharide;
- + 4. nonreducing disaccharide;
- 5. polysaccharide.

283. Cellulose is:

- 1. monosaccharide;
- 2. oligosaccharide;
- + 3. homopolysaccharide;
- 4. heteropolysaccharide;
- 5. reducing disaccharide.

284. Starch is:

- 1. monosaccharide;
- 2. oligosaccharide;
- + 3. homopolysaccharide;
- 4. heteropolysaccharide;
- 5. reducing disaccharide.

285.Heparin is:

- 1. monosaccharide;
- 2. oligosaccharide;
- 3. homopolysaccharide;
- + 4. heteropolysaccharide;
- 5. reducing disaccharide.

286. Hyaluronic acid is:

- 1. monosaccharide;

- 2. oligosaccharide;
- 3. homopolysaccharide;
- + 4. heteropolysaccharide;
- 5. reducing disaccharide.

287. What information is true for sucrose:

- + 1. can be hydrolyzed at acidic solution;
- 2. can be hydrolyzed at basic solution;
- 3. can be oxidated by Tollen's reagent;
- 4. can be oxidated by Tollen's reagent and in conditions of Trommer's test;
- 5. oxo-cyclo tautomerization is possible.

288. What information is true for maltose:

- 1. oxo-cyclo tautomerization is not possible;
- 2. is hydrolyzed at basic solution;
- 3. is not oxidated by Tollen's reagent and in conditions of Trommer's test;
- + 4. is reducing disaccharide;
- 5. is hydrolyzed at acidic and basic solution.

289. What information is true for starch:

- + 1. consists of amilose and amilopectine;
- 2. is hydrolyzed with D-fructose forming;
- 3. macromolecules consist of β -D-glucopyranose units;
- 4. can be hydrolyzed at basic solution;
- 5. is found in organism of animals.

290. What information is true for glycogen:

- 1. has structure like structure of amilose;
- 2. consists of alfa-D-galactopyranose units;
- + 3. has very branching structure;
- 4. consists of β -D-glucopyranose units;
- 5. is a reducing disaccharide.

291. What information is true for cellulose:

- + 1. consists of beta-D-glucopyranose units;
- 2. D-glucose units are chained in macromolecule by alfa- (1,4)-glycosidic linkage;
- 3. has branching structure;
- 4. is not hydrolyzed in acidic solution;
- 5. consists of alfa-D-glucopyranose units.

292. The products of maltose hydrolysis reaction are:

- 1. D-glucose and D-galactose;
- + 2. D-glucose;
- 3. D-galactose;
- 4. D-fructose;
- 5. L-glucose.

293. The products of lactose hydrolysis reaction are:

- 1. D-glucose and D-fructose;
- 2. D-glucose;
- 3. D-galactose;
- 4. D-fructose;
- + 5. D-glucose and D-galactose.

294. The products of sucrose hydrolysis reaction are:

- 1. D-glucose;
- 2. D-glucose and D-galactose;
- 3. D-galactose;
- 4. D-fructose and D-galactose;
- + 5. D-glucose and D-fructose.

295. The products of cellobiose hydrolysis reaction are:

- 1. D-glucose and D-galactose;
- + 2. D-glucose;
- 3. D-galactose;
- 4. D-fructose;
- 5. L-glucose.

296. Heparin is:

- 1.unbranched polymer of D-glucose connected by α -1,4-glycosidic linkages;
- 2.unbranched polymer of D-glucose connected by β -1,4-glycosidic linkages;
- 3. cellulose derivative;
- + 4. D-glucuronic acid-2-sulfate- β -1,4-N-sulfo-D-glucosamine-6-sulfate- β -1,4;
- 5. D-glucuronic acid- β -1,3-N-acetyl-D-Glucosamine- β -1,4.

297. Hyaluronic acid is:

- 1.homopolysaccharide;
- 2.unbranched polymer of D-glucuronic acid units connected by β -1,4-glycosidic linkages;
- 3. unbranched polymer of D-glucuronic acid units connected by α -1,4-glycosidic linkages;
- 4. D-glucuronic acid-2-sulfate-β-1,4-N-sulfo-D-glucosamine-6-sulfate-β-1,4;
- + 5. D-glucuronic acid- β -1,3-N-acetyl-D-Glucosamine- β -1,4.

Amino acids.

298.	Which	of the	followin	ig natura	l alfa-	amino	acids	have	the	structure	of 2S	6, 6-
dian	ninohexa	anoic a	acid:									

- 1. glycine;
- 2. asparagine;
- 3. arginine;
- 4. glutamic acid;
- + 5. lysine.

299. Which of the following natural alfa-amino acids are essential:

- 1. Asn;
- + 2. Met, Phe, Lys;
- 3. Asn, Ala;
- 4. Phe, Ala;
- 5. Val, Lys, Asn.

300. Essential amino acids are:

- + 1. Try, Tht;
- 2. Cys, Asn;
- 3. Ala;
- 4. Val, Cys;
- 5. Try, Ala.

301. Achiral molecule has the following natural alfa-amino acid:

- 1. Glytamine;
- 2. Isoleucine;
- 3. Proline;
- + 4. Glycine;
- 5. Arginine.

302. Neutral alfa-amino acids are:

- + 1. Val, Gly, Ser;
- 2. Glu, Ile;
- 3. Arg;
- 4. Tyr, Glu, Asp;
- 5. Asp.

303. Neutral alfa-amino acidis:

- 1. Lys;
- + 2. Ile;
- 3. Arg;

- 4. Glu;
- 5. Asp.

304. Neutral alfa-amino acidis:

- +1. Val;
- 2. His;
- 3. Arg;
- 4. Glu;
- 5. Asp.

305. Non polar amino acid is:

- 1. Ser;
- 2. His;
- 3. Cys;
- 4. Glu;
- + 5. Leu.

306. Non polar amino acid is:

- 1. Asn;
- 2. His;
- + 3. Phe;
- 4. Glu;
- 5. Lys.

307.Polar amino acid is:

- 1. Pro;
- + 2. Ser;
- 3. Phe;
- 4. Glu;
- 5. Ile.

308. Polar amino acid is:

- + 1. Gln;
- 2. Glu;
- 3. Phe;
- 4.Asp;
- 5. His.

309. Negative charged amino acid is:

- 1. Ser;
- + 2. Glu;
- 3. Lys;

- 4.Ala; - 5. Phe.
310.Negative charged amino acid is: - 1. Arg; - 2. Tyr; + 3. Asp; - 4.Val; - 5. Cys.
311.Positive charged amino acid is: - 1. Asp; - 2. Asn; + 3. His; - 4.Val; - 5. Ser.
312.Positive charged amino acid is: + 1. Arg; - 2. Tyr; - 3. Asp; - 4.Val; - 5. Cys.
313.Positive charged amino acid is: - 1. Glu; - 2. Thr; - 3. Met; - 4.Leu; + 5. Lys.
314.Amino acid 2-amino-4-methylpentanoic acidis:

- + 1. Leucine;
- 2. Valine;
- 3. Alanine;
- 4.Glycine;
- 5. Tryptophan.
- 315.Amino acid2-amino-3-mercaptopropanoic acid is:
- 1. Isoleucine;
- 2. Methionine;
- 3. Glutamine;

+ 4.Cysteine; - 5. Serine.
316.Amino acid2-amino-3(4-hydroxyphenyl)-propanoic acidis: + 1. Tyrosine; - 2. Proline; - 3. Glutamine; - 4.Cysteine; - 5. Arginine.
317. Basic alfa-amino acid is: - 1. Ala; - 2. Ile; - 3. Ser; - 4. Glu; + 5. Arg.
318. Acidic alfa-amino acid is: - 1. Thr; + 2. Asp; - 3. Gln; - 4. Cys; - 5. Val.
319. Nonpolar natural alfa-amino acid is: - 1. Gly; + 2. Leu; - 3. Asp; - 4. Tyr; - 5. Glu.
320. Polar natural alfa-amino acid is: - 1. Ala; - 2. Val; + 3. Ser; - 4. Ile; - 5. Glu.
321. For identification of alfa-amino acids can be used qualitative reaction with: - 1. CH ₃ CH ₂ OH (H ₂ SO ₄); + 2. ninhydrine; - 3. Br ₂ ;

- 4. CH₃COCl;
- 5. CH₃I.
- 322. Reaction with nitric acid (HNO₃(concd)) occurs for alfa-amino acids:
- 1. cysteine;
- 2. asparagine;
- 3. isoleucine;
- + 4. tyrosine;
- 5. valine.
- 323. Qualitative reaction with (CH₃CO)₂O Pb occurs for:
- 1. serine;
- + 2. cysteine;
- 3. tyrosine;
- 4. praline;
- 5. asparagine.
- 324. Specific reations of alfa-amino acids in heating are:
- 1. formation of salts;
- 2. formation of lactides;
- 3. formation of lactones;
- + 4. formation of diketopiperasines;
- 5. formation of lactams.
- 325. Decarboxylation reaction occurs easily in:
- + 1. alfa-aminoacids:
- 2. beta-aminoacids;
- 3. gamma-aminoacids;
- 4. delta-aminoacids;
- 5. epsilon-aminoacids.
- 326. Diketopiperasine forms in heating:
- + 1. 2-aminopropanoic acid;
- 2. beta-alanine;
- 3. 2-hydroxypropanoic acid;
- 4. 4-aminobutanoic acid;
- 5. 3-aminopentanoic acid.
- 327. In heating beta-amino acids usually occurs:
- 1. decarboxylation;
- 2. formation of lactones;
- + 3. formation of conjugated unsaturated acids;

- 4. formation of diketopiperasines;
- 5. formation of lactams.
- 328. Alfa-aminoacid lysine (with pI 9,8)has in solution at pH 5 the predominant form of:
- 1. anion;
- + 2. cation;
- 3. dipolar ion;
- 4. nonionized molecules;
- 5. anion or dipolar ion.
- 329. Alfa-amino acid asparagin (with pI 5,41) has in solution at pH 5,41 the predominant form of:
- 1. anion:
- 2. cation;
- + 3. dipolar ion;
- 4. nonionized molecules;
- 5. anion or cation.
- 330. Alfa-amino acid threonine (with pI 5,6) has in solution at pH 10 the predominant form of:
- + 1. anion;
- 2. cation;
- 3. dipolar ion;
- 4. nonionized molecule;
- 5. cation or dipolar ion.
- 331. Alfa-amino acid Glytamine (with pI 5,65) has in solution at pH 1 the predominant form of:
- 1. anion:
- + 2. cation;
- 3. dipolar ion;
- 4. nonionized molecule;
- 5. dianion.
- 332. Cysteine is the amino acid that containin its side chain:
- 1. disulfide linkage;
- 2. hydroxy group;
- 3. carboxy group;
- + 4. thiol group;
- 5. aldehyde group.

Peptides and proteins.

- 333. Macromolecules of peptides and proteins consist of:
- 1. alfa-hydroxy carboxylic acids;
- 2. beta-oxo carboxylic acids;
- 3. dicarboxylic acids;
- 4. gamma-amino carboxylic acids;
- + 5. alfa-amino carboxylic acids.
- 334.Proteins consist of:
- + 1. alfa-amino acids;
- 2. beta-oxo carboxylic acids;
- 3. dicarboxylic acids;
- 4.hydrocarbons;
- 5. nucleotides.
- 335. In chemical nature peptides and proteins are:
- 1. polyesters;
- + 2. polyamides;
- 3. polyglycosides;
- 4. polynucleotides;
- 5. polyterpenes.
- 336. The chemical nature peptide bond is:
- 1. alcohol;
- 2. ester;
- 3. glycoside;
- 4. amine;
- + 5. amide.
- 337. Proteins and peptides differ in:
- + 1. macromolecular mass and number of amino acid residues in molecule;
- 2. chemical nature of macromolecules:
- 3. number of monosaccharide units;
- 4.type of glycosidic linkages;
- 5. nature of peptide bond.
- 338. Chemical nature of peptide bond is:
- 1. carboxylic acid;
- 2. primary amine;
- + 3. amide;
- 4. ester;

- 5. glycoside.
- 339. The structure and properties of peptide bond is characterized by the following:
- -1. sp³ hybridization of each atoms;
- -2. tetrahedral configuration;
- +3. p,(pi)-conjugation forms delocalized electron structure and, as the result rotation is restricted about the C-N bond;
- -4. C-N bond is weak and easy broken in a hydrolysis;
- -5. rotation about the C-N bond is free.
- 340. Primary structure of the tripeptide glycylvalylphenylalanine is:
- 1. Gln-Ser-Phe;
- 2. Phe-Val-Phe:
- 3. Val-Ser-Gly;
- 4. Gln-Val-Phe;
- + 5. Gly-Val-Phe.
- 341. Primary structure of the tetrapeptide prolylarginylserylglycine is written in example:
- 1. Gly-Ser-Arg-Pro;
- + 2. Pro-Arg-Ser-Gly;
- 3. Glu-Asp-Ser-Gly;
- 4. Pro-Asp-Ser-Glu;
- 5. Pro-Ser-Gly.
- 342. Primary structure of polipeptides and proteins gives information about the following:
- -1. the conformation of the macromolecule;
- +2. the sequence of constituent (alfa)-amino acids;
- -3. the local conformation of polypeptide backbone;
- -4. possibility to be destroyed in the denaturation process;
- -5. the dimensional shape of the macromolecule.
- 343. The isoelectric point of tripeptide Ala-Val-Tyr is in the following pH solution:
- -1. acidic:
- +2. almost neutral;
- -3. basic;
- -4. pH=8-10;
- -5.pH=10-12.

- 344. The isoelectric point of tripeptide Met-Pro-Lys is in the following pH solution:
- -1. acidic;
- -2. neutral;
- +3. basic;
- -4. weak acidic;
- -5.pH=3-5.
- 345. The isoelectric point of tripeptide Ser-Asp-Gln is in the following pH solution:
- +1. acidic:
- -2. neutral;
- -3. basic;
- -4. weak basic;
- -5.pH=10-12.
- 346. N-terminal (alfa)-amino acid residue of polypeptide is identified by the following method:
- -1. partial hydrolysis;
- -2. using of enzymes called carboxypeptidases;
- +3.Sanger method;
- -4. Hydrolysis with enzyme called tripsin;
- -5. Hydrolysis with enzyme called chymotrypsin.
- 347. N-terminal (alfa)-amino acid residue of polypeptide is identified by the following method:
- -1. partial hydrolysis;
- -2. Hydrolysis with enzyme called tripsin;
- -3.using of enzymes called carboxypeptidases;
- +4.Edman degradation;
- -5. Hydrolysis with enzyme called chymotrypsin.
- 348. C-terminal (alfa)-amino acid residue of polypeptide is identified by the following method:
- -1. partial hydrolysis;
- +2. using of enzymes called carboxypeptidases;
- -3.Sanger method;
- -4. Hydrolysis with enzyme called tripsin;
- -5. Hydrolysis with enzyme called chymotrypsin.
- 349. The reagent of Edman degradation as N-terminal residue polypeptide analysis is:

- -1. 2,4-dinitrofluorobenzene;
- +2. phenyl isothiocyanate;
- $-3. \text{ H}_2\text{O} / \text{H}^+;$
- $-4. H_2O / OH^-$;
- -5. benzyl chloroformate.
- 350. The reagent of Sanger method as N-terminal residue polypeptide analysis is:
- +1. 2,4-dinitrofluorobenzene with following hydrolysis inH₂O / H⁺;
- -2. phenyl isothiocyanate;
- -3. chymotrypsin;
- -4. di-tert-butyl carbonate;
- -5. benzyl chloroformate.
- 351. Protection of amino group of the first amino acid to the polypeptide synthesis is carried out by the following reaction:
- -1. hydrolysis;
- -2. chelate complex formation;
- -3. hydration;
- +4. acylation with benzyl chloroformate;
- -5. alkylation.
- 352. The reagent for protection of amino group of the first amino acid to the polypeptide synthesis is the following:
- $-1. H_2O / H^+;$
- +2. di-tert-butyl carbonate;
- $-3. H_2 / Pt;$
- -4. Br₂/ NaOH;
- $-5.Cu(OH)_2$.
- 353. Activation of carboxyl group of the first amino acid to the polypeptide synthesis is carried out by the following reaction:
- -1. formation of salt with Na₂CO₃;
- -2. chelate complex formation;
- +3. formation of mixed anhydride with ethyl chloroformate;
- -4.hydration;
- -5. esterification.
- 354. The sequence of operations of peptide synthesis strategy is the following:
- +1. "protection" of the amino group and "activation" of the carboxyl group of the first amino acid, "protection" of the carboxyl group of the second amino ac-

- id, then substitution reaction to the peptide bond formation, then hydratation and then hydrolysis to the removal of "protected" groups.
- -2. "protection" of only the amino group of the first amino acid, then substitution reaction to the peptide bond formation, then hydratation to the removal of "protected" group;
- -3. only "activation" of the carboxyl group of the second amino acid, then substitution reaction to the peptide bond formation;
- -4. only "protection" of the carboxyl group of the second amino acidand then hydrolysis to the removal of "protected" group.
- -5. only substitution reaction between two amino acids to the peptide bond formation.
- 355. Secondary structuren of polipeptides and proteins gives information about the following:
- -1. the conformation of the macromolecule;
- -2. the sequence of constituent (alfa)-amino acids;
- +3. the local conformation of polypeptide backbone;
- -4. possibility to be destroyed in the denaturation process;
- -5. the dimensional shape of the macromolecule.
- 356. The secondary structures of polypeptides and poteins are the following:
- -1. micells;
- -2. lipid bilayer;
- +3. (alfa)-helixes and (beta)-pleated sheets;
- -4. double helixes;
- -5. globules and fibrillas.
- 357. The adjacent coils of (alfa)-helix in the secondary structure of peptides and proteins are linked by the following bonds:
- -1. covalent;
- +2. hydrogen;
- -3. ionic;
- -4. hydrophobic interactions;
- -5. peptide.
- 358. Peptides and proteins macromolecules of their ondary structure are linked by the following bonds:
- Epherated) sheet sec-

- -1. covalent;
- +2. hydrogen;
- -3. ionic;
- -4. hydrophobic interactions;
- -5. peptide.

- 359. Tertiary structuref polipeptides and proteins gives information about the following:
- -1. the structures of side-chains of constituent (alfa)-amino acids;
- -2. the sequence of constituent (alfa)-amino acids;
- -3. the local conformation of polypeptide backbones;
- -4. possibility to be destroyed in the denaturation process;
- +5. the three-dimensional shape of the macromolecule that arises from further foldings superimposed on the coils of helixes.
- 360. The tertiary structures of polypeptides and poteins are the following:
- -1. micells;
- -2. lipid bilayer;
- -3. (alfa)-helixes;
- -4. (beta)-pleated sheets;
- +5. globules and fibrillas.
- 361. The locations of the side chains of nonpolar, hydrophobic amino acids in globular proteins usually are the following:
- +1. in the interior of protein, out of contact with the aqueous solvent;
- -2. on the surface of the protein;
- -3. most often on the surface, but some times in the interior;
- -4. in contact with aqueous solvent;
- -5. the location is not important.
- 362. The locations of the side chains of polar charged amino acids in globular proteins usually are the following:
- -1. in the interior of protein;
- +2. on the surface of the protein, in contact with aqueous solvent;
- -3. most often on the surface, but some times in the interior;
- -4.out of contact with the aqueous solvent;
- -5. the location is not important.
- 363. The locations of the side chains of uncharged polar amino acids in globular proteins usually are the following:
- -1. only in the interior of protein, out of contact with the aqueous solvent;
- -2. only on the surface of the protein;
- +3. most often on the surface, but some times in the interior;
- -4. only in contact with aqueous solvent;
- -5. the location is not important.

- 364. Peptides and proteins macromolecules of their tertiary structure are linked by the following bonds:
- -1. only covalent;
- -2. only hydrogen;
- +3. Disulfide, hydrogen and ionic;
- -4. only hydrophobic interactions;
- -5. peptide.
- 365. The qualitative test for discovery of peptide bonds in the structures of polipeptides and proteins is:
- -1. iodoform test;
- -2. xanthoproteinic test;
- -3. reaction with lead(II) acetate;
- -4. reaction with ninhydrin;
- +5. biuret test.
- 366. The qualitative test for discovery of aromatic fragments of aromatic side chains in the aromatic amino acid residues of polipeptides and proteins is:
- -1. iodoform test;
- +2. xanthoproteinic test;
- -3. reaction with lead(II) acetate;
- -4. reaction with ninhydrin;
- -5. biuret test.
- 367. The qualitative test for discovery of thiol and sulfides groups of side chains in the sulfurous amino acid residues of polipeptides and proteins is:
- -1. iodoform test;
- -2. xanthoproteinic test;
- +3. reaction with lead(II) acetate;
- -4. reaction with ninhydrin;
- -5. biuret test.
- 368. Macromolecules of peptides and proteins consist of:
- 1. alfa-hydroxy carboxylic acids;
- 2. beta-oxo carboxylic acids;
- 3. dicarboxylic acids;
- 4. gamma-amino carboxylic acids;
- + 5. alfa-amino carboxylic acids.
- 369. In chemical nature peptides and proteins are:
- 1. polysters;
- + 2. polyamides;

- 3. polyglycosides;
- 4. polynucleotides;
- 5. polyterpenes.

370. Proteins and peptides differ in:

- + 1. macromolecular mass and number of amino acid residues in molecule;
- 2. chemical nature of macromolecules;
- 3. number of monosaccharide units;
- 4.type of glycosidic linkages;
- 5. nature of peptide bond.

371. Chemical nature of peptide bond is:

- 1. carboxylic acid;
- 2. primary amine;
- + 3. amide;
- -4. ester;
- 5. glycoside.
- 372. Primary structure of the tripeptide glycylvalylphenylalanine is:
- 1. Gln-Ser-Phe;
- 2. Phe-Val-Phe;
- 3. Val-Ser-Gly;
- 4. Gln-Val-Phe;
- + 5. Gly-Val-Phe.
- 373. Primary structure of the tetrapeptide prolylarginylserylglycine is written in example:
- 1. Gly-Ser-Arg-Pro;
- + 2. Pro-Arg-Ser-Gly;
- 3. Glu-Asp-Ser-Gly;
- 4. Pro-Asp-Ser-Glu;
- 5. Pro-Ser-Gly.

Nucleosides, Nucleotides, Nucleic acids,

- 374. Pyrimidinic bases is:
- + 1. uracil;
- 2. uric acid (2,6,8-thrihydroxypurine);
- 3. adenine;
- 4. guanine;
- 5. imidazole (1,3-diazacyclopenta-2,4-diene).

375. Pyrimidinic bases is:

- + 1. tymine;
- 2. adenine;
- 3. arginine;
- -4. guanine;
- 5. glutamine.

376. Pyrimidinic bases is:

- 1. adenine;
- +2. cytosine;
- 3. histidine;
- -4. guanine;
- 5. alanine.

377. Pyrimidinic bases is:

- 1. naphthalene;
- 2. adenine;
- -3. guanine;
- + 4. tymine;
- 5. imidazole (1,3-diazacyclopenta-2,4-diene).

378. Purinic bases are:

- 1. uric acid (2,6,8-trihydroxypurine);
- + 2. adenine;
- 3. uracil;
- 4. tymine;
- 5. cytosine.

379. Purinic bases are:

- 1. asparagine;
- 2. proline;
- 3. uracil;
- 4. tymine;
- + 5. guanine.

380. More stable tautomeric form of uracil is:

- 1. lactimic;
- 2. imino-lactimic;
- + 3. lactamic.
- 4. amino-lactamic;
- 5. enolic.

381. More stable tautomeric form of cytosine is:

- 1. lactimic:
- 2. imino-lactimic;
- 3. lactamic;
- + 4. amino-lactamic;
- 5. enolic.

382. More stable tautomeric form of guanine is:

- 1. lactimic;
- 2. imino-lactimic;
- 3. lactamic;
- + 4. amino-lactamic;
- 5. enolic.

383. Monomeric units of RNA are:

- 1. ribose:
- + 2. ribonucleotides;
- 3. phosphoric acid;
- 4. deoxyribonucleotides;
- 5. heterocyclic bases.

384. Monomeric units of nucleic acids are:

- 1. aminoacids;
- + 2. nucleotides;
- 3. alcohols:
- 4. fatty acids;
- 5. heterocyclic bases.

385. Monomeric units of DNA are:

- 1. deoxyribose;
- 2. heterocyclic bases;
- 2. ribonucleotides;
- 3. phosphoric acid;
- + 4. deoxyribonucleotides.

386. Products of acidic hydrolysis of ribonucleotides are:

- + 1. heterocyclic base, prosphoric acid, ribose;
- 2. ribonucleoside;
- 3. ribose, prosphoric acid;
- 4. prosphoric acid;
- 5. deoxyribose, phosphate-ion.

387. Products of basic hydrolysis of deoxyribonucleotides are:

- 1. deoxyribonucleoside;
- 2. deoxyribose, heterocyclic base;
- 3. deoxyribose;
- 4. heterocyclic base, phosphoric acid;
- + 5. deoxyribonucleoside, phosphate-ion.

388. Products of acidic hydrolysis of deoxyribonucleotides are:

- 1. deoxyribose, heterocyclic base;
- + 2. deoxyribose, heterocyclic base, phosphoric acid;
- 3. heterocyclic base, prosphoric acid, ribose;
- 4. deoxyribose, phosphate-ion;
- 5. deoxyribonucleoside.

389. Products of acidic hydrolysis of adenosine are:

- 1. deoxyribose, adenine;
- 2. deoxyribose, adenine, phosphoric acid;
- + 3. adenine, ribose;
- 4. ribose, phosphate-ion;
- 5. ribose, phosphoric acid.

390.Products of acidic hydrolysis of Guanosine are:

- 1. deoxyribose, Guanine;
- 2. deoxyribose, Guanine, phosphoric acid;
- + 3. Guanine, ribose;
- 4. ribose, phosphate-ion;
- 5. ribose, phosphoric acid.

391. Products of acidic hydrolysis of 5`-Thymidilic acid are:

- 1. deoxyribose, thymine;
- + 2. deoxyribose, thymine, phosphoric acid;
- 3. thymine, ribose;
- 4. ribose, phosphate-ion;
- 5. ribose, phosphoric acid.

392. Products of acidic hydrolysis of adenosine 5-monophosphateare:

- 1. deoxyribose, adenine;
- + 2. ribose, adenine, phosphoric acid;
- 3. adenine, ribose;
- 4. ribose, phosphate-ion;
- 5. ribose, phosphoric acid.

393. Products of acidic hydrolysis of Guanosine 5`-monophosphate are:

- 1. guanine, deoxyribose;
- 2. ribose, phosphoric acid.
- 3. guanine, ribose;
- 4. ribose, phosphate-ion;
- + 5. ribose, guanine, phosphoric acid;

394. Products of acidic hydrolysis of 5`-Uridylic acid are:

- + 1. ribose, uracil, phosphoric acid;
- 2. ribose, uracil, phosphate-ion;
- 3. uracil, ribose;
- 4. ribose, phosphate-ion;
- 5. uracil, deoxyribose;

395. Products of acidic hydrolysis of 5`- cytidylic acid are:

- 1. ribose, phosphate-ion;
- 2. ribose, cytosine, phosphate-ion;
- 3. cytosine, ribose;
- + 4. ribose, cytosine, phosphoric acid
- 5. cytosine, deoxyribose;

396. Products of basic hydrolysis of 5`-Thymidilic acid are:

- + 1. phosphate-ion, thymidine;
- 2. deoxyribose, thymine, phosphate-ion;
- 3. thymine, ribose;
- 4. ribose, phosphate-ion;
- 5. ribose, phosphoric acid.

397. Products of basic hydrolysis of adenosine 5-monophosphateare are:

- 1. deoxyribose, adenine;
- + 2. adenosine, phosphate-ion;
- 3. adenine, ribose;
- 4. ribose, phosphate-ion;
- 5. ribose, phosphoric acid.

398. Products of basic hydrolysis of Guanosine 5`-monophosphate are:

- 1. guanine, deoxyribose;
- 2. ribose, phosphoric acid.
- 3. guanine, ribose;
- + 4. guanosine, phosphate-ion;
- 5. ribose, guanine, phosphoric acid;

399. Products of basic hydrolysis of 5`-Uridylic acid are:

- 1. ribose, uracil, phosphoric acid;
- + 2. uridine, phosphate-ion;
- 3. uracil, ribose;
- 4. ribose, phosphate-ion;
- 5. uracil, deoxyribose;

400. Products of basic hydrolysis of 5`- Cytidylic acid are:

- + 1. cytidine, phosphate-ion;
- 2. ribose, cytosine, phosphate-ion;
- 3. cytosine, ribose;
- 4. ribose, cytosine, phosphoric acid
- 5. cytosine, deoxyribose;

401. Heterocyclic bases of DNA are:

- 1. adenine, uracil;
- + 2. guanine, thymine;
- 3. uracil, guanine;
- 4. arginine;
- 5. cytosine, histidine.

402. Heterocyclic bases of RNA are:

- 1. thymine, adenine;
- 2. thymine, guanine;
- 3. uracil, alanine;
- + 4. uracil, cytosine;
- 5. proline.

403. Heterocyclic bases of DNA are:

- 1. uracil, thymine;
- + 2. thymine, cytosine;
- 3. tryptophan, adenine;
- 4. deoxyribose, cytosine;
- 5. phenylalanine.

404. Heterocyclic bases of RNA are:

- 1. heparin;
- 2. adenine, thymine;
- 3. ribose, uracil;
- 4. cytosine, thymine.
- + 5. uracil;

405. Thymine is:

- 1. heterocyclic base of RNA;
- + 2. heterocyclic base of DNA;
- 3. nucleotide of RNA;
- 4. nucleotide of DNA;
- 5. nucleic acid.

406. Adenine is:

- + 1. heterocyclic base;
- 2. aminoacid;
- 3. nucleotide of RNA;
- 4. nucleotide of DNA;
- 5. nucleic acid.

407. Guanine is:

- 1. aminoacid;
- 2. nucleotide;
- 3. polysaccharide;
- 4. nucleic acid.
- + 5. heterocyclic base;

408. Uracil is:

- 1. nucleotide:
- + 2. heterocyclic base;
- 3. polysaccharide;
- 4. nucleic acid.
- 5. aminoacid;

409. 5`-Thymidilic acid is:

- 1. Nucleotide of RNA;
- + 2. Nucleotide of DNA;
- 3. heterocyclic base;
- 4. nucleic acid.
- 5. aminoacid;

410. Adenosine 5-monophosphate is:

- + 1. Nucleotide of RNA;
- 2. heterocyclic base;
- 3. nucleic acid.
- 4. polysaccharide;
- 5. Nucleotide of DNA;

411. Guanosine 5`-monophosphate is:

- 1. heterocyclic base;
- 2. nucleic acid.
- 3. monosaccharide:
- + 4. Nucleotide of RNA;
- 5. Nucleotide of DNA;

412. 5`-Uridylic acid is:

- 1. Amino acid;
- 2. nucleic acid.
- + 3. Nucleotide of RNA;
- 4. Nucleotide of DNA;
- 5. Carboxylic acid;

413. 5`- Cytidylic acid is:

- + 1. Nucleotide of RNA;
- 2. Nucleotide of DNA;
- 3. nucleic acid.
- 4. Carboxylic acid;
- 5. Amino acid;

414. Heterocyclic bases of DNA are:

- 1. adenine, guanine, uracil, thymine, cytosine;
- + 2. adenine, guanine, thymine, cytosine;
- 3. uracil, adenine, guanine;
- 4. deoxyribose, adenine, guanine, thymine, cytosine;
- 5. cytosine, ribose, guanine, thymine.

415. Heterocyclic bases of RNA are:

- 1. thymine, adenine, guanine, uracil, cytosine;
- 2. adenine, thymine, guanine, cytosine;
- 3. ribose, uracil, adenine, guanine;
- + 4. adenine, guanine, uracil, cytosine;
- 5. cytosine, thymine, guanine.

416. Choose conditions for hydrolysis reaction of nucleosides:

- 1. water;
- + 2. acidic aqueous solution;
- 3. basic aqueous solution;
- 4. concentrated basic solution;
- 5. concentrated solution of salts.

- 417. Which of the following reactional centres form hydrogen bonds between complementaric bases:
- 1. nucleophylic;
- 2. electrophylic;
- + 3. acidic and basic;
- 4. basic and electrophylic;
- 5. nucleophylic and electrophylic.
- 418. Which of the following reactional centres of nucleotides participate in hydrolysis reactions:
- 1. basic;
- 2. acidic;
- 3. nucleophylic;
- + 4. electrophylic;
- 5. nucleophylic and electrophylic.
- 419. Guanine pairs with following base in DNA:
- 1. adenine;
- + 2. cytosine;
- 3. tymidine;
- 4. 6-N-methyladenine;
- 5. uracil.
- 420. Thymine pairs with following base in DNA:
- + 1. adenine;
- 2. cytosine;
- 3. uracil;
- 4. guanine;
- 5. hypoxanthine (6-hydroxypurine).
- 421. Cytosine pairs with following base in DNA:
- 1. thymine;
- 2. thymine or uracil;
- 3. uracil;
- + 4. guanine;
- 5. purine.
- 422. Adenine pairs with following base in DNA:
- + 1. thymine;
- 2. cytosine;
- 3. uracil;
- 4. guanine;

- 5. purine.
- 423. RNA nucleosides is:
- 1. adenosine 5-monophosphate;
- 2. 5`-Thymidilic acid;
- + 3. uridine;
- 4. cytosine;
- 5. uracil.
- 424. DNA nucleosides is:
- 1. Guanosine 5`-monophosphate;
- + 2. 2`-Deoxythymidine;
- 3. 5`-Adenylic acid;
- 4. cytidine;
- 5. adenosine.
- 425. RNA nucleotides are:
- 1. 5`-Uridylic acid;
- + 2. 2`-Deoxyadenosine 5`-monophosphate;
- 3. 2`-Deoxycytidine;
- 4. 5`-Thymidilic acid;
- 5. 2`-Deoxythymidine 5`-monophosphate.
- 426. DNA nucleotides are:
- + 1. 2`-Deoxythymidine 5`-monophosphate;
- 2. 2`Deoxygyanosine;
- 3. adenosine 5-monophosphate;
- 4. 2`-Deoxycytidine;
- 5. 5`-Uridylic acid.
- 427. Monomeric units of nucleic acids are:
- 1. Ribose:
- 2. Ribonucleosides:
- 3. Phosphoric acid;
- + 4. Deoxyribonucleotides;
 - 5. Heterocyclic bases.
- 428. The products of the acidic hydrolysis of RNA nucleotides are:
- + 1. Heterocyclic bases, ribose, phosphoric acid;
- 2. Ribonucleosides:
- 3. Ribose;
- 4. 2`-Deoxynucleosides;

- 5. Phosphate ion.
- 429. The products of the basic hydrolysis of DNA nucleotides are:
- 1. 2`-Deoxynucleosides, phosphoric acid;
- 2. Heterocyclic bases;
- 3. 2`-Deoxyribose;
- 4. 2`-Deoxyribose, phosphoric acid;
- + 5. 2`-Deoxynucleosides, phosphate ion.
- 430. Hydrolysis of nucleosides undergoes by following conditions:
- 1. aqueous solution;
- + 2. acidic solution;
- 3. basic solution;
- 4. alcohol solution;
- 5. aqueous solution or concd. salt solution.
- 431. Nucleic acids carry out:
- 1. the receptor functions;
- + 2. the storage of the genetic information and translation of the genetic information to proteins;
- 3. the energy functions;
- 4. syntesis of monosaccharides;
- 5. syntesis of polysaccharides.
- 432. Primary structure of RNA is represented by:
- 1. linear polypeptide chain;
- 2. helical polysaccharide chain;
- 3. double helix;
- + 4. single chain of polynucleotide;
- 5. linear polysaccharide chain.
- 433. Secondary structure of DNA is represented by:
- 1. helical polysaccharide chain;
- 2. linear polypeptide chain;
- + 3. double helix of polynucleotides;
- 4. single chain of polynucleotides;
- 5. linear polysaccharide chain.
- 434. Chemically nature of ATP:
- 1. it is polyribonucleotide;
- + 2. it is nucleosidepolyphosphate;
- 3. it is polypeptide;

- 4. it is coenzyme of oxidoreductases;
- 5. contains in structure esteric bonds.

435. ATP is:

- 1. found in nucleic acid;
- 2. found in peptides;
- + 3. important energy source;
- 4. important source of monosaccharides;
- 5. coenzyme of oxidoreductases.

436. NAD+:

- 1. is hydrolyzed in aqueous solution;
- 2. is found in nucleic acids;
- + 3. is coenzyme of oxidoreductases;
- 4. is polypeptide;
- 5. is nucleosidepolyphosphate.

Saponified lipids.

437. Lipids are:

- 1.low-molecular water-soluble substances;
- 2. high-molecular water-soluble substances;
- 3. water-insoluble biological polymers;
- + 4. low-molecular water-insoluble substances;
- 5. gaseous in the ordinary term substances.

438. Lipids are classified according to hydrolyzation into:

- 1. alfa-amino acids, peptides, proteins;
- + 2. saponified and non-saponified;
- 3. monosaccharides, oligosaccharide, polysaccharide;
- 4. nucleosides, nucleotides;
- 5. ribonucleic acid, desoxyribonucleic acid.

439. According to chemical structure saponified lipids are:

- 1. Isoprenoids;
- 2. derivatives of perhydrocyclopentanophenanthrene;
- + 3. esters;
- 4. polyamides;
- 5. polyhydric alcohols and hemiacetales.

440. According to chemical structure non-saponified lipids are as:

- 1. esters:

- 2. polyesters;
- 3. polyamides;
- + 4. isoprenoids;
- 5. polyhydric alcohols and acetales.

441. Saponified lipids are:

- 1. sterols;
- 2.bile acids;
- 3. terpenoids;
- + 4. phospholipids;
- 5.estrogens.

442. Non-saponified lipids are:

- + 1. Steroids, terpenes and terpenoids;
- 2. fats and oils;
- 3. fats and waxes;
- 4. glycolipids;
- 5. prospnolipids.

443. Saponified lipids are classified into:

- 1. non-hydrolyzed compounds;
- 2. monomers and polymers;
- 3. terpenes (terpenoids) and steroids;
- + 4. simple and complex lipids;
- 5. esters and isoprenoids.

444. Non-saponified lipids are classified into:

- 1. simple and complex lipids;
- 2. fats, waxes, phospholipids;
- 3. proteins and peptides;
- 4. RNA and DNA;
- + 5. terpenes (terpenoids) and steroids.

445. Simple saponified lipids are:

- 1. terpenes and terpenoids;
- 2. steroids;
- 3. glycolipids;
- + 4. fats (and oils);
- 5. phospholipids.

446. Complex saponified lipids are:

- 1. terpenes and terpenoids;

- 2. steroids;
- 3. waxes:
- 4. fats (and oils);
- + 5. Phospholipids.
- 447. Most of natural fats are formed by fatty acids and:
- 1. monohydric alcohols;
- 2. dihydric alcohols glycol;
- + 3. trihydric alcohol glycerol;
- 4. heterofuctional alcohols;
- 5. any alcohols.
- 448. The following residues predominate in the molecules of fats:
- -1. non-saturated fatty acids;
- -2. oleic acid;
- -3. linolenic acid;
- +4. saturated fatty acids;
- -5. linoleic acid;
- 449. Saturated fatty acid is:
- +1. palmitic acid
- -2. oleic acid;
- -3. linolenic acid;
- -4. palmitooleic acid
- -5. linoleic acid;
- 450. Saturated fatty acid is:
- -1. linoleic acid
- -2. oleic acid:
- -3. linolenic acid;
- +4. stearic acid
- -5. palmitooleic acid;
- 451. Saturated fatty acid is:
- -1. linoleic acid;
- -2. oleic acid;
- -3. linolenic acid;
- -4. palmitooleic acid
- +5. myristic acid;
- 452. Unsaturated fatty acid is:
- -1. palmitic acid

- +2. oleic acid:
- -3. ethanoic acid;
- -4. stearic acid
- 5. myristic acid;

453. Unsaturated fatty acid is:

- -1. stearic acid
- -2. palmitic acid
- -3. ethanoic acid;
- -4. myristic acid;
- +5. linolenic acid;

454. Following fatty acid contains 16 carbon atoms:

- -1. stearic acid
- +2. palmitic acid
- -3. linolenic acid;
- -4. myristic acid;
- -5. linolenic acid;

455. Following fatty acid contains 18 carbon atoms:

- +1. stearic acid
- -2. palmitic acid
- -3. palmitooleic acid;
- -4. myristic acid;
- -5. propanoic acid;

456. The following residues predominate in the molecules of oils:

- +1. non-saturated fatty acids;
- -2. stearic acid:
- -3. palmitic acid;
- -4. saturated fatty acids;
- -5. butyric acid;

457. Which of the following are the saturated fatty acids:

- -1. methanoic acid;
- +2. stearic acid;
- -3. arachidonic acid;
- -4. oleic acid;
- -5. linolenic acid;

458. Which of the following are non-saturated fatty acids:

-1. palmitic acid;

- -2. stearic acid:
- +3. oleic acid;
- -4. butyric acid;
- -5. myristic acid;
- 459. Which of the following compounds are the fats:
- +1. 3-linoleoil-2-oleoil-1-stearoilglycerol;
- -2. 1-palmitoil-2-oleoil-L-glycero-3-phosphocholine;
- -3. ethylacetate;
- -4. cetylpalmitate;
- -5. C₃₁H₆₃OH
- 460. Complex saponified lipids are the following:
- -1. fats;
- +2. glycerophospholipids;
- -3. oils:
- -4. waxes;
- -5. steroids;
- 461. According to chemical nature glycerophospholipids are:
- -1. Fatty acids
- -2. Polyatomic alcohols
- -3. ethers
- +4. Esters of L-phosphatidic acid
- -5. Esters of monoatomic alcohols and fatty acids
- 462. Components of the cellular membrane bilayer are ambivalent because of their structure. They are:
- -1. Solid fats;
- -2. Oils;
- -3. Waxes;
- -4. Terpenoids;
- +5. Glycerophospholipids;
- 463. Saponified lipids as esters are able to undergo hydrolysis in heating:
- -1. Only in acidic medium;
- -2. Only in basic medium;
- +3. Both in acidic and basic medium;
- -4. In alcohol solution;
- -5. Only in distilled water;

- 464. The products of fats hydrolysis in basic medium are:
- -1. C₁₅H₃₁COOH+C₁₆H₃₃ONa;
- $-2. C_{15}H_{31}COOH+C_{16}H_{33}OH;$
- -3. C₁₅H₃₁COONa+C₁₆H₃₃ONa;
- +4. C₁₅H₃₁COONa+C₁₆H₃₃OH;
- -5. There's no correct answer;
- 465. Products of hydrolysis of 2-linoleoil-3-oleoil-1-stearoil-glycerol in basic medium in heating are glycerol and:
- -1. C₁₇H₃₁COOH, C₁₇H₃₃COOH, C₁₇H₃₅COOH;
- -2. C₁₇H₃₃COONa, C₁₇H₃₅COONa, C₁₅H₃₁COONa;
- -3. C₁₇H₃₃COOH, C₁₇H₃₅COOH, C₁₅H₃₁COOH;
- -4. C₁₉H₃₁COONa, C₁₇H₃₃COONa, C₁₇H₃₅COOH
- +5. C₁₇H₃₁COONa, C₁₇H₃₃COONa, C₁₇H₃₅COONa
- 466. The product of hydrogenation of 3-lineoyl-2-palmitoyl-1-stearoylglycerol on the metal catalyst is:
- -1. 3-(10,13-dihydroxystearoyl)-2-palmitoyl-1-stearoylglycerol;
- -2. 1,2,3-tripalmitoyl glycerol;
- +3. 2-palmitoyl-1,3-distearoylglycerol;
- -4. 1,2,3-tristearoylglycerol;
- -5. 3-lineoyl-2-palmitoyl-1-oleoylglycerol;
- 467. We can expect the decolouration of the iodine or bromine solution when shaked with the following substances:
- +1. 3-linoleoyl-2-oleoyl-1-stearoylglycerol;
- -2. 3-palmitoyl-1,2-distearoylglycerol;
- -3. 1,2,3-tristearoylglycerol;
- -4. C_6H_{14} .
- -5. 1,2,3-tripalmitoyl glycerol;
- 468. Saponified lipids are oxidized in mild conditions (KMnO₄, H₂O), if there are following residues in their molecules:
- -1. Only saturated carboxylic acids;
- +2. Non-saturated carboxylic acids;
- -3. OH group is present;
- -4. amino group is present;
- -5. Aromatic ring is present;
- 469. In organism remnants of the fatty acids are oxidized by the following ways listed:
- -1. Hydroxylation;

- +2. Peroxide oxidation and enzyme-mediated oxidation;
- -3. oxidation by KMnO₄;
- -4. oxidation by $K_2Cr_2O_7$;
- -5. oxidation by strong acid;

Non-saponified lipids. Steroids.

- 470. Which of the lipids are isoprenoids according to their chemical structure:
- -1. Waxes:
- -2. Fats and oils:
- -3. Phospholipids;
- -4. Glycerophospholipids;
- +5. Steroids:
- 471. The following information is true for beta-karotene:
- -1. It is a vitamin of A group;
- -2. It is fat:
- -3. It is steroid:
- +4. It is an example of natural polyene compound and a precursor of vitamin A;
- -5. The reactions of unsaturated compounds and primary alcohols are cheractaristic reactions;
- 472. The structural basis of steroids molecules is the carbon skeleton of the following compound:
- -1. Mentane:
- -2. Kamphane;
- -3. 1-methyl-4-isopropylcyclohaxane;
- +4. Perhydrocyclopentanophenantrene;
- -5. Perhydronaphthaline;
- 473. Structure of steroid molecules are characterized by:
- -1. Planar structure;
- 2. Symmetric molecule structure with several chiral centres;
- +3. Possibility for stereoisomery;
- -4. All the carbon atoms are in the same plane;
- -5. Two planes of symmetry;
- 474. For indication of substituents configuration in chiral centers of steroid molecule the following stereochemic nomenclature is used:
- -1. D-, L-;
- +2. alpha-, beta-;
- -3. radical-functional;

- -4. substitutive -5. R-,S-; 475. In molecules of natural steroids C and D rings have junction: -1. only trans-; -2, only cys-; -3. trans- or cys-; +4. commonly trans-; -5. commonly cys-; 476. The hydrocarbon of female sex hormones steroids group is: -1. cardenolid: +2. estran; -3. cholestan: -4. pregnane; -5. androstane; 477. The hydrocarbon of bile acids steroids group is: -1. cardenolid; -2. estran; -3. cholestan; +4. cholane -5. pregnane; 478. Which of the following corresponds to steroids of bile acids group: -1. they are strong cardiac compounds; +2. glycocholic and taurocholic acids according to chemical structure may be considered as functional derivates of cholic acid; -3. they are forming in liver from androstane; -4. the hydrocarbon base is estran; -5. are the estrane derivates: 479. Which of the lipids are isoprenoids according to their chemical structure? -1. Waxes: -2. Fats:
- 480. The following information is true for beta-carotene: -1. It is a vitamin of B group;
- -2. It is vitamin of D-group;

-3. Phospholipids;

-4. Oils;

+5. Steroids:

- -3. It is steroid:
- +4. It is an example of natural polyene compound and a precursor of vitamin A;
- -5. It is phospholipid;
- 481. Structures of steroid molecules are characterized by:
- -1. Planar structure:
- 2. Symmetric molecule structure with several chiral centres;
- +3. Possibility for stereoisomerism;
- -4. All the carbon atoms are in the same plane;
- -5. Two planes of symmetry;
- 482. Symbol α (alfa) designates substituent that lies toward the general plane of steroid ring system:
- -1. on the top side (up);
- +2. on the bottom (down);
- -3. in the same plane as cycles;
- -4. on the same side as the most senior group;
- -5. on the same side as angular methyl groups.
- 483. Symbol β (beta) designates substituent that lies toward the general plane of steroid ring system:
- +1. on the top side (up);
- -2. on the bottom (down);
- -3. in the same plane as cycles;
- -4. on the same side as the most senior group;
- -5. trans to angular methyl groups.
- 484. $5-\alpha$ (alfa) steroid has A and B rings junction as:
- -1. only *cis*-;
- +2. only trans-
- -3. both *cis* and *trans*-;
- -4. planar;
- -5. no cis- neither trans-
- 485. 5-β(beta) steroid has A and B rings junction as:
- +1. only *cis*-;
- -2. only trans-
- -3. both *cis* and *trans*-;
- -4. planar;
- -5. no cis- neither trans-

486. In molecules of natural steroids B and C rings have junction: +1. only trans-; -2, only cys-; -3. trans- or cys-; -4. planar; -5. commonly cys-;
487. In molecules of natural steroids A and B rings have junction: -1. only trans-; -2, only cys-; +3. trans- or cys-; -4. commonly trans-; -5. commonly cys-;
488. The hydrocarbon of male sex hormones steroids group is: -1. cardenolid; +2. androstane; -3. cholestane; -4. cholane -5. pregnane;
489. The hydrocarbon of sterols is: -1. cardenolid; -2. estrane; +3. cholestane; -4. cholane -5. pregnane;
 490. The hydrocarbon of pregnancy hormone steroids group is: -1. cardenolid; -2. estrane; -3. cholestane; -4. cholane +5. pregnane;
 491. The hydrocarbon of adrenocortical hormones steroids group is: -1. cardenolid; -2. estran; -3. cholestan; -4. cholane

+5. pregnane;

- 492. The hydrocarbon of cardiac steroids group is:
- +1. cardenolid;
- -2. estran:
- -3. cholestan;
- -4. cholane
- -5. pregnane;
- 493. The steroid hydrocarbons differ to each other mainly with:
- -1. the presence and number of double bonds in the ring A;
- -2. the nature of functional groups in ring A;
- -3. the presence or absence of angular methyl groups;
- -4. the nature of functional groups in ring B;
- +5. the nature of R group (substituent) at position 17 of ring D.
- 494. The absence of R group at position 17 of ring D of perhydrocyclopentanophenantrene ring system is structural characteristic of the following steroid family:
- -1. sterols;
- -2. bile acid;
- -3. adrenocortical hormons;
- +4. estrogens;
- -5. cardiac steroids.
- 495. The absence of R group at position 17 of ring D of perhydrocyclopentanophenantrene ring system is structural characteristic of the following steroid family:
- -1. sterols;
- +2. androgenes;
- -3. adrenocortical hormons;
- -4.bile acids:
- -5. cardiac steroids.
- 496. The ethyl R group at position 17 of ring D of perhydrocyclopentanophenantrene ring system is structural characteristic of the following steroid family:
- -1. sterols:
- -2. bile acids;
- +3. adrenocortical hormons;
- -4. estrogens;
- -5. cardiac steroids.

- 497. The *sec*-pentyl R group at position 17 of ring D of perhydrocyclopentanophenantrene ring system is structural characteristic of the following steroid family:
- -1. sterols:
- +2. bile acids;
- -3. adrenocortical hormons;
- -4. estrogens;
- -5. cardiac steroids.
- 498. The R group containing eight carbon at position 17 of ring D of perhydrocyclopentanophenantrene ring system is structural characteristic of the following steroid family:
- +1. sterols;
- -2. bile acids:
- -3. adrenocortical hormons;
- -4. estrogens;
- -5. cardiac steroids.
- 499. The unsaturated lactone group at position 17 of ring D of perhydrocyclopentanophenantrene ring system is structural characteristic of the following steroid family:
- -1. sterols;
- -2. bile acids;
- -3. adrenocortical hormons;
- -4. estrogens:
- +5. cardiac steroids.
- 500. The following information is characteristic of cholesterol:
- -1. it is female sex hormone, contains aromatic ring A.
- -2. It is a regulator of carbohydrate, protein and lipid metabolism, water and electrolyte balance.
- +3. It is the secondary alcohol; it serves as intermediate in the biosynthesis of all of the steroids in the body.
- -4. It is cardiac aglycone, contains five-membered unsaturated lactone cyclic group.
- -5. it is male sex hormon.
- 501. The following information is characteristic of estrogens:
- +1. They are female sex hormones, contain aromatic ring A.
- -2. They are regulators of carbohydrate, protein and lipid metabolism, water and electrolyte balance.
- -3. They serves as detergents.

- -4. They are cardiac aglycones, contain five-membered unsaturated lactone cyclic group.
- -5. They are derivatives of cholane.
- 502. The following information is characteristic of adrenocortical hormones:
- -1. They are female sex hormones, contain aromatic ring A.
- +2. They are regulators of carbohydrate, protein and lipid metabolism, water and electrolyte balance, contained tertiary alcohol goup at 17 atom.
- -3. They all are the secondary alcohols and serve as intermediates in the biosynthesis of all of the steroids in the body.
- -4. They are cardiac aglycones, contain five-membered unsaturated lactone cyclic group.
- -5. They are derivatives of estrane.
- 503. The following information is characteristic of cardiac aglicone group steroids:
- -1. They are female sex hormones, contain aromatic ring A.
- -2. They are detergents.
- -3. They all are the secondary alcohols and serve as intermediates in the biosynthesis of all of the steroids in the body.
- +4. They are cardiac aglycones, contained five-membered unsaturated lactone cyclic group.
- -5. They are derivatives of estrane.

QUESTIONS FOR THEORETICAL EXAM

1. Theoretical base of the structure and reactivity of organic compounds.

1.1 Introduction. Classification and nomenclature of organic compounds.

- 1. Classification of organic compounds according to the structure of carbon skeleton and according to the functional groups.
- 2. Principal rules of IUPAC nomenclature of organic compounds; substitutive and radicofunctional nomenclature.

1.2 Chemical bond and mutual influence of atoms in organic compounds.

- 3. Electronic structure of carbon atom and heteroatoms (N, O). Hybridization.
- 4. Chemical bonding in organic compounds. Main characteristics of the σ -and π -bonds in organic compounds. Hydrogen bonds.
- 5. Conjugation (π , π and p, π -conjugation). Conjugated systems with an open chain: 1, 3 diens, polyenes, allylic radical).
- 6. Conjugated systems with a closed chain. Aromaticity: criterions (conditions) of aromaticity, Huckel's rule of aromaticity. Aromaticity of benzenoid (benzene, naphthalene, phenanthrene), nonbenzenoid compounds. Conjugation (delocalization) energy. Thermodynamic stability of biologically important molecules with opened and closed conjugated systems.
- 7. Mutual influence of atoms in organic compounds: inductive effect and mesomeric effect. Electron–withdrawing and electron–releasing substituents. Electron density delocalization in the molecule. Reaction centres.

1.3 Stereochemistry of organic compounds. Configuration and conformation of organic compounds.

- 8. Configuration and conformation of organic compounds. The relationship between steric structure of organic compounds and the hybridization type of a carbon atom: sp^3 , sp^2 , sp hybridization. Molecular models (ball-and-stick models, space-filling models); three-dimensional (stereo-chemical) formulas. Newman and Fischer projection formulas.
- 9. Chirality. Chiral molecules. The chiral carbon atom. A stereocenter. Enantiomerism. Optical activity. Relative configuration. The D-, L-system of a stereochemical designation. Glyceraldehyde as a configurational standard. Absolute configuration of stereoisomers. Notion of the R-, S –system of a stereochemical designation.
- 10. Stereoisomerism of molecules with one stereocenter. Stereoisomerism of molecules with more than one stereocenter: enantiomers and diastereomers. Meso compounds. Racemate, racemic mixtures. Notion of methods of racemic mixtures separation. π -Diastereomers.

- 11. Conformations of open chain compounds. Newman projection formulas. Torsional and Van Der Waals strains in the molecules. Energy characteristics of alkanes` conformations.
- 12. The primary formation of five- and six-membered cycles. Stability of conformations. Axial and equatorial bonds. 1,3-diaxial interaction. Conformational inversion of cyclohexane.

1.4 Reactivity of hydrocarbons.

- 13. Chemical reaction as a process. Terms: reactants (a substrate, a reagent), products (the product of interest, the by- product), a reaction center, an activation energy, the rate of the reaction, the mechanism of the reaction. Classification of organic reactions according to the result (substitution, addition, elimination reactions; rearrangements; oxidation-reduction reactions) and mechanisms such as radical reactions, ionic reactions (electrophilic, nucleophilic).
- 14. Types of reagents: radical, nucleophilic, electrophilic, acidic, basic. Types of bond cleavage in organic compounds and forming species: free radicals as the result of homolysis, carbocations and carbonions as the result of heterolysis). Electronic and steric structures of these intermediates. Factors of their relative stability.
- 15. Reactivity of saturated hydrocarbons. Free–radical substitution reactions as homolytical reactions with participation of C–H bonds at a sp³ hybridized carbon atom. The mechanism of free radicals substitution reactions on the example of the halogenation of alkanes. Free-radical substitution reactions as regionselective reactions. Ways of free radicals formation. Notion of chain processes. The role of free radical oxidation reactions in biological processes. Active forms of oxygen, peroxides.
- 16. Electrophilic addition reactions to alkenes as heterolycal reactions with participation of π -bond between two sp² hybrid carbon atoms. The mechanism of the hydration reaction. The acidic catalysis. The effect of static and kinetic factors on regioselectivity of addition reactions. Markovnikov's rule.
- 17. Electrophilic addition to conjugated systems: hydration of α , β unsaturated carboxylic acids. Qualitative reactions for the unsaturated hydrocarbons (for the double bond).
- 18. Electrophilic aromatic substitution reactions as heterolytical reactions with participation of the π -electron cloud of an aromatic system. The mechanism of the reaction. The role of catalysts in the electrophile formation.
- 19. Electrophilic aromatic substitution reactions. Effect of substituents in an aromatic ring on its reactivity in electrophilic (aromatic) substitution. Orienting effect of substituents. Halogenation and alkylation reactions in vivo.

1.5 Reactivity of alcohols, phenols, thiols and amines. Acid-base properties of organic compounds.

- 20. Reaction centers of alcohols, phenols, thiols and amines. Acidity or basicity: Bronsted-Lowry and Lewis theories. Qualitative and quantitative characteristics of acidic and basic properties of organic compounds.
- 21. The acidic and basic properties: the chemical nature of the atom in acidic and basic centers, electronic effects of substituents, solvatation effect. Toxicity of strong acids and bases. Amphoterism. The hydrogen bond as specific manifestation of acid and basic properties.
- 22. Nucleophilic substitution reactions at sp³-hybrid carbon atom. S_{N1} and the S_{N2} mechanisms. Stereochemistry of nucleophilic substitution reactions.
- 23. Nucleophilic substitution of the hydroxyl group in alcohols. The role of acid catalysis.
- 24. The alkylation reactions of alcohols, thiols, amines. The alkylation in vivo.
- 25. Elimination reactions (dehydration) of alcohols. The biologically important dehydration reactions of alcohols.
- 26. Oxidation reactions of alcohols, phenols, thiols. Reduction reactions of disulfides. NAD⁺-NADH system; hydride transfer as one of the stages of the biological oxidation–reduction reactions with participation of this system. Phenols and thiols as antioxidants.

1.6 Reactivity of aldehydes and ketones.

- 27. Reaction centers of aldehydes and ketones. Nucleophilic addition reactions. The mechanism of nucleophilic addition reaction. Reactions of carbonyl compounds with water, alcohols, amines. Formation of cyclic hemiacetals. The biological role of acetalization reactions
- 28. Nucleophilic addition reactions. The aldol addition reactions. Reversibility of nucleophilic addition reactions. The biological role of aldol addition reactions.
- 29. Nucleophilic addition-elimination reactions of aldehydes and ketones with amines. Toxicity of aldehydes. Aldehydes as disinfectants and sterilizing agents.
- 30. Oxidation and reduction reactions of carbonyl compounds in vitro and in vivo. Qualitative reactions for aldehyde group and for acetone.

1.7 Reactivity of carboxylic acids and their derivatives.

- 31. Reaction centers of carboxylic acids. Acidic properties of mono- and dibasic, saturated, unsaturated and aromatic carboxylic acids.
- 32. Nucleophilic substitution reactions at the sp²-hybrid carbon atom of carboxylic acids and their derivatives. The acylation reactions such as formation of carboxylic acid anhydrides, haloanhydrides, esters, amides. Hydrolysis reactions of derivatives of carboxylic acids.

- 33. The acylating by carboxylic acid anhydrides, acid chlorides, carboxylic acids, esters, thioesters. The acylation ability of carboxylic acids derivatives. Relative reactivity of esters and thioesters. Biological importance of esters and thioesters. Acylcoenzyme A. Acylphosphates. Biologically important acylation reactions that proceed with participating of acylphosphates. Notion about phosphorilation reactions.
- 34. Amides of carboxylic acids. The structure of amide-group. Acid-base properties of amides. Hydrolysis of amides. Amide of benzoic acid.
- 35. Derivatives of carbonic acid: the urea (carbamide) as the complete amide of the carbonic acid, carbamic acid. Acid-base properties and biological importance of carbamic acid and carbamide. Biuret. Urethanes, ureides, ureidoacids in the medicine. Biological importance of creatine and phosphocreatine.

2. Biologically important heterofunctional compounds.

- 2.1 Poly- and heterofunctional compounds: participating in biological processes and using in medicine (compounds, which are origin of the most important medicament groups).
- 36. Classification of poly- and heterofunctional compounds. Acid-base properties. Typical reactivity of poly- and heterofunctional compounds.
- 37. Specific features of chemical behaviour of poly- and heterofunctional compounds: features of acid and base properties, cyclization and chelates formation. Chelate complex formation as the qualitative test for a diol fragment.
- 38. Intramolecular cyclization (γ and δ -hydroxyaldehydes, γ and δ -hydroxy- and aminoacids, dicarboxylic acids with 4 or 5 carbon atoms) intermolecular cyclization (α hydroxy- and aminoacids). Cyclic hemiacetals, cyclic anhydrides, lactides, diketopiperasines, lactones, lactames.
- 39. Decarboxylation reactions. The elimination reactions of β -hydroxy- and β -amino acids. Tautomerization: keto–enol tautomerization and lactam–lactim tautomerization.
- 40. Polyalcohols. Their examples: ethylene glycol, glycerol, inositol, xylitol, sorbitol. Esters of polyhydric alcohols with inorganic acids (nitro-glycerol, glycerol and inositol phosphates) and with fatty acids.
- 41. Dihydric phenols. Their examples: hydroquinone, resorcinol, catechol. Oxidation of dihydric phenols. Hydroquinone-quinone system. Phenols as antioxidants. Tocopherols.
- 42. Dicarboxylic acids. Their examples: oxalic acid, malonic acid, succinic acid, glutaric acid, fumaric acid. The transformation of succinic acid to fumaric acid as an example of a biologically important dehydrogenation reaction.
- 43. Amino alcohols. Their examples: 2-aminoethanol, choline, acetylcholine. Forming of choline from L-serine. Amino phenols. Their examples: dopamine, noradrenaline (norepinephrine), adrenaline (epinephrine).

- 44. Hydroxy-acids. Lactic acid, malic acid, tartaric acid, citric acid. Oxidation reactions of lactic acid and malic acid with participating of NAD⁺. Citric acid. Citrates: preservation of donor blood. Dehydration of citric acid in vivo.
- 45. Oxo-acids (aldehyde and keto acids). Their examples: pyruvic acid, acetoacetic acid, oxaloacetic acid, α -ketoglutaric acid. Acid properties and reactivity. The decarboxylation reaction of β -ketobutyric acid and the oxidizing decarboxylation reactions of pyruvic acid. Keto-enol tautomerization. β -hydroxybutyric acid, β -ketobutyric acid, acetone as representatives of "ketone bodies", their biological and diagnostic importance.
- 46. The heterofunctional benzene derivatives as medicaments. Salicylic acid and its derivatives (acetylsalicylic acid, methyl-salicylate, phenyl-salicylate).
- 47. p-Aminobenzoic acid and its derivatives (benzocain, novocaine). Biological role of p-aminobenzoic acid (folic acid as the growth factor). Modern anesthetics.
 - 48. Sulfanilic acid and its amide. Sulfanamides. Notion of antimetabolites.

2.2 Biologically important heterocyclic compounds. Alkaloids.

- 49. Heterocycles with one heteroatome. Pyrrole, indole, pyridine, quinoline. Heterocycles with several heteroatoms. Pyrazole, imidazole, pyrimidine, purine. Electronic and spacial structure of pyrrolic and pyridinic heteroatoms. Aromaticity of heterocycles. Influens of heteroatoms on reactivity of pyrrole and pyridine in $S_{\rm E}$ reactions.
- 50. Heterocycles with several heteroatoms. Acid-base properties of heterocyclic compounds. The tautomerisation on the example of imidazole. Biologically important pyridine derivatives: nicotinic amide, pyridoxal, isonicotinic acid and its derivatives.
- 51. Barbituric acid and its derivatives (phenobarbital). The hydroxypurines: hypoxanthine, xanthine, uric acid. Notion about alkaloids.

3. Biopolymers and their structural units. Low-molecular bioregulators. 3.1 Carbohydrates.

- 52. Monosaccharides. Classification of monosaccharides. Aldoses, ketoses; trioses, tetroses, pentoses, hexoses. Stereoisomerism of monosaccharides. Dand L-families. Biological importance of monosaccharides and their derivatives.
- 53. Structures of the most important pentoses (D-ribose, D-xylose, 2-deoxy-D-ribose) and hexoses (D-glucose, D-mannose, D-galactose, D-fructose). Amino sugars (D-glucosamine, D-mannosamine, D-galactosamine) and their properties. Neuraminic acid, sialic acids.
- 54. Open-chain structures and cyclic forms. Furanoses and pyranoses; α and β -anomers. Fischer projection formulas and Haworth formulas. A cyclo-oxo tautomerization. Mutarotation. Conformations of pyranose forms of monosaccharides. Physical properties of monosaccharides.

- 55. Chemical properties of monosaccharides. Nucleophilic substitution at an anomeric atom in cyclic forms of monosaccharides. O- and N-glycosides. Hydrolysis of glycosides. Biologically important phosphorylation reactions of monosaccharides. Phosphates of monosaccharides.
- 56. Oxidation of monosaccharides. Reducing properties of aldoses. Aldonic, aldaric, uronic acids. Reduction of monosaccharides to alditols (xylitol, glucitol (sorbitol), mannitol); application of alditols in medicine. Epimerization reaction of monosaccharides, the reversible transformation of aldoses to ketoses.
- 57. Nucleophilic addition reaction with participation of oxo-group of openchain form of glucose (glycylation reactions of peptides). Ascorbic acid. Its structure, properties, and biological importance.
- 58. Oligo- and polysaccharides. Common characteristic and classification of polysaccharides. Oligosaccharides. Disaccharides: maltose, cellobiose, lactose, sucrose. Structures, the cyclo-oxo tautomerization. Reducing properties. Hydrolysis.
- 59. Maltose, cellobiose, lactose. The conformational structure. The role of lactose oligosaccharides in formation of not pathogenic microflora in the intestines, which is necessary for normal digestion.
- 60. Polysaccharides. Homo- and heteropolysaccharides. Homopolysaccharides: starch (amylose, amylopectine), glycogen, dextran, cellulose. Primary structure, hydrolysis. Notion about secondary structure (amylose, cellulose). Pectins (polygalacturonic acid). Plasma replacing solutions on the basis of dextran and starch.
- 61. Heteropolysaccharides: hyaluronic acid, chondroitin sulfates. Primary structure. Notion of mixed biopolymers: proteoglycans, glycoproteins, glycolipids.

3.2 Amino acids. Peptides and proteins.

- 62. Amino acids that can be obtained from proteins. Classification of naturally occurring amino acids taking into account different signs: acid and base properties, chemical nature of a side chain and its substituents. Structure, nomenclature. Stereoisomerism.
 - 63. Acid and base properties, dipolar ions. Essential amino acids.
- 64. The formation of α -amino acids: hydrolysis of proteins, synthesis from α -halo acids. Reducing amination reactions and transamination reactions. Pyridoxal catalysis.
- 65. Chemical properties of α -amino acids as heterofunctional compounds. Formation of intracomplex salts. Esterification, acylation, alkylation, deamination reactions, formation of amines. Qualitative tests for α -amino acids.
- 66. Biologically important reactions of α -amino acids. Decarboxylation of α -amino acids the way of formation of biogenic amines and biological regulators (2-aminoethanol, histamine, tryptamine, serotonin, dopamine, γ -amino butyric acid), their biological importance. Notion about neuromediators.

- 67. Oxidative and not oxidizing deamination reactions. Hydroxylation reactions: phenylalanine \rightarrow tyrosine, tyrosine \rightarrow 3, 4-dihydroxyphenylalanine, tryptophan \rightarrow 5-hydroxytryptophan, proline \rightarrow 4-hydroxyproline. Cysteine oxidation. Disulfide bond.
- 68. Peptides. Electronic and steric structure of a peptide bond. Hydrolysis of polypeptides. Individual representatives of polypeptides: aspartame, glutathione, neuropeptides, insulin.
- 69. Establishment of primary structure of polypeptides. Notion about the strategy of peptide synthesis.
- 70. Primary structure of proteins. Notion of secondary, tertiary (domains) and quaternary structures. Hemoglobin, heme group structure. Notion of complex proteins: glycoproteins, phosphoproteins, metalloproteins, hemoproteins, nucleoproteins.

3.3 Nucleic acids.

- 71. Nucleic (heterocyclic) base that can be obtained from nucleic acids. Pyrimidines (uracil, thymine, cytosine) and purines (adenine, guanine). Aromatic properties. A lactim–lactam tautomerization. Deamination reactions.
- 72. Nucleosides. Nucleotides. Structure of mononucleotides that can be obtained from nucleic acids. Nomenclature. Nucleotides hydrolysis.
- 73. Primary structure of nucleic acids. The phosphate diester linkage. Ribonucleic and deoxyribonucleic acids. Nucleotides found in RNA, nucleotides found in DNA. Hydrolysis of nucleic acids. Structure and properties of m-RNA, t-RNA, r-RNA.
- 74. Notion of the secondary structure of DNA. The role of hydrogen bonds in formation of the DNA secondary structure. Complementarity of heterocyclic bases. Hydrogen bonds in complementary pairs of heterocyclic bases.
- 75. Medicaments on base of the modified heterocyclic bases. Change of heterocyclic base structures caused with chemical mutagens, UV irradiation and radiation.
- 76. Nucleoside mono- and polyphosphates. AMP, ADP, ATP. The role of ATP as the accumulator and carrier of free energy in cell. Nucleoside cyclophosphates (cyclic AMP, cyclic GMP) as secondary mediators in the regulation of cell metabolism.
- 77. Notion of coenzymes. Structures of NAD⁺ and its phosphate (NADPh⁺). NAD⁺-NADH system; hydride transfer as one of the stages of the biological oxidation–reduction reactions with participation of this system.

3.4 Lipids.

- 78. Classification. Biological importance. Neutral fats. Notion of the structure of waxes.
- 79. Common natural fatty acids that can be obtained from lipids: palmitic, stearic, oleic, linoleic, linilenic, arachidonic acids. Features of unsaturated fatty

acids, ω -nomenclature. The role of free fatty acids in the energy reservation and thermoregulation

- 80. Phospholipids. Phosphatidic acids. Phosphatidylethanolamines (cephalins), phosphatidylserines, phosphatidylcholines (lecithines), phosphatidylinositols as structural components of cellular membranes. Notion about composition and the role of surfactant.
 - 81. Sphingolipids and glycolipids, the role in myelinization of nerve fibers.
- 82. Rancidness of fats that is free radical chain process as the model of the peroxidation of polyunsaturated fatty acids in the cell membranes, its mechanism and its biological role. The role of the peroxide lipid oxidation in realization of damage by environment factors. Notion about antioxidant protection systems.

3.5 Low-molecular bioregulators.

- 83. Steroids. Notion about their biological role. Gonan (steran, perhydrocyclopentanophenanthrene), stereochemical structure of 5α , 5β series of steroids. Physical properties of steroids. Hydrocarbons that are parent structures of steroid groups: estrane, androstane, pregnane, cholane, cholestane.
- 84. Steroid hormones. Sex hormones: estrogens, androgens; progestins; adrenocortical hormones. Structure, biological role.
- 85. Bile acids: cholic acid, conjugated bile acids (glycocholic, taurocholic acids), their structure, their biological role.
- 86. Cholesterol as one of sterols, its conformational structure. Its properties, its role in metabolism and structure of cell membranes, in development of cardiac pathology. 7-Dehydrocholesterol, its transformation to vitamin D_3 (cholecalciferol). Ergosterol, its transformation to vitamin D_2 (ergocalciferol). The role of vitamin D in regulation of calcium-phosphorus metabolism.

APPROXIMATE LIST OF EXAMINATION PROBLEMS Carbohydrates.

- 1. Direct oxidation of an aldose affects the aldehyde group first, converting in to a carboxylic acid, and most oxidazing agents that will attack 2° alcohol groups. Cleary, then, a laboratory synthesis of a uronic acid from an aldose requires profecting these groups from oxidation. Keeping this in mind, suggest a method for carrying out a specific oxidation that would convert D-galactose to D-galacturonic acid.
- 2. Write the structure of the aldonic acids and aldaric acids obtained by oxidation of each of the following monosaccharides.

- 3. Write the structure of the products, if any, of the reaction of α -D-galactopyranose with each of the following reagents.
 - (a) CH₃OH/HCl;
 - (b) (CH₃CO)₂O / CH₃COONa;
 - (c) $Cu(OH)_2 / t^0$;
 - (d) Br_2/H_2O .
- 4. Write the structure of the products, if any, of the reaction of mannopyranose with each of the following reagents.
 - (a) CH₃OH/HCl;
 - (b) (CH₃O)₂SO₂/NaOH;
 - (c) Br_2/H_2O ;
 - (d) HNO_3 .
- 5. Write the reaction of the acid-catalyzed hydrolysis of methyl α -D-glucopyranoside and its pentamethyl derivative.
- 6. Write the reaction of the acid-catalyzed and base-catalyzed hydrolysis of esters of β -D-mannopyranose (resulted from reaction of β -D-mannopyranose with acetic anhydride).
- 7. Write the structure of the product of the reactions of β -lactose and β -cellobiose with each of the following reagents:
 - a) HOH/H⁺
 - b) Br₂/HOH
 - c) CH₃COCl/CH₃COO⁻Na⁺
 - d) (CH₃O)₂SO₂/NaOH
- 8. Write the structure of the product of the reaction of α -maltose with each of the following reagents:

- a) HOH/H⁺
- b) Br_2/H_2O
- c) (CH₃CO)₂O/CH₃COO⁻Na⁺
- d) Tollen's reagent/t⁰

Amino acids. Peptides and proteins.

- 9. Write the structure of the predominant form of each of the following amino acids at the pH of blood-7,4.
 - a) Valine; b) Glutamic acid; c) Lysine; d) Glycine.
- 10. Write the structure of the predominant form of each of the following aminoacids at the pH of blood 7,4.
 - a) Lys, b) Gly, c) Met, d) Asp.
- 11. Write the structure of the predominant form of each of following amino acids at the pH of blood 7,4.
 - a) Ser; b) Glu; c) His; d) Gly
 - 12. Write the structure of the product of each of the following reactions:
 - (e) Histidine decarboxylase
 - (f) Write the scheme of the deamination reaction of Glu.
- 13. Write the structure of the predominant form of each of the following aminoacids at the pH of blood 7,4.
 - a) Arg, b) Val, c) Glu, d) Ser.
- 14. Write the structure of the predominant form of lysine in each solution of the following pH:
 - a) pH=0,2; b) pH=5; c) pH=9,8; d) pH=13
- 15. Write the structure of the predominant form of threonine in each solution of the following pH:
 - a) pH=0,2; b) pH=5; c) pH=11.
- 16. Write the structure of the predominant form of aspartic acid in each solution of the following pH:
 - a) pH=0.2; b) pH=3; c) pH=7.4; d) pH=13
- 17. Write the structure of the predominant form of tyrosine in each solution of the following pH:
 - a) pH=0,2; b) pH=5; c) pH=9,5; d) pH=13
- 18. Write the structure of the product of each of the following transamination reactions:
 - a) 2-oxopropanoic acid + Glutamic acid transaminase
 - b) 2-oxobutandioic acid + alanine ----
 - 19. Write the structure of the product of each of the following reactions:
 - (a). 2-oxopropanoic acid + Glutamic acid aminotransferase
 - (b). 2-oxobutandioic acid + methionine aminotransferase

20. Write the structure of tripeptide Ala-Met-Glu and write its structure of the predominant form in each solution of the following pH.

21. Write the sructure of tripeptide Leu-Asn-Glu in solution at:

(a)
$$pH=1$$
; (b) $pH=3$; (c) $pH=11$

22. Write the sructure of tripeptidel Phe-Val-Lys in solution at:

(a)
$$pH=1$$
; (b) $pH=7.4$; (c) $pH=13$.

- 23. Show all steps in the synthesis of Gly-Met-Ser using the benzyloxycarbonyl group as a protecting group.
- 24. Aspartame a widely used nonnutritive sweetener, is the methyl ester of the dipeptide Asp-Phe. Draw the full structure of aspartame. The isoelectric point of aspartame is 5,9. Draw the structure present in aqueous solution at this pH.
- 25. Write the reactions showing how 2,4-dinitrofluorobenzene could be used to identify the N-terminal amino acid of Val-Ala-Gly.
- 26. What products would you expect (after hydrolysis) when Val-Lys-Gly is treated with 2,4-dinitrofluorobenzene?

Nucleic acids.

- 27. The most stable tautomeric form of guanine is the lactam form. This is the form normally present in DNA and it pairs specifically with cytosine. If guanine tautomerazes to the abnormal lactim form, it pairs with thymine. Write structural formulas showing the hydrogen bonds in these base pairs.
- 28. Uridine and 2-deoxyguanosine are stable in dilute base/ In dilute acid, however, they undergo rapid hydrolysis yielding a sugar and heterocyclic base. Write the reaction of nucleosides hydrolysis.
- 29. Write the structure of mRNA portion with following nucleotides sequences:

- 30. Write the structure of the nucleoside formed by combining each of the following pairs of heterocyclic bases and pentoses.
 - a) Guanine and ribose;
- c) Cytosine and ribose;
- b) Thymine and 2-deoxyribose; d) Adenine and 2-deoxyribose.
- 31. Write the structures of 5'-guanilic acid, 5'-uridilic acid. Write the hydrolysis reaction of nucleotides UMP and GMP in dilute acid and dilute base.
- 32. Write the structures of 5'-guanilic acid, 5'-cytidilic acid. Write the hydrolysis reaction of nucleotides CMP and GMP in dilute acid and dilute base.
- 33. Write the structures of 2'-deoxyguanosine-5'-monophosphate, 5'-cytidylic acid. Write the reaction of acid and base-catalyzed hydrolylis of nucleotides d-GMP, CMP.

- 34. Write the structures of 5'-adenylic acid; 2'-deoxythymidine-5'-monophosphate. Write the reaction of acid and base-catalyzed hydrolylis of nucleotides d-TMP, AMP
- 35. Write the structures of 2'-deoxyguanosine-5'-monophosphate, 5'-adenylic acid; 2'-deoxythymidine-5'-monophosphate; 5'-cytidylic acid. Write the reaction of acid and base-catalyzed hydrolylis of nucleotides d-TMP, AMP.
- 36. Write the structure of mRNA portion with following nucleotides sequence: 5'-end U-A-C 3'-end.
- 37. Write the structure of mRNA portion with following nucleotides sequences: 5'-end G-U-A 3'-end.
- 38. Write the structures of 2'-deoxyadenosine-5'-phosphate, 5'-cytidilic acid. Write the hydrolysis reaction of nucleotides in dilute acid and dilute base.
- 39. A portion of one chain of a DNA molecule has the following nucleotides sequence 5'-end A-G-A-C-T-A-T-G-C-A-T 3'-end. Write the sequence of nucleotides with letters in the complementary chain of this portion of the DNA molecule. Draw the structure of the portion of one chain of DNA molecule with following nucleotides sequence: 5'-end A-C-T 3'-end.
- 40. A portion of one chain of a DNA molecule has the following nucleotides sequence 5'-end A-G-G-C-T-A-T-T-C-G-T 3'-end. Write the sequence of nucleotides with letters in the complementary chain of this portion of the DNA molecule. Draw the structure of the portion of one chain of DNA molecule with following nucleotides sequence: 5'-end G-C-T 3'-end.

Lipids. Steroids.

- 42. Write the scheme of acid-catalyzed and base-catalyzed hydrolysis of:
 - a) 1-O-stearoyl-2-O-linoleoyl-3-O-palmitoylglycerol;
 - b) 1-O-myristoyl-2-O-oleyl-3-O-linolenoylglycerol.

Name the products of this reactions.

- 43. Write the scheme of acid-catalyzed and base-catalyzed hydrolysis of:
 - a) 1-O-stearoyl-2-O-linoleoyl-3-O-palmitoylglycerol;
 - b) 1-O-myristoyl-2-O-linolenoy-3-O-oleoylglycerol.

Name the products of these reactions.

- 44. Write the structure of triacylglycerol formed by combining of the following fatty acids with glycerol: palmitic acid, oleic acid, stearic acid. Write the acid-catalyzed hydrolysis for this triacylglycerol.
- 45. Write the structure of triacylglycerol formed by combining of the following fatty acids with glycerol: linolenic acid, palmitic acid, stearic acid. Write the base-catalyzed hydrolysis for this triacylglycerol.
- 46. Write the structure of triacylglycerol formed by combining of the following fatty acids with glycerol: linoleic acid, palmitic acid, linolenic acid. Write the acid-catalyzed hydrolysis for this triacylglycerol.

- 47. Write the structure of triacylglycerol formed by combining of the following fatty acids with glycerol: linoleic acid, stearic acid, linolenic acid. Write the base-catalyzed hydrolysis for this triacylglycerol.
- 48. Write the structure and name triacylglycerol formed by combining of oleic acid, linoleic acid, stearic acid with glycerol. Write the reaction of acid-catalyzed hydrolylis for this triacylglycerol.
- 49. Write the structure of phosphatidyl serine contained stearic acid and linolenic acid and show it's the hydrophilic and hydrophobic portions.
- 50. Write the structure of lecithin (phosphatidyl choline) contained palmitic acid and linoleic acid and show it's the hydrophilic and hydrophobic portions.
- 51. Write the structure of cephalin (phosphatidyl colamine(2-aminoethanol)) contained stearic acid and oleic acid and show it's the hydrophilic and hydrophobic portions.
- 52. Norethynodrel, a synthetic steroid that has been widely used in oral contraceptives, has the systematic name 17α -ethynyl- 17β -hydroxy-5(10)-estren-3-one. Give a three-dimensional formula for norethynodrel. (Ethynyl radical is C=CH).
- 53. The adrenocortical steroids are apparently involved in the regulation of a large number of biological activities including carbohydrate, protein, and lipid metabolism, water and electrolyte balance, and reactions to allergic and infammatory phenomena. Write the structures of adrenocortical hormones:
 - a) Cortisone 17α, 21-dihydroxy-4-pregnene-3,11,20-trione.
 - b) Cortisole 11β, 17α, 21-trihydroxy-4-pregnene-3,20 dione.
- 54. Androsterone, a secondary male sex hormone, has the systematic name 3α -hydroxy- 5α -androstan-17-one. Give a three-dimensional formula for androsterone.

TABLES

The IUPAC system for naming of alkanes

Number of	Structure	Name	Number of	Structure	Name
carbon			carbon atoms		
C_1	CH ₄	Methane	C ₁₇	H ₃ C-(CH ₂) ₁₅ ·CH ₃	Heptadecane
C_2	H ₃ C-CH ₃	Ethane	C_{18}	$H_3C^-(CH_2)_{16}\cdot CH_3$	Octadecane
C ₃	H ₃ C-CH ₂ -CH ₃	Propane	C ₁₉	H ₃ C-(CH ₂) ₁₇ ·CH ₃	Nonadecane
C_4	H ₃ C-(CH ₂) ₂ -CH ₃	Butane	C_{20}	H ₃ C-(CH ₂) ₁₈ ·CH ₃	Eicosane
C_5	H ₃ C ⁻ (CH ₂) ₃ -CH ₃	Pentane	C ₂₁	H ₃ C ⁻ (CH ₂) ₁₉ ·CH ₃	Heneicosane
C_6	H ₃ C-(CH ₂) ₄ -CH ₃	Hexane	C ₂₂	H ₃ C-(CH ₂) ₂₀ -CH ₃	Docosane
C ₇	H ₃ C-(CH ₂) ₅ -CH ₃	Heptane	C ₂₃	H ₃ C-(CH ₂) ₂₁ -CH ₃	Tricosane
C_8	H ₃ C-(CH ₂) ₆ -CH ₃	Octane	C ₃₀	H ₃ C-(CH ₂) ₂₈ ·CH ₃	Triacontane
C ₉	H ₃ C-(CH ₂) ₇ -CH ₃	Nonane	C ₃₁	H ₃ C-(CH ₂) ₂₉ ·CH ₃	Hentriacontane
C ₁₀	H ₃ C-(CH ₂) ₈ -CH ₃	Decane	C ₄₀	H ₃ C-(CH ₂) ₃₈ -CH ₃	Tetracontane
C ₁₁	H ₃ C-(CH ₂) ₉ -CH ₃	Undecane	C ₅₀	H ₃ C-(CH ₂) ₄₈ ·CH ₃	Pentacontane
C ₁₂	H ₃ C ⁻ (CH ₂) ₁₀ -CH ₃	Dodecane	C ₆₀	H ₃ C ⁻ (CH ₂) ₅₈ ·CH ₃	Hexacontane
C ₁₃	H ₃ C ⁻ (CH ₂) ₁₁ -CH ₃	Tridecane	C ₇₀	H ₃ C ⁻ (CH ₂) ₆₈ ·CH ₃	Heptacontane
C ₁₄	H ₃ C-(CH ₂) ₁₂ -CH ₃	Tetradecane	C ₈₀	H ₃ C-(CH ₂) ₇₈ -CH ₃	Octacontane
C ₁₅	H ₃ C ⁻ (CH ₂) ₁₃ -CH ₃	Pentadecane	C ₉₀	H ₃ C ⁻ (CH ₂) ₈₈ -CH ₃	Nonacontane
C ₁₆	H ₃ C-(CH ₂) ₁₄ -CH ₃	Hexadecane	C ₁₀₀	H ₃ C-(CH ₂) ₉₈ ·CH ₃	Hectane

Alkyl groups

Alkane	Alkyl group	Name/Abbreviation
CH ₄ Methane	CH ₃ -	Methyl-/Me-
H ₃ C-CH ₃ Ethane	H ₃ C-CH ₂ -	Ethyl-/Et-
H ₃ C-CH ₂ -CH ₃ Propane	H ₃ C-CH ₂ -CH ₂ - H ₃ C-CH- CH ₃	Propyl-/Pr Isopropyl-/ <i>i</i> -Pr-
H ₃ C-CH ₂ -CH ₃ -CH ₄ Butane	H ₃ C-CH ₂ -CH ₃ -CH ₃ - H ₃ C-CH ₂ -CH- CH ₃	n-Butyl-/n-Bu- secondary-Butyl-/sec- Bu-
CH ₃ H ₃ C-C-CH ₃ CH ₃	H ₃ C—CH-CH ₂ — CH ₃ CH ₃ H ₃ C—C— CH ₃ CH ₃	Isobutyl-/i-Bu- Tertiary-Butyl-/tert-Bu-

Functional groups priority range. (the order of priority of functional groups decreases from top to bottom)

Functional group	Prefix	Suffix
0	Carboxy-	-oic acid
OH OH		-carboxylic acid
Q	Sulfo-	-sulfonic acid
— <u>s</u> _OH		
0		
0	R-oxycarbonyl-	-oate
$-C^{\prime}$ OR		-carboxylate
O	Halocarbonyl-	-oyl halide
—c.	Tuiocuroonyi	-carbonyl halide
Hal		
0_0	Carbomoyl-	-amide
-c		-carboxamide
$N(H,R)_2$		
–C≡N	Cyano-	-nitrile
		-carbonitrile
0	Formyl-	-al
H_C_		-carbaldehyde
0	Охо-	-one
-C_	S No	
-OH	Hydroxy-	-ol
–SH	Mercapto-	-thiol
$-N(H,R)_2$	Amino-	-amin
\ /	Alkenyl-	-ene
C=C	1	
/ -C=C-	A 11 1	
_C=C—	Alkynyl-	-yne

Functional groups work as prefixes

Functional group	Prefix name
-Halogens (-F,-Cl,-Br,-I)	Halo-(fluoro-, chloro-, bro-
	mo-, iodo-)
-OR	Alkoxy-
-SR	Alkylthio-
-NO2	Nitro-
-N=O	Nitroso-

RADICOFUNCTIONAL NOMENCLATURE Functional groups work as suffixes

Functional group	Suffix
ν0	Sulfonic acid
—S <u>~</u> OH	
O O	
-OH	alcohol
-SH	thioalcohol
-NH ₂ / -NH- / —N—	amine
-O-	ether
Hal (-F, -Cl, -Br, -I)	halide
	ketone
—C≡N	cyanide

Electronegativities of some of the elements

			Н			
			2.1			
Li	Be	В	C	N	О	F
1.0	1.5	2.0	2.5	3.0	3.5	4.0
Na	Mg	Al	Si	P	S	Cl
0.9	1.2	1.5	1.8	2.1	2.5	3.0
K						Br
0.8						2.8

Electronic effects of substituents

Substituent	Inductive effect	Resonance effect	Electron-donating or elec-
	(I)	(M)	tron – accepting group
			(ED*, EA**)
- Alk (- R)			
- CH_3 , - C_2H_5 and so on	+ I		ED
- O	+ I	+ M	ED
- NH ₂ (-NHR, - NR ₂)	a) - I	+ M	ED(+M>-I)
	b) - I		EA
- OH (- OR)	a) - I	+ M	ED (+M > -I)
, , ,	b) - I		EA
Halogens:	a) - I	+ M	EA (-I > + M)
- F, - Cl, - Br, - I	b) - I		EA
C = O	a) - I	- M	EA
	b) - I		EA
- COOH	a) - I	- M	EA
- COOH	b) - I		EA
SO II	a) - I	- M	EA
- SO ₃ H	b) - I		EA
NO	a) - I	- M	EA
- NO ₂	b) – I		EA
	•		

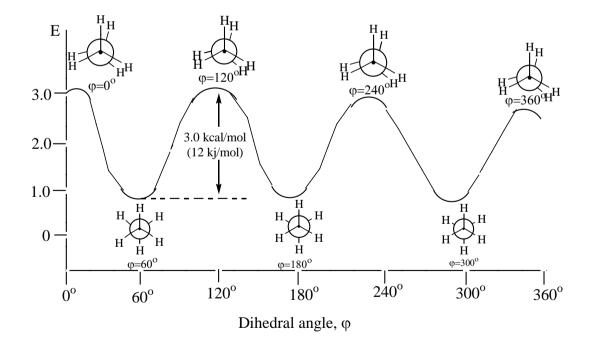
Classification of the reagents

Electrophilic reagents		Nucleophilic	reagents
Positive charged ions	Neutral molecules	Negative charged ions	Neutral molecules
H^{\oplus} , Br^{\oplus} , $-C^{\oplus}$ O H^{\oplus} , Br^{\oplus} , $-C^{\oplus}$ O H^{\oplus} , Br^{\oplus} , $-C^{\oplus}$ O	$ \begin{array}{c} \delta^{+} \\ -C \longrightarrow X \\ \delta = S \\ O \end{array} $	⊖ ⊝ ⊝ ⊝ H, Br, HO, RO ⊝ ⊝ HS, RS	H ₂ O, ROH, RSH, NH ₃ , RNH ₂

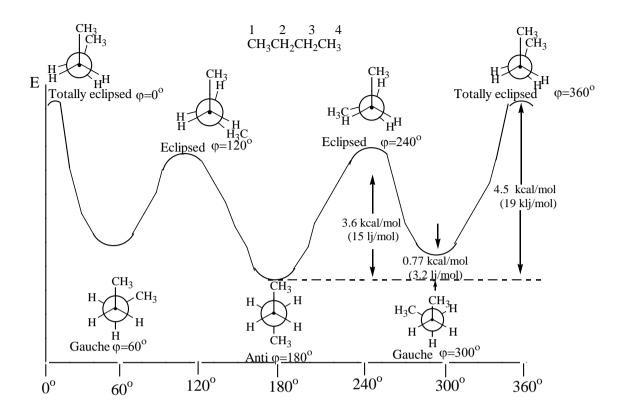
Classification of substituents according to the orientation characteristics

	Meta-or	rientants		
Activating s	Activating substituents Deactivating substituents			
(electron-dona	ating groups)	(electron-acception groups)	uents	
			(electron-acception	
	,		gro	ups)
+ I	+ M > - I	- I > + M		
- Alk	- NH ₂	- F	-C = N	$-NO_2$
$(-CH_3, -C_2H_5)$	- NHR	- C1	-COOH	⊕ ² -NH3
and so on)	- NR ₂	- Br	-COOR	-NR ₃
	- NHCOR - OH	- I	C#7	-SO ₃ H
	- 011		-C\H	2 3 3 2 2
	- OR		-C(1)	

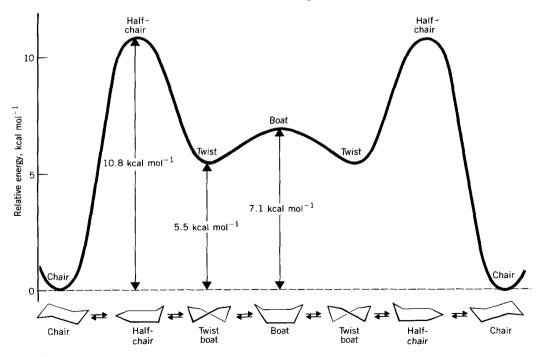
Conformations of ethane



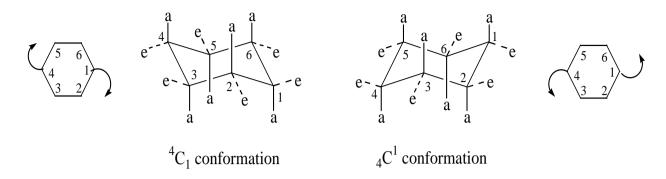
Conformations of butane



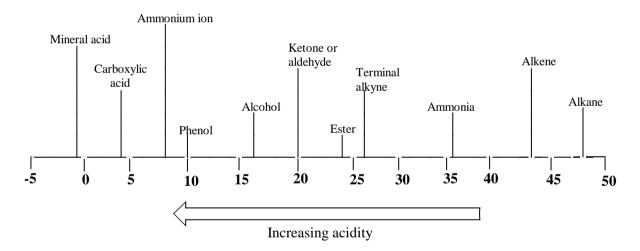
Conformations of cyclohexane



Chair conformations of cyclohexane



A graphical representation of pKa values for some of important categories of Bronsted-Lowry acids



Relative strength of acids and their conjugate bases

	ACID	APPROXIMATE pK_a	CONJUGATE BASE	_
Strongest Acid	HSbF ₆	>-12	SbF ₆ ⁻	Weakest Base
	HI	-10	I-	
	H_2SO_4	-9	HSO ₄ ⁻	
	HBr	-9	Br	
	HCI	-7	CI-	
$\langle \rangle$	$C_6H_5SO_3H$	-6.5	$C_6H_5SO_3^-$	
	H_3O^+	-1.74	H_2O	
	HNO ₃	-1.4	NO_3^-	
	CF ₃ CO ₂ H	0.18	CF ₃ CO ₂ ⁻	<u>=</u>
ngth	HF	3.2	F-	increasing base strength
Increasing acid strength	CH ₃ CO ₂ H	4.76	CH ₃ CO ₂ ⁻	ng ba
g acic	NH_4^+	9.2	NH_3	se str
reasin	C ₆ H ₅ OH	9.9	$C_6H_5O^-$	ength
2	CH ₃ NH ₃ ⁺	10.6	CH_3NH_2	
	H_2O	15.74	OH-	
	CH₃CH₂OH	16	CH ₃ CH ₂ O ⁻	
	(CH ₃) ₃ COH	18	(CH ₃) ₃ CO ⁻	7
	НС≡СН	25	HC≡C ⁻	*
	\mathbf{H}_{2}	35	H-	
	NH_3	38	$\mathrm{NH_2}^-$	
	$CH_2 = CH_2$	44	$CH_2 = CH^-$	
Weakest Acid	CH ₃ CH ₃	50	$\mathrm{CH_{3}CH_{2}^{-}}$	Strongest Base

Tautomerism of organic compounds

Tautomerism	Tautomerism equilibrium	Example
Keto-enol tau- tomerism	$C - C' = C'$ $H^{\delta^{+}} O^{\delta^{-}} OH$	$\begin{array}{ccc} \text{CH}_3\text{-C-CH}_2\text{-C-OC}_2\text{H}_5 &\longrightarrow\\ \text{O} & \text{O}\\ \text{CH}_3\text{-C=CH-C-OC}_2\text{H}_5\\ \text{OH} & \text{O} \end{array}$
Lactam-lactim tautomerism	$- N - C \longrightarrow - N = C$ H^{δ^+}	$\begin{array}{c c} NH_2 & NH_2 \\ \hline N & N \\ N & OH \\ H & \\ \end{array}$
Cyclo-oxo tau- tomerism	Aldoses CO H (CHOH) _n (CHOH) _n CH ₂ CH ₂ OH CHOH) _n CH ₂ OH CHOH) _n OH CHOH) _n OH CH ₂ OH CHOH) _n OH CH ₂ OH CHOH) _n OH CH ₂ OH CH CH ₂ OH CH	D-glucose Fischer pyranose proiection CH2OH formula HO H OH OH H OH OH OH OH OH OH OH OH OH
	Ketoses $ \begin{array}{ccc} CH_2OH & CH_2OH \\ C = O & CH_2OH \\ (CHOH)_n & (CHOH)_n O \\ CH_2OH & CH_2 \end{array} $	Prischer projection Furanose formula HOH ₂ C CH ₂ OH HOH _α C OH OH HOH _α C OH OH OH GHO OH G

Nomenclature of di- and polysaccharides

Name	IUPAC name
Sucrose	α-D-glucopyranosyl-1,2 β-D-fructofuranoside
Maltose	4-O-(α-D-glucopyranosyl)-α, β-D-glucopyranose
Cellobiose	4-O-(β-D-glucopyranosyl)-α, β-D- glucopyranose
Lactose	4-O-(β-D-galactopyranosyl)-α, β-D- glucopyranose
Starch	Consist of amylose and amylopectin
a) amylose	(α-D-glucopyranosyl-1,4) _n -α, β-D- glucopyranose
b) amylopectin	$(\alpha$ -D-glucopyranosyl-1,4) _n - α , β -D-glucopyranose with
	branching α , $1\rightarrow 6$
Glycogen	$(α - D-glucopyranosyl-1,4)_n-α, β-D-glucopyranose$
	with branching α , $1\rightarrow 6$
Cellulose	(β-D-glucopyranosyl-1,4) _n - α , β-D- glucopyranose
Chondroitin-4-sulfate	[D-glucuronic acid –β-1,3-N-acetyl-D-galactosamine-
	4-sulfate] _n
Heparin	[D-glucuronic acid –2-sulfate-β-1,4-N-sulfo-D-
	glucosamine-6-sulfate] _n
Hyaluronic acid	[D-glucuronic acid –β-1,3-N-acetyl-D-glucosamine] _n -
	[β-1,4-D-glucuronic acid-β-1,3-N-acetyl-D-
	glucosamine] _m

Structures of amino acids

No	Name	Structure	Abbreviation	IUPAC name	pI
		1. Non po	lar amino acids		
1.	Glycine	O 	Gly	2-aminoethanoic acid	5,97
2.	Alanine	О H ₂ N—СН-С—ОН СН ₃	Ala	2-aminopropanoic acid	6,02
3.	Valine*	O 	Val	2-amino-3- methylbutanoic ac- id	5,97

4.	Leucine*	$\begin{array}{c} \text{O} \\ \text{II} \\ \text{H}_2 \text{NCH-COH} \\ \text{CH}_2 \\ \text{CH-CH}_3 \\ \text{CH}_3 \end{array}$	Leu	2-amino-4- methylpentanoic acid	5,98
5.	Isoleucine*	O 	Ile	2-amino-3- methylpentanoic acid	6,02
6.	Phenylalanine*	H ₂ N—CH-C—OH	Phe	2-amino-3- phenylpropanoic acid	5,98
7.	Tryptophan*	О H ₂ N—СН-С—ОН H ₂ С	Trp	2-amino-3(indolyl-3)-propanoic acid	5,88
8.	Methionine*	O 	Met	2-amino-3- methyltiobutanoic	5,75
9.	Proline	C=O N OH	Pro	Pyrrolidin-2- carboxylic acid	6,10
		2. Pola	r amino acids		
1.	Serine	O 	Ser	2-amino3- hydroxypropanoic acid	5,68
2.	Threonine*	O 	Thr	2-amino-3- hydroxybutanoic acid	6,58
3.	Cysteine	O 	Cys	2-amino-3- mercaptopropanoic acid	5,02

4.	Tyrosine	H ₂ N—CH-C—OH CH ₂ OH	Tyr	2-amino-3(4- hydroxyphenyl)- propanoic acid	5,65
5.	Asparagine	$\begin{array}{c} & \text{O} \\ \parallel \\ \text{H}_2\text{NCH-COH} \\ \downarrow \\ \text{CH}_2 \\ \downarrow \\ \text{C=-O} \\ \downarrow \\ \text{NH}_2 \end{array}$	Asn	2-amino-3- carbamoylpropano- ic acid	5,41
6.	Glutamine	$\begin{array}{c} & \text{O} \\ \\ \text{H}_2\text{NCH-COH} \\ & \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{C=-O} \\ \\ \text{NH}_2 \end{array}$	Gln	2-amino-4- carbamoylbutanoic acid	5,65
		3. Negative cl	harged amino a		
1.	Aspartic acid	O 	Asp	2-aminobutandioic acid	2,97
2.	Glutamic acid	O 	Glu	2- aminopentandioic acid	3,22
		4. Positive ch	arged amino a	cids	
1.	Histidine	H ₂ N—CH-C—OH N—CH ₂	His	2-amino-3- (imidozolyl-5)- propanoic acid	7,58
2.	Lysine*	О 	Lys	2,6- diaminohexanoic acid	9,74
3.	Arginine	O 	Arg	2-amino-5- guanidinopentanoic acid	10,7

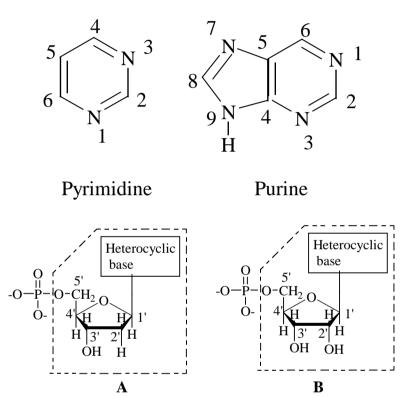
^{* -} essential amino acids.

pK_a values for the 20 common amino acids

α-Amino Acid	$\begin{array}{c} p(K_a)_1 \\ (\alpha\text{-COOH} \\ Group) \end{array}$	$p(K_a)_2 (\alpha-NH_3^+ Croup)$	pK _{aR} (Side Chain Group)	pI
Alanine	2.3	9.9	-	6.0
Arginine	1.8	9.0	12.5	10.8
Asparagine	2.1	8.8	-	5.4
Aspartic acid	2.0	9.9	3.9	3.0
Cysteine	1.9	10.8	8.3	5.0
Glutamic acid	2.1	9.5	4.1	3.2
Glutamine	2.2	9.1	-	5.7
Glycine	2.3	9.8	-	6.0
Histidine	1.8	9.3	6.0	7.6
Isoleucine	2.3	9.8	-	6.1
Leucine	2.3	9.7	-	6.0
Lysine	2.2	9.2	10.8	9.8
Methionine	2.1	9.3	-	5.8
Phenylalanine	2.2	9.2	-	5.5
Proline	3.0	10.6	-	6.3
Serine	2.2	9.2	-	5.7
Threonine	2.1	9.1	-	5.6
Tryptophan	2.4	9.4	-	5.9
Tyrosine	2.2	9.1	10.1	5.7
Valine	2.3	9.7	-	6.0

Nomenclature of nucleic bases

Name	IUPAC name
Adenine	6-aminopurine
Guanine	2-amino-6-hydroxypurine
Cytosine	4-amino-2-hydroxypyrimidine
Thymine	2,4-dihydroxy-5-methylpyrimidine
Uracil	2,4-dihydroxypyrimidine



The general structure of a nucleotide found in DNA and RNA.

Nomenclature of fatty acids

Name	Condense formula	IUPAC name
Myristic acid	$(C_{14}); C_{13}H_{27}COOH$	Tetradecanoic acid
Palmitic acid	$(C_{16}); C_{15}H_{31}COOH$	Hexadecanoic acid
Stearic acid	$(C_{18}), C_{17}H_{35}COOH$	Octadecanoic acid
Palmitooleic acid	$(C_{16}); (\Delta 9); C_{15}H_{29}COOH$	Cis – 9-hexadecenoic acid
Oleic acid	$(C_{18}); (\Delta 9); C_{17}H_{33}COOH$	Cis -9-octadecenoic acid
Linoleic acid	$(C_{18}); (\Delta 9,12); C_{17}H_{31}COOH$	Cis,cis-9,12-
		octadecadienoic acid
Linolenic acid	$(C_{18}); (\Delta 9, 12, 15);$	Cis, cis, cis-9,12,15-
	$C_{17}H_{29}COOH$	octadecatrienoic acid

Nomenclature of steroids Names of steroid hydrocarbons

R	NAME
—Н	Androstane
—H (with —H also replacing	Estrane
-CH ₃)	
-CH ₂ CH ₃	Pregnane
-CHCH ₂ CH ₂ CH ₃	Cholane
ČH ₃	
-CHCH ₂ CH ₂ CH ₂ CH ₂ CHCH ₃	Cholestane
CH ₃ CH ₃	

Nomenclature of steroids

Family of ster-	Name	IUPAC name	
oids			
Estrogens	Estrone	3-hydroxy-1,3,5(10)-estratrien –17-one	
	Estradiol	1,3,5(10)-estratriene-3,17β-diol	
Androgens	Androsterone	3-α-hydroxy-5α-androstan-17-one	
	Testosterone	17β- hydroxy-4-androsten-3-one	
Progestin	Progesterone	4-pregnene-3,20-dione	
Adrenocortical	Cortisone	17α,21-dihydroxy-4-pregnene-3,11,20-	
hormones		trione	
	Cortisol	17α, 11β, 21-trihydroxy-4-pregnen-3,20-	
		dion	
Bile acid	Cholic acid	3α,7α,12α-trihydroxy-5β-cholan-24-oic ac-	
		id	
Sterols	Cholesterol	5-cholesten-3β-ol	
	Ergosterol	24-methyl-5,7,22-cholestatrien-3β-ol	

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