## МИНИСТЕРСТВО ЗДРАВООХРАНЕНИЯ РЕСПУБЛИКИ БЕЛАРУСЬ БЕЛОРУССКИЙ ГОСУДАРСТВЕННЫЙ МЕДИЦИНСКИЙ УНИВЕРСИТЕТ КАФЕДРА БИООРГАНИЧЕСКОЙ ХИМИИ

О. Н. РИНЕЙСКАЯ, Е. М. ЕРМОЛЕНКО, С. В. ГЛИННИК

# БИООРГАНИЧЕСКАЯ ХИМИЯ BIOORGANIC CHEMISTRY

Практикум для студентов-стоматологов

3-е издание, исправленное



Минск БГМУ 2022

УДК 577.1(076.5)(075.8)-054.6 ББК 28.072я73 Р51

Рекомендовано Научно-методическим советом университета в качестве практикума 20.04.2022 г., протокол № 4

Рецензенты: канд. биол. наук, доц. В. В. Хрусталёв; канд. мед. наук, доц. В. Э. Бутвиловский

#### Ринейская, О. Н.

Р51 Биоорганическая химия = Bioorganic chemistry : практикум для студентов-стоматологов / О. Н. Ринейская, Е. М. Ермоленко, С. В. Глинник. – 3-е изд., испр. – Минск : БГМУ, 2022. – 108 с.

ISBN 978-985-21-1046-4.

Содержит методические рекомендации для подготовки к лабораторным занятиям по биоорганической химии на английском языке. К каждой теме даны цель занятия, вопросы для обсуждения, письменные задания, а также указана литература для подготовки. Приведены описания и протоколы лабораторных опытов. Первое издание вышло в 2019 году.

Предназначен для студентов 1-го курса медицинского факультета иностранных учащихся, обучающихся на английском языке по специальности «Стоматология».

УДК 577.1(076.5)(075.8)-054.6 ББК 28.072я73

ISBN 978-985-21-1046-4

<sup>©</sup> Ринейская О. Н., Ермоленко Е. М., Глинник С. В., 2022

<sup>©</sup> УО «Белорусский государственный медицинский университет», 2022

#### **REGISTRATION FORM**

Student name\_\_\_\_

№	Theme	Date	Mark	Signature of teacher
1.	Classification and nomenclature of organic compounds			
2.	Chemical bond structure and atom effects in the organic molecules			
3.	Stereoisomerism, its role for biological activity demonstration			
4.	Hydrocarbons			
5.	Monofunctional hydrocarbon derivatives			
6.	Biologically important reactions of aldehydes and ketones			
7.	Carboxylic acids and their derivatives.  Concluding test «Theoretical fundamentals of basic classes of organic compound structure and reactivity»			
8.	Poly-and heterofunctional compounds			
9.	Organic compounds using in dentistry			
10.	Carbohydrates. Monosaccharides			
11.	Oligo- and polysaccharides			
12.	Structure and reactivity of amino acids			
13.	Peptides. The levels of protein organization			
14.	Nucleosides. Nucleic acids			
15.	Lipids. Structure, properties. Lipid peroxidation			
16.	Steroids			
17.	Concluding test «Biopolymers and their structural components»			
18.	CONCLUDING SESSION			

#### LABORATORY SAFETY RULES

- 1. Dress appropriately for the lab. Wear white lab coat. Tie back long hair.
- 2. Know what safety equipment is available and how to use it. This includes eyewash place, fire blanket, fire extinguisher and sand.
- 3. Know the dangers of the chemicals in use, and read labels carefully. Do not taste or sniff chemicals.
- 4. Dispose of chemicals according to instruction. Use designated disposal sites, and follow the rules. Never return unneeded chemicals to the original containers.
- 5. Always add acids and bases to water slowly to avoid splattering. This is especially important when using strong acids and bases that can generate significant heat, form steam, and splash out of the container.
- 6. Never point test tubes at yourself or others. Be aware of reactions that are occurring so that you can remove them from the heat if necessary.
  - 7. Do not eat or drink in the lab! It is too easy to take in some dangerous substance accidentally.
- 8. Follow all directions. Never occasionally mix chemicals. Pay attention to the order in which chemicals are to be added to each other, and do not deviate!
- 9. After the end of the experiment each student should submit an account of the work that have been done, then to wash up chemical crockery, clean a workplace and ask the student on duty to check it.

#### Responsibilities of the student on duty:

- to get all the necessary equipment from the laboratory assistant;
- to keep an order the laboratory room;
- student on duty should leave the laboratory the last, after receiving permition from the lab assistant.

I agree		20	year	
C	(date)		•	(signature)

#### **PRECAUTIONS**

#### Work with alcohol lamps

Careless work with an alcohol lamp can result in a fire, that is why it is necessary to follow the below requirements:

- the wick of an alcohol lamp should tightly enter the aperture of a metal bush; the topping should be put forward for 1 cm and fluffed up;
- the bush should close the aperture of a alcohol lamp tightly; the alcohol lamp should be filled with alcohol no more than 2/3 of the volume;
- the lighting of an alcohol lamp should be carried only by matches, it is strictly forbidden to light an alcohol lamp from another alcohol lamp, because the bush can stoop and coming out steams of alcohol can be fired;
  - to blow out an alcohol lamp only by covering it with bell-glass;
- when heating up substances in chemical glassware it is necessary to heat them at the top or mid-range flame, not touching a wick, because a wick is always cool, and when hot glass contacts with it, glass may burst.

#### Work with chemical glassware

Heating substances in glassware should be performed gradually, slightly rotating it and cautiously shaking from time to time. When heating a test tube with a liquid on the open fire, splasing of a liquid is possible. Because of this fact, the aperture of a test tube should be directed aside from you and from your neighbours. Especially it is necessary to avoid injuring the eyes with hot splashes, that it is why it is forbidden to bend forward to the test tube and look inside. When heating the test tube, it should be kept at the angle of inclined position (45°), so that splashes will hit walls of a glassware and will not be thrown outside. If the liquid starts to rise in an exhaust tube, it is necessary to let down a test tube immediately, so that the fluid level in it will become lower than the end of an exhaust tube.

#### Work with inflammable liquids (IL)

IL (diethyl ether, alcohol, toluene, acetone, acetoacetic ether) are kept always in a fume hood. Experiments with these substances are carried out under draught, far from open fire and the turned on small stoves. If an ignition of the IL happened in a vessel, it is necessary to cover it quickly with a fire-prevention blanket. If the burning liquid has been spilt, it must be extinguished by sand. If the clothes begin to fire, it is necessary to wrap up quickly and densely in a fire-prevention blanket.

#### Work with acids and alkalis

Concentrated solutions of nitric, sulfuric, hydrochloric acids, nitrosulfuric acid are kept in a fume hood. All experiments with concentrated acids and alkalis are carried out only in the fume hood. It is necessary to cover carelessly spilt on the floor acids and alkalis by sand and after that to clean up.

#### **Work with toxicants**

Toxic organic substances — aniline, methyl amine, toluene, picric acid are kept in a fume hood. It is necessary to be cautious with these substances, not to inhale their steams, to avoid injuring the hands as they can penetrate through the skin. In case of emergency when these substances got on hands, it is necessary to wash up quickly the hands with warm water and soap. If inhaled the steams — immediately to go out in the fresh air.

#### First-aid treatment in case of accidents:

- in case of hands are cut with glass first of all it is necessary to remove all the splinters out of the wound, then to treat the wound with an alcohol solution of iodine and to put a bandage;
- in case of thermal burns happen it is necessary to treat the burnt place with the 70 % solution of ethanol;
- in case of burns are caused by solutions of acids or alkalis it is necessary to wash up the burnt site with water quickly and to put an aseptic bandage;
- in case of acids or alkalis hit the eyes it is necessary wash them with water carefully and to refer the victim to the outpatient clinic;
- in case of skin burns caused by bromine it is necessary quickly to wash the injured place off with ethanol and to put anti-burn emulsion;
- in case of burns caused by hot organic liquids it is necessary to wash out the injured place with ethanol;
- in case of burns caused by liquid phenol it is necessary to massage the emerged sites of white skin with a glycerin until normal skin color is restored then to wash with water and to put the gauze bandage moistened with a glycerin solution;
- after providing the first-aid treatment it necessary to address to the health center of the university or to the outpatient clinic.

#### 

**Objective:** to study composition unity, configuration and conformation concept for organic molecules.

#### **Recommended literature:**

- 1. Ryneiskaya, O.N. Bioorganic chemistry / O.N. Ryneiskaya [et al.]. 2020. P. 6-13.
- 2. Ryneiskaya, O.N. Bioorganic chemistry/ O.N. Ryneiskaya [et al.]. 2018. P. 6-13.
- 3. Zurabyan, S. E. Fundamentals of Bioorganic Chemistry / S. E. Zurabyan. 2012. P. 27–39.

#### **Problems for discussion:**

- 1. Introduction into bioorganic chemistry: the definition of subject, objects learned by bioorganic chemistry.
- 2. Classification of organic compounds: a) according to the carbon chain structure; b) according to the functional groups.
- 3. Nomenclature of organic compounds: a) trivial (or common) nomenclature; b) systematic nomenclature IUPAC.

#### **Exercises**

1. Write the formulas of the following compounds:

methane	ethane		propane	butane
ethene	propene		but-1-ene	but-2-ene
ethanol	2-methylprop	ene	propan-2-ol	butan-2-ol
pentan-1-ol		propano	one	ethanethiol
methanoic acid		propano	ic acid	benzene
phenol		benzoic	acid	toluene

ethanedioic acid	butanedioic ac	cid	butenedioic acid
2-aminopropanoic acid		2-oxopentanedioic ac	eid

2. Give the IUPAC names for the following compounds:

H <sub>3</sub> C C O	H <sub>3</sub> C CH <sub>2</sub> C O	H <sub>2</sub> C C C O	OH   
HOOC CH <sub>2</sub> COOH	СООН	H <sub>2</sub> N COOH	H <sub>2</sub> N—CH-COOH   CH <sub>2</sub>   SH

#### TEST CONTROL (ANSWERS TO TEST ON 106 P.)

1. Give the name for the heterocycle:

N N N

1) pyrrole;

2) purine;

3) pyridine;

4) pyrimidine.

2. Give the IUPAC name for the following compound

- 1)  $\alpha$ -ketopropionoic acid;
- 3) pyruvic acid;
- 2) 2-oxopropanoic acid;
- 4) oxaloacetic acid.

 $H_3C$  COOH

3. Choose the IUPAC name of the amino acid (threonine)

- 1) 2-hydroxypentanoic acid;
- 3) 2-amino-3-aminopropanoic acid;
- 2) 2-aminobutanoic acid;
- 4) 2-amino-3-hydroxybutanoic acid.

CH-COOF | | CH-OH | | CH<sub>3</sub>

4. Choose the IUPAC name of the deoxyribose

- 1) 1,3,4,5,6-pentahydroxyhexanone-2;
- 2) 2,3,4,5,6-pentahydroxyhexanal;
- 3) 2,3,4,5-tetrahydroxypentanal;
- 4) 3,4,5-trihydroxypentanal.

H CO I CH<sub>2</sub> I CHOH I CHOH

ĊH<sub>2</sub>OH

5. Choose the IUPAC name of the following compound 1) 2-amino-3-imidazolylpropanoic acid; 2) 2-amino-3-indolylpropanoic acid; 3) 2-amino-4-imidazolylpropanoic acid; 4) 2-hydroxy-3-imidazolylpropanoic acid
6. Select the structural formula of the 1-methoxypropanol:
H <sub>3</sub> C CH <sub>2</sub> OH CH <sub>2</sub> OCH <sub>3</sub> H <sub>3</sub> C OCH <sub>3</sub> H <sub>3</sub> C OCH <sub>3</sub> OCH <sub>5</sub>
7. Choose the name of the following compound: 1) propanoic acid; 2) propanal; 3) butanal; 4) butanoic acid.  O  H <sub>3</sub> C  CH <sub>2</sub> CH <sub>2</sub> H
8. Select the IUPAC name of the following compound:  1) acetone; 2) propanone; 3) propanoic acid. 0 II C CH <sub>3</sub>
9. Select unsaturated compound(s): 1) but-2-ene; 2) ethane; 3) cyclohexene; 4) benzene.
10. Select the trivial name of the compound:  1) 2-hydroxypropanoic acid; 2) alanine;  3) lactic acid; 4) malic acid.
PRACTICAL PART
1. Antioxidant activity of ascorbic acid.  Take the two test tubes. In both tubes, place 2 drops of ethanol* <sup>1</sup> . To one of them add a few crystals of ascorbic acid* with a glass spatula. Then add 1 drop of KMnO <sub>4</sub> solution (14) and 2 drops of H <sub>2</sub> SO <sub>4</sub> solution (23) to each tube, and shake. Heat each tube to the boil and discoloration of the solution. Note the appearance of apples smell in one of the test tubes.  Observed changes:

<sup>1</sup> Notice: reagents marked with (\*) are in the fume hood.

Write a scheme of the reaction:

Conclusion:

Signature of teacher:

## LABWORK № 2 CHEMICAL BOND STRUCTURE AND ELECTRONIC EFFECTS IN THE ORGANIC MOLECULES

**Objective**: to develop knowledge about chemical bond structure, dimensional and electronic effects of substituents.

#### **Recommended literature:**

- 1. Ryneiskaya, O.N. Bioorganic chemistry / O.N. Ryneiskaya [et al.]. 2020. P. 14-35.
- 2. Ryneiskaya, O.N. Bioorganic chemistry / O.N. Ryneiskaya [et al.]. 2018. P. 14-35.
- 3. Zurabyan, S. E. Fundamentals of Bioorganic Chemistry / S. E. Zurabyan. 2012. P. 13–25, 40–49.

#### **Problems for discussion:**

- 1. An electronic and dimensional structure of sp<sup>2</sup>-hybridized carbon atom.
- 2. Conjugated systems. Conjugation energy.
- 3. Cyclic conjugated systems. Aromaticity. Huckel's rule. Aromaticity of benzoic and non-benzoic systems.
  - 4. Aromaticity of heterocyclic systems (pyrrole, pyridine).
  - 5. Inductive effect. Mesomeric effect.
  - 6. Electron donating and electron withdrawing substituents.

#### **Exercises:**

but-1,3-diene

Write the formulas of the following compounds. Indicate compounds with conjugated system.

hex-2,4-diene

pent-1,4-diene	but-2-ene
2. Determine the type of conjugated system:	
2-methylbut-1,3-diene	propanoic acid
2 methylout 1,5 diene	propuliore dela
propenal	pyrrole
propenoic acid	pyridine

3. Define aromaticity by the means of Huckel's rule for the compounds:

benzene	pyridine
pyrrole	imidazole
pyrimidine	purine

4. Electronic effects — ...

Show the electron density distribution in the molecules with inductive and mesomeric effects:

1-chlorobutane	propanal
benzaldehyde	propenal
ethanol	phenol

#### TEST CONTROL

1. Indicate formulas of compounds with conjugated double bonds:

- 1) ethene; 3) cycloheptatrienyl cation;
- 2) pent-1,3-diene; 4) propenoic acid.
- 2. Indicate formulas of compounds with conjugated p- $\pi$  double bonds:





$$H_2C$$
 $CH$ 
 $C$ 
 $H$ 

3. Compounds (1) benzene;	with conjugated (2) naphthalene;		s are following: entadienyl anion;	4) vinylamine.
2) nitrogen give	es in the conjud	lated system 2		in the sp <sup>2</sup> -hybridization; efficient aromatic system; e aromatic system.
<b>5. What electro</b> 1) +I, -M;	nic effect(s) does 2) –I;	<b>hydroxyl group</b> 3) –I, +M;	possess in propanol: 4) –I, –M.	
<b>6. Which substi</b> 1) – COOH;	tutions possess e	lectron donor pr 3) – OH;	operties towards ber 4) –NHCH <sub>3</sub> .	nzene:
7. What electron 1) +I, -M;	nic effect(s) does 2) –I;	hydroxyl group 3) –I, +M;	possess in phenol: $4) - I, -M.$	
8. How many el 1) 14;	lectrons are in cy 2) 8;	clic conjugated s 3) 12;	system of quinoline: 4) 10.	
9. Which of the	following compo	ounds are aroma	tic:	
1)	2)	3) H C H	4)	
<ul><li>A) benzyl alcoho</li><li>B) phenol;</li><li>C) ethanol;</li><li>D) chlorobenzen</li></ul>	2) –l 3) –l	[, -M; [ < +M; [; [ > +M.		
		PRACTICA	L PART	
	ube, place 1 drop rated solution of b	romine water*. No	ote the appearance of t	of ammonia solution* and the characteristic staining.
Observed chang	ges			
ОН -	$NH_3, Br_2 \rightarrow HO$	$N = \sqrt{\frac{1}{2}}$	0	
		indophenol		
Conclusion:				
Signature of tead	cher:			

## LABWORK ightharpoonup 3 STEREOISOMERISM, ITS ROLE FOR BIOLOGICAL ACTIVITY DEMONSTRATION

**Objective:** to study the dimensional organization and discuss a stereoisomerism role for interaction specificity on a molecular scale understanding

#### **Recommended literature:**

- 1. Ryneiskaya, O.N. Bioorganic chemistry / O.N. Ryneiskaya [et al.]. 2020. P. 26-40.
- 2. Ryneiskaya, O.N. Bioorganic chemistry / O.N. Ryneiskaya [et al.]. 2018. P. 26-40.
- 3. Zurabyan, S. E. Fundamentals of Bioorganic Chemistry / S. E. Zurabyan. 2012. P. 76–81, 149–161.

#### **Problems for discussion:**

- 1. Stereoisomerism. Classification of stereoisomers.
- 2. A spatial structure of a sp<sup>3</sup>-hybridized carbon atom. Configuration. Stereochemical formulas. Molecular models.
  - 3. Ethane configuration and conformations, torsion strain. Newman projections.
  - 4. Buthane conformations. Van der Waals strain. Long-chain compound conformations.
- 5. Carbocyclic compound conformations, angle strain. Cyclohexane conformations. A cyclohexane ring in the biologically important compounds.
- 6. Chiral and achiral molecules. Chiral centers. Optical activity is the property inherent chiral molecules.
  - 7. Fischer's projective formulas. Enantiomers.
- 8. Relative D-,L-nomenclature of stereoisomers. Glyceraldehyde as the configuration standard. R, S-system of a configuration designation.
  - 9. Racemic mixtures. Methods of racemic substance division.
  - 10. Diastereoisomerism. Stereoisomers of tartaric acid.
  - 11. Cys-, trans-isomerism. Stereoisomers of butenedioic and oleic acids.

#### **Exercises**

- 1. Write all possible conformations by means of Newman projections for the following compounds.
  - a) ethane

- b) butane
- 2. Write the structural formulas for the following Newman projections:



3. I	Draw the possible chair c	conformations of	the cyclohexanol.	
4. I	Draw the preferred confo	ormation of the 2-	methylcyclohexanol.	
diastereor		for the following	g compounds. Indicate	e pairs of enantiomers and
b) 2	2-hydroxybutanedioic ac	id		
c) 2	2-amino-3-hydroxybutan	oic acid (2 chiral	centers)	
6. V	Write R- and S-isomers f	or the 2-hydroxy	propanoic acid.	
		Test co	NTROL	
_	sive interaction between er Waals strain; 2) ar	n electron clouds	in the C-H bond is ca 3) Baeyer strain;	alled: 4) torsion strain.
2. Indica	te compounds with chir nydroxybutanedioic acid;	al centers:	obutanoic acid;	i, corsion strain.

## 3. Various spatial arrangement of the atoms in molecular that differ only after rotation about C-C single bonds are:

1) enantiomers;

2) configuration;

3) diastereomers;

4) conformation.

#### 4. Less stable butane conformation —is:

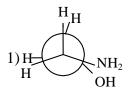
1) stagged;

2) eclipsed;

3) skew;

4) zigzag.

#### 5. Select conformations with the maximal Van der Waals strain:



#### 6. Less stable 1,3-dimethylcyclohexane conformation is:

## 3) CH<sub>3</sub> CH<sub>3</sub> 4)

#### 7. Select compounds with 2 chiral centrals:

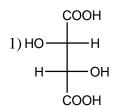
1) 2-amino-3-methylpentanoic acid;

3) 2-amino-3-methylbutanoic acid;

2) 2,3-dihydroxybutandioc acid;

4) 2-hydroxyethanoic acid.

#### 8. Select L-stereoisomers:



#### 9. Select names for the corresponded structures:

OH CI CI OH OH CH3 
$$H_3C$$
 COOH  $H_3C$  COO

1) R-2-chloropropanoic acid

3) S-2-hydroxypropanal

2) R-2-hydroxypropanal

4) S-2-chloropropanoic acid

#### 10. Diastereoisomers — are:

- 1) pairs of stereoisomers which concern to each other as a subject and its display in an ideal plane mirror, possess in achiral surrounding identical chemical and physical properties, except for a sign on optical rotation;
- 2) pairs of stereoisomers of the same substance not being a mirror image of one another and possessing various chemical and physical properties;
- 3) pairs of stereoisomers of the same substance not being a mirror image of one another and possessing the same chemical and physical properties;
- 4) pairs of stereoisomers which consist in migration of some groups within a molecule and is an accompanied by redistribution of electron density.

Signature of teacher:

#### LABWORK Nº 4 **HYDROCARBONS**

**Objective:** to develop knowledge about classification and mechanisms of organic reactions; to develop skills of carrying out of qualitative tests for double bond detection in organic compounds.

#### **Recommended literature:**

- 1. Ryneiskaya, O.N. Bioorganic chemistry / O.N. Ryneiskaya [et al.]. 2020. P. 46-52.
- 2. Ryneiskaya, O.N. Bioorganic chemistry / O.N. Ryneiskaya [et al.]. 2018. P. 46-52.
- 3. Zurabyan, S. E. Fundamentals of Bioorganic Chemistry / S. E. Zurabyan. 2012. P. 52–57, 75, 82–96.

#### **Problems for discussion:**

- 1. Organic reaction mechanism definition. Homolytic and heterolytic mechanisms of bond cleavage. Classification of reagents in organic reactions
  - 2. Organic reactions classification according to the direction and result of reaction.
  - 3. Reactions of radical substitution (S<sub>R</sub>). Alkanes and cycloalkanes.
- 4. Electrophilic addition (A<sub>E</sub>) to alkenes: hydrogenation, halogenation, hydrohalogenation and hydration reactions. The Markovnikov's rule.
- 5. Mechanism of electrophilic substitution reactions (S<sub>E</sub>) in aromatic compounds. I and II sort directing substitutients.

#### **Exercises:**

1. Indicate the type of reagent:

+CH <sub>3</sub>	НОН	·СH <sub>3</sub>	CH <sub>3</sub> –Cl	CH <sub>3</sub> – OH

2. Write the scheme of chlorination reaction of propane. Indicate mechanism.							
3. Write the sc a) ethene	chemes of polymeriz	ation reaction of:					
b) propenoic a	cid						
c) 2-methylpro	openoic acid						

a) HCl to propene			
b) HBr to propenoic ac	id		
c) HOH to butenedioic	acid		
5. Describe the reaction a) chlorination of benze		alyst)	
b) alkylation of toluene	e with CH3 – CH2	2 – Cl (AlC	l <sub>3</sub> as catalyst)
	Те	ST CONTRO	vI.
<b>1. Nucleophile reagents are</b> 1) H ; 2) HOH;	: 3) C <sub>2</sub> H <sub>5</sub> OH;	4) H <sup>+</sup> ;	5) CH <sub>3</sub> NH <sub>2</sub> .
2. Select properties of free (1) molecular contain polar co 2) covalent bonds breaks as (3) acids and bases catalyze (14) require violent conditions	radicals reaction ovalent bond; a result of hemol hese reactions;	ns: ysis;	
3. Electrophilic addition really cyclohexene; 2) but-2-enoic acid;	3) ethane;	_	

4. Write the schemes of addition reaction:

4. The following product is mainly formed as a result of interaction of 2-methylpenten-1 and HCl:

- 1) 4-methyl-3-chloropentane;
- 3) 2-methyl-2-chloropentane;
- 2) 4-methyl-2-chloropentane;
- 4) 2-methyl-1-chloropentane.

5. The following product is mainly formed as a result of interaction of 2-chloropropaneand aniline with catalyst:



6. Hydration reaction is:

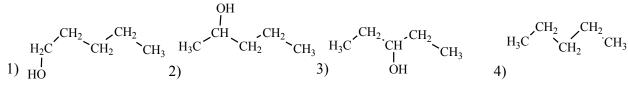
- 1) hydrogen addition;
- 3) hydrogen elimination;
- 2) water addition;
- 4) water elimination.

7. Select scheme(s) of electrophilic addition reaction(s):

1) 
$$H_{2}C \stackrel{\text{C}}{=} C_{CH_{3}} + H_{2}O \stackrel{\text{H}^{+}}{=} \cdots$$
2)  $H_{3}C \stackrel{\text{CH}_{3}}{=} + Cl_{2} \stackrel{\text{t}}{=} \cdots$ 
3)  $H_{2}C \stackrel{\text{CH}_{2}}{=} + Br_{2} \stackrel{\text{...}}{=} \cdots$ 

4) 
$$H_2C \nearrow CH_2 + Br_2 \longrightarrow ...$$

8. Indicate product of following reaction: pent-1-ene + HOH -->



9. Select reactions which goes according Marcovnicov rules:

- 1) ethane hydration;
- 4) butene-2 hydrohalogenation;
- 2) propenoic acid hydration;
- 5) butene-1 hydrohalogenation.
- 3) propene hydration;

10. Indicate compound possessing strongest reaction ability in the S<sub>E</sub> mechanism:

1) benzene;

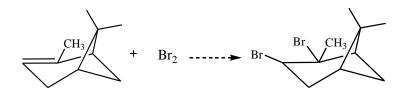
3) benzoic acid;

2) toluene;

4) pyridine.

#### PRACTICAL PART

1. Qualitative test on the alkenes with bromine water.



**Accomplishment:** to 4 drops of bromine water\* add 2 drops of  $\alpha$ -pinene\* and shake.

Observed changes:

_ ssel (ea changes)	 	
· ·		
Conclusion:		
t ancilisian:		
Conciusion.		

#### 2. Qualitative test on the alkenes with potassium permanganate.

$$\alpha$$
-pinene +  $[O]$  +  $H_2O$  .....  $KMnO_4$  HO  $CH_3$   $\alpha$ -pinenglycol

**Accomplishment:** to 3 drops of KMnO<sub>4</sub> (14) solution add 1 drop of α-pinene\* and shake.

Observed cha	anges:	 	 	
Conclusion:				

Signature of teacher:

#### LABWORK № 5 MONOFUNCTIONAL HYDROCARBON DERIVATIVES

**Objective:** to study structure and properties of monofunctional hydrocarbon derivatives; acidity and basicity of organic compounds; to generate skills for qualitative determination of organic compound acidity and basicity.

#### **Recommended literature:**

- 1. Ryneiskaya, O.N. Bioorganic chemistry / O.N. Ryneiskaya [et al.]. 2020. P. 53-59.
- 2. Ryneiskaya, O.N. Bioorganic chemistry / O.N. Ryneiskaya [et al.]. 2018. P. 53-59.
- 3. Zurabyan, S. E. Fundamentals of Bioorganic Chemistry / S. E. Zurabyan. 2012. P. 61–73, 101–119.

#### **Problems for discussion:**

- 1. The Brensted theory of organic compound acidity and basicity. The Lewis electronic theory of organic compound acidity and basicity. Classification of organic acids.
- 2. The quantitative and qualitative characteristics of acidity. The factors influencing on the acidic properties of organic compounds.
- 3. Oxidation reactions of alcohols, thiols and phenols. Antioxidants and their role in processes of vital activity.
  - 4. Basicity. The factors influencing on the basic properties of organic compounds.
  - 5. Amphoteric properties of organic compounds. Hydrogen bonds.
  - 6. Nucleophilic substitution reaction at sp<sup>3</sup>-hybrid carbon atom. Elimination reaction.

Exercises 1. Brensted acid —		
Brensted base —		
Lewis acid —		
Lewis base —		

2. Indicate acidic and basic centers at the following compounds:

$HO$ $CH_2$ $OH$ $H_2N$ $CH_2$ $NH_2$	H <sub>2</sub> N CH <sub>2</sub> CH OH	O H <sub>2</sub> N-CH-C-OH CH <sub>2</sub> CH <sub>2</sub> S S CH <sub>3</sub>
---------------------------------------	--	--

- 3. Compare acidity of compounds in the following groups:
- a) ethanol and ethanthiol

- b) ethanoic and ethanedioic acids
- 4. Indicate the acidic centers at the N-acetyltyrosine

HO 
$$\longrightarrow$$
 CH<sub>2</sub>-CH-NH- $\overset{\text{O}}{\overset{\text{C}}{\text{C}}}$ -CH<sub>3</sub>

- 5. Compare basicity of compounds in the following groups:
- a) ethylamine and aniline

b) methylamine and dimethylamine

- c) methylamine and dimethylamine
- 6. Show the strongest basic center at the procaine molecule. Write the reaction of procaine with hydrochloric acid.

7.

$$\begin{array}{c} O \\ \parallel \\ C \\ O \end{array} \begin{array}{c} CH_2 \\ CH_2 \end{array} \begin{array}{c} N \\ C_2H_5 \end{array}$$

8. Indicate reactive sites in the following molecules:

HO CH <sub>2</sub> CH <sub>3</sub> CH CH <sub>3</sub>	H <sub>3</sub> C CH <sub>2</sub> -NH <sub>2</sub>	H <sub>3</sub> C CH <sub>3</sub> CH SH	CH <sub>2</sub> -CI
---	---	--	---------------------

- 9. Write the schemes of interaction reactions of:
- a) 1-chloropropane and aqueous NaOH solution
- b) propanol-1 and HBr
- c) 2-bromo-2-methylpropane and alcoholic solution of NaOH
- 10. Write the scheme of dehydration reactions of 2-hydroxybutanedioic acid in vivo.
- 11. Write the ethanol oxidation reaction in vitro and in vivo.

- 12. Write the scheme of oxidation reaction:
- a) methanethiol
- b) 2-amino-3-mercaptopropanoic acid

#### TEST CONTROL

#### 1. Acidity increases in the following row of acids:

- 1) acetic acid, oxalic acid, malonic acid;
- 3) oxalic acid, malonic acid, acetic acid;
- 2) acetic acid, malonic acid, oxalic acid;
- 4) malonic acid, acetic acid, oxalic acid.

#### 2. Basicity according to the Bransted theory is ability of molecular or ion:

- 1) accept electrons;
- 2) donate electrons;
- 3) donate proton;
- 4) accept proton.

#### 3. Indicate the correct statement about acidity comparison:

- 1) conjugation stabilizes anion and increase acidity;
- 2) electron donors increase acidity;
- 3) electron withdrawers increase acidity;
- 4) solvation effect influence on anion stability and acidity.

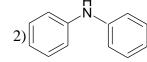
#### 4. Select substances which are capable to link heavy metals:

- 1) 2-amino-3-mercaptopropanoic acid;
- 3) 2,3-dimercaptopropanol-1;

2) propanol-2;

4) diethyl disulfide.

#### 5. Basicity decreases in the following row of amines:



3) CH<sub>3</sub>NH<sub>2</sub>

#### 6. Acidity according to the Lewis theory is the ability of molecule or ion:

- 1) to accept proton;
- 2) to accept electrons; 3) to donate electrons;
- 4) to donate proton.

#### 7. Indicate the factors which influence on the basicity:

- 1) polarizability of the basic site elements is in the same period of the periodic table;
- 2) electronegativity of the basic site elements is in the same period of the periodic table;
- 3) electronegativity of the basic site elements is in the same group of the periodic table;
- 4) polarizability of the basic site elements is in the same group of the periodic table.

#### 8. Give characteristics for interaction reaction between butene-2 and H<sub>2</sub>O (in acidic medium):

- 1) S<sub>N</sub> mechanism;
- 3) S<sub>E</sub> mechanism;
- 2) water is electrophile;
- 4) A<sub>E</sub> mechanism.

#### 9. Give characteristics for interaction reaction between benzene and isopropyl chloride (with AlCl<sub>3</sub>presence):

1) Cl<sup>+</sup> is electrophile;

- 3) S<sub>E</sub> mechanism;
- 2) alkylation of benzene is result of this reaction;
- 4) S<sub>N</sub> mechanism.

#### 10. Find the accordance between scheme of the reaction and typical reaction mechanism:

- A) toluene +  $CH_3Br$  (FeBr<sub>3</sub>);
- $1) S_R;$

B) propene + HCl;

- 2)  $A_E$ ;
- C) ethane  $+ Cl_2$  (light);

- 3)  $S_E$ ;
- D) tert-butyl alcohol+ HBr (conc.).
- 4) S<sub>N</sub>.

#### PRACTICAL PART

#### 1. Oxidation of primary alcohols

Alcohol oxidation reaction is carried out in narrow term. Primary alcohols are oxidized to aldehydes.

3 CH<sub>3</sub>CH<sub>2</sub>OH + K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> + 4H<sub>2</sub>SO<sub>4</sub> ···· 
$$\rightarrow$$
 H<sub>3</sub>C  $\rightarrow$  C H + K<sub>2</sub>SO<sub>4</sub> + Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> + 7H<sub>2</sub>O ethanol

**Accomplishment:** add 2 drops of  $H_2SO_4$  (23) dilute solution and 3 drops of  $C_2H_5OH^*$  to 3 drops of  $K_2Cr_2O_7$  (24). Carefully mix and heat.

Observed changes:	 	
Conclusion:		

#### 2. Qualitative test on polyols.

Unlike primary alcohols polyols react not only with alkali metals but with some metal hydroxides. In reaction of glycerine with copper (II) hydroxide complex compound is formed:

**Accomplishment:** to 2 drops of NaOH (21) solution add 2 drops of solution CuSO<sub>4</sub> (26), shake, add 2 drops of glycerine (4), shake.

Observed cha	anges:	 	 	_
Conclusion:			 	

#### 3. Sodium phenoxide production and its decomposition

Phenols possess more strong acidic properties than alcohols because stability of phenoxide anion raises according to negative charge delocalization along bond conjugate system. Phenols unlike alcohols are capable to react with alkalis. Water-soluble sodium phenoxide is formed. Mineral acids replace phenol from phenoxides.

$$C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O$$

$$C_6H_5ONa + H_2SO_4 \rightarrow C_6H_5OH + NaHSO_4$$

**Accomplishment:** to 10 drops of phenol water emulsia\*add on drops solution of NaOH (21) until transparent solution has been obtained. Add on drops dilute solution of H<sub>2</sub>SO<sub>4</sub> (23), and again emulsia is formed.

Observed changes:	 		
Conclusion:	 	 	·

#### 4. Qualitative test on phenol

This is a qualitative test on the hydroxyl group bound with unsaturated carbon atom. Phenol as an acid reacts with ion  $Fe^{3+}$  forming the complex compound.

**Accomplishment:** to 10 drops of phenol water emulsia\* add 1–2 drops of solution of FeCl<sub>3</sub> (8), shake.

Observed cha	anges:	 	 	
Conclusion: _		 	 	

#### 5. Comparison of the methyl amine and aniline basic properties

Aliphatic radicals possessing positive inductive effect +I increase electronic density on the nitrogen atom therefore aliphatic amines are stronger bases than ammonia NH<sub>3</sub>.

In aromatic amines nitrogen atom unshared electronic pair participates in the aromatic ring  $\pi$ -electronic system therefore aniline is weaker base than methyl amine.

**Accomplishment:** one litmus band is moistened with water solution of methylamine\* and another is with water solution of aniline\*.

Observed changes:	 	 
Conclusion:	 	 
Signature of teacher:		

### LABWORK $\[Mathbb{N}\]$ 6 BIOLOGICALLY IMPORTANT REACTIONS OF ALDEHYDES AND KETONES

**Objective:** to study features of aldehydes and ketones reactivity and develop skills to carring out of qualititative reactions on aldehydes, ketones.

#### **Recommended literature:**

- 1. Ryneiskaya, O.N. Bioorganic chemistry / O.N. Ryneiskaya [et al.]. 2020. P. 60-67.
- 2. Ryneiskaya, O.N. Bioorganic chemistry / O.N. Ryneiskaya [et al.]. 2018. P. 60-67.
- 3. Zurabyan, S. E. Fundamentals of Bioorganic Chemistry / S. E. Zurabyan. 2012. P. 121–133.

#### **Problems for discussion:**

- 1. An electronic structure of a carbonyl group. The reactive centers in aldehydes and ketones.
- 2. Mechanism of nucleophilic addition reaction  $(A_N)$ . Addition of water and alcohols. Reactions of aldehydes and ketones with amines. Reduction reactions.
  - 3. Reaction of CH-acidic center. Aldol condensation reactions. Haloform reactions.
- 4. Oxidation reactions are qualitative tests on aldehyde group. Oxidation reactions of ketones. Disproportionation reactions.
  - 5. Formaldehyde. Application in medicine. Toxicity.

#### **Exercises**

1. Indicate reactive centers in the carbonyl compound molecules:

O H	$H_3C$ $C$ $CH_2$ $CH_3$
-----	--------------------------

- 2. Write down the equation reaction acetalization: interaction ethanal with 2 mol methanol.
- 3. Describe the mechanism of intramolecular acetalization reaction to form cyclic hemiacetal of 5-hydroxyhexanal.

- 4. Write the interaction reaction of ethanal and methylamine.
- 5. Write reaction schemes of ethanal reduction in vivo and in vitro.

6. Write the scheme of aldol condensation reaction of 2-methylpropanal.

7. Write the scheme of oxidation reaction of ethanal.

8. Describe the mechanism of dismutation reaction for the formaldehyde.

#### TEST CONTROL

#### 1. Indicate reaction sites in the 2,2-dimethylpropanal molecule:

- 1) CH-acidic site on  $\alpha$ -carbon atom;
- 2) basic site on the oxygen atom;
- 3) electrophilic site on the carbonyl carbon atom;
- 4) nucleophile site on the carbonyl carbon atom.

#### 2. Find the accordance between the carbonyl compounds and its reduction product:

- A) 2-methylpropanal;
- 1) 2-hydroxybutandioic acid;
- B) 2-oxopropanoic acid;
- 2) 2-methylpropan-1-ol;
- C) 2-oxobutandioic acid;
- 3) propan-1-ol;

D) propanal.

4) 2-hydroxypropanoic acid.

#### 3. Select the product of methanal and ethanol (1:2) interaction in acidic medium:

- 1) 2-methoxyethanol;
- 3) ethoxymethanol;
- 2) diethoxymethane;
- 4) 1,1-dimethoxyethane.

#### 4. Select the hydrolysis product of the represented hemiacetal:

- 1) 4-hydroxy-5-methylhexanal;
- 3) 5-hydroxy-5-methylhexanal;
- 2) 5-hydroxyhexanal;
- 4) 5-hydroxy-5-methylheptanal.

#### 5. Schiff's bases forms as a result of interaction between:

- 1) methylamine and ethanal;
- 3) propanal and ethylamine;
- 2) methylamine and benzoic acid; 4) methylamine and ethylamine.

#### 6. In aldol condensation reaction could undergo:

- 1) 2-methylpropanal; 2) propanal;
- 3) benzaldehyde;
- 4) 2,2-dimethylpropanal.

#### 7. For qualitative detection of the aldehyde group are used:

- 1) Shiffs reagent;
- 2) FeCl<sub>3</sub>; 3) Cu(OH)<sub>2</sub>, heating;
- 4) Ag<sub>2</sub>O in ammonia solution.

#### 8. Choose carbonyl compound with the highest reactive ability in A<sub>N</sub> reactions:

- 1) propanone;
- 2) butan-2-one; 3) ethanal;
- 4) methanal.

#### 9. Select the product of 2-oxopropanoic acid reduction:

OH OH CH2 COOH 
$$(CH_2)^{OH}$$
  $(CH_2)^{OH}$   $(CH_2)^{OH}$ 

#### 10. Represented substance forms as a result of interaction between:

- methylamine and ethanal;
   ethylamine and methanol;
   ethylamine and methylamine 4) ethylamine and methylamine.

#### PRACTICAL PART

#### 1. Formaldehyde oxidation with Cu(OH)2 in alkaline medium

Qualitative tests on aldehydes are connected with easy oxidizability of aldehyde group with oxides or metal hydroxides in medium at heating, thus aldehydes turn into carboxylic acids with the same number of carbon atoms and the ion of metal is reduced. The Trommer's reagent (fresh obtained copper (II) hydroxide) is used as an oxidizer.

$$CuSO_4 + 2 NaOH \rightarrow Cu(OH)_2 + Na_2SO_4$$
 
$$R - CHO + 2Cu(OH)_2 \xrightarrow{OH^-, t} R - COOH + 2CuOH + H_2O$$
 
$$2 CuOH \longrightarrow Cu_2O + H_2O$$

**Accomplishment:** to 3 drops of formaline (32) add 5 drops of NaOH solution (21) and 1–2 drops of CuSO<sub>4</sub> (26). Mixture is heated to boiling point.

Observed cha	anges:	 	 	
Conclusion:		 	 	

#### 2. Reaction of formaldehyde with Shiff's reagent

Reaction goes according to the A<sub>N</sub> mechanism with the Shiff's reagent without heating. **Accomplishment:** to 2 drops of the Shiff's reagent\* add 3 drop of formaldehyde solution (32).

Observed change	es:	 	
Conclusion:		 	

#### 3. Disproportiation reaction of formaldehyde

Disproportionation reaction is interaction of two aldehyde molecules when one aldehyde molecule is reduced to alcohol due to another aldehyde molecule is oxidized to a carboxylic acid. Water formaldehyde solution has acidic medium of reaction.

$$2 \text{ HCHO} \rightarrow \text{HCOOH} + \text{CH}_3\text{OH}$$

**Accomplishment:** to 3–4 drops of formaline (32) add 1 drop of methyl red indicator\*.

Observed ch	anges:		
<b>Conclusion:</b>			

#### 4. Acetone detection by transformation to iodoform (iodoform reaction)

Iodoform reaction is connected with ability of carbonyl containing compounds to substitute hydrogen atom at  $\alpha$ -carbon atom on halogen and the following cleavage of carbon-carbon bond with iodoform (CHI<sub>3</sub>) formation.

 $I_2 + NaOH \longleftrightarrow HIO + NaI$ 

to disappearing of color, then pour 1–2 acetone drops*.					
Observed changes:					
Conclusion:					
5. Colored reaction on the acetone with sodium nitroprusside.  Reaction with sodium nitroprussiate Na <sub>2</sub> [Fe(CN) <sub>5</sub> NO] is used in a clinical practice to discovery of acetone in urine at a diabetes. Aromatic carbonyl compounds do not yield this reaction.  Accomplishment: to 3dropsacetone* add 2 drops of sodium nitroprussiate Na <sub>2</sub> [Fe(CN) <sub>5</sub> NO] (35) and 2 drops of NaOH (21) solution. In 2–3 minutes add 2 drops of acetic acid (36).					
Observed changes:					
Conclusion:					
Signature of teacher					

**Accomplishment:** to 3 drops of Lugol (47) solution (I<sub>2</sub> in KI solution) add NaOH solution (21)

### LABWORK № 7 CARBOXYLIC ACIDS AND THEIR DERIVATIVES

**Objective:** to study features of carboxylic acids reactivity and develop skills to carring out of qualititative reactions on carboxylic acids.

#### **Recommended literature:**

- 1. Ryneiskaya, O.N. Bioorganic chemistry / O.N. Ryneiskaya [et al.]. 2020. P. 68-75.
- 2. Ryneiskaya, O.N. Bioorganic chemistry / O.N. Ryneiskaya [et al.]. 2018. P. 68-75.
- 3. Zurabyan, S. E. Fundamentals of Bioorganic Chemistry / S. E. Zurabyan. 2012. P. 135.

#### **Problems for discussion:**

- 1. Reactions sites of carboxylic acids and derivatives.
- 2. Acidic properties of carboxylic acids.
- 3. Decarboxylation reaction. Biogenic amines. Cyclic anhydrides.
- 4. Nucleophilic substitution reactions. Esterification reaction.
- 5. Amides, acyl chlorides, anhydrides. Their hydrolysis.

#### **Exercises**

1. Indicate reactive sites at the carboxylic acid molecule:

2. Compare the acidity of ethanoic and ethanedioic acids. Write the reaction of salt formation of the stronger acid with Ca(OH)<sub>2</sub>.

3. Write down the decarboxylation reaction a) propanedioic acid (malonic)	of the following compounds:
b) 2-aminopentanedioic acid	
4. Write the dehydration reaction of pentane	dioic acid.
5. Write the formulas of the functional deriv	atives of carboxylic acids:
anhydride of acetic acid	acetyl chloride
ethylethanoate	ammonia acetate
full amide of oxalic acid	full amide of carbonic acid
6. Write the esterification reaction of the me	thanoic acid with ethanol.

7. Write down the acidic hydrolysis reaction of the following compound:

8. Write down the alkaline hydrolysis reaction of the following compound:

$$\begin{array}{c}
O \\
C \\
OH
\end{array}$$
OH

9. What products would be obtained from the hydrolysis of each of the following amides:

$$\begin{array}{c} O \\ \parallel \\ C \\ NH_2 \end{array} \qquad \begin{array}{c} O \\ \parallel \\ H_3C \end{array} \qquad \begin{array}{c} C \\ N \\ H \end{array}$$

10. Mark the ester, amide, anhydride bonds at the coenzyme A molecule. Write the scheme of acetyl coenzyme A formation (using short formula for coenzyme A — CoA-SH).

11. Write the scheme of acylation reaction:

$$\begin{array}{c|cccc}
CH_2OH & O & O \\
OH & OH & H_3C & SCoA
\end{array}$$

#### TEST CONTROL

#### 1. Arrange in order of decreasing of reactivity in $S_N$ reactions of the following compounds:

#### 2. Find accordance between compound and its decarboxylation products:

- A) ethandioic acid; 1) propanone;
- B) 2-amino-3-hydroxypropanoic acid; 2) 2-aminoethanol; C) propandioic acid; 3) ethanoic acid;
- D) 3-oxobutanoic acid. 4) methanoic acid.

#### 3. Methyl salicylate forms as a result of acidic hydrolysis of:

- 1) methanol and o-hydroxybenzoic acid;
- 2) o-hydroxybenzoic acid and methanoic acid;
- 3) p-hydroxybenzoic acid and methanol;
- 4) o-hydroxybenzoic acid and phenol.

#### 4. Choose correct statement(s):

- 1) RS-group possess less +M effect than RO-group;
- 2) RS-ions more stable than RO-ions and are more easily leaving group;
- 3) RO-ions more stable than RS-ions and are more easily leaving group;
- 4) partial positive charge on carbonyl carbon atom in thioesters is higher than its in esters.

#### 5. Electron density distribution in propanoic acid molecule is characterized by presence:

- 1) O H acidic site in the carboxyl group;
- 2) nucleophile site on the carbon atom of carboxylic group;
- 3) C H acidic site in the alkyl group;
- 4) basic site on the oxygen atom in the carboxyl group;
- 5) electrophilic site on the carbon atom of carboxylic group.

#### 6. Indicate type of the following reaction $CH_3COCl + CH_3OH \rightarrow CH_3COOCH_3 + HCl$ :

- 1) elimination; 3) electrophilic substitution;
- 2) nucleophilic substitution; 4) nucleophilic addition.

#### 7. Indicate acids which are stronger than acetic acid?

1) 2-chloroacetic acid; 2) hydrochloric acid; 3) propanoic acid; 4) formic acid.

#### 8. To increase reactive ability of carboxylic acids we should:

- 1) conduct reaction in alkaline medium;
- 2) conduct reaction in acidic medium;
- 3) enter more strong electron withdrawer in aside chain;
- 4) enter more strong electron withdrawer in a carboxyl group.

#### 9. Select functional derivatives of carboxylic acids:

1) ethanoic acid; 2) ethyl chloride; 3) acetic anhydride; 4) methyl benzoate.

#### 10. Choose products of the butandioic acid heating in acidic medium:

1) H<sub>2</sub>O; 2) CO<sub>2</sub>; 3) propanoic acid; 4) succinic anhydride.

#### PRACTICAL PART

#### 1. Ethyl acetate formation

To detect the carboxylic acids the esters production reaction can be used if esters have specific smell. The reaction is carried out according to the nucleofilic substitution mechanism  $(S_N)$ .

$$CH_3COONa + H_2SO_4 \rightarrow CH_3COOH + NaHSO_4$$
  
 $CH_3COOH + C_2H_5OH \rightarrow CH_3COOC_2H_5 + H_2O$ 

**Accomplishment:** to 3 drops of ethanol\* add 5 drops of H<sub>2</sub>SO<sub>4</sub> concentrated solution\* and waterless CH<sub>3</sub>COONa (42), heat. Pour solution to another test-tube with water.

Observed changes:
Conclusion:
2. Oxalic acid decarboxylation Result of the oxalic acid decarboxylation is carbon dioxide which forms CaCO <sub>3</sub> when mixed with the lime water (solution of Ca(OH) <sub>2</sub> ).
$HOOC - COOH \xrightarrow{t} CO_2 + HCOOH$
$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 \downarrow + H_2O$ Accomplishment: in dry test-tube add crystal oxalic acid* (mass $\approx 0.5$ g). Test-tube is closed by flatus tube and heat. The end of flatus tube put into test-tube with 15 drops of lime water (Ca(OH) <sub>2</sub> ) (2).
Observed changes:
Conclusion:

Signature of teacher:

## CONCLUDING TEST «THEORETICAL FUNDAMENTALS OF BASIC CLASSES OF ORGANIC COMPOUND STRUCTURE AND REACTIVITY»

**Remind the program material** from the theme  $N_0 = 1$  to  $N_0 = 6$ .

**Recommended literature:** study the literature from the theme  $N_2$  1 to  $N_2$  6.

#### **Questions to the concluding test(computer test):**

- 1. Conformations. Newman projections. Types of strains. Energetic characteristic of eclipsed, gauche and staggered conformations (butane). Conformational structure of hydrocarbon radicals of fatty acids (palmitic and stearic acids). Cyclohexane conformations. Types of strains (angle, torsion, Van-der-Waals). Inversion of cycle. 1,3-diaxial interaction.
- 2. Configuration of organic compounds. Stereoisomerism. Fischer projections. Relative configuration and D, L-convention. Glyceraldehyde as the configurational standart. Stereoisomerism of molecules with one chiral centre (lactic acid as an example). Enantiomers. Optic activity. Racemic mixtures. Absolute configuration of stereoisomers. R, S-convention. Relationship of spatial structure with biological activity.
- 3. Electronic effects in organic molecules (inductive and mesomeric), their role in the reactivity centers in the molecule. Electron donors and withdrawers.
  - 4. Conjugation ( $\pi$ , $\pi$  and p, $\pi$ -conjugations). Conjugated systems with open chain (butadiene-1,3).
- 5. Conjugated systems with close chain. Aromaticity, criteries of aromaticity, Huchel's rule (benzene, naphtaline, phenantrene).
  - 6. Acidity and basicity of organic compounds; Brensted and Lewis theories.
- 7. Acidic properties of organic compounds (alcohols, phenols, thiols, carboxylic acids, amides). Factors of anion stability.
- 8. Basic properties of organic compounds (alcohols, ethers, thioesters, amines). Comparing of basic properties of aliphatic and aromatic amines; salt formation.
- 9. Classification of organic reactions (substitution, addition, elimination, isomerisation, red-ox, acid-basic interaction). Classification of organic reactions on the mechanism of covalent bond cleavage (radical and ionic). Electronic and spatial structure of free radicals, carbocations and carboanions.
- 10. Oxidation reactions of organic compounds (alcohols, thiols, phenols). Antioxidants (2,3-dimercaptopropanol, ascorbic acid, phenols and others).
- 11. Radical substitution reactions. Propane chlorination as an example of free radical substitution. Initiators of radical reactions. Antioxidants.
- 12. Electrophilic addition reactions of alkenes. Hydration reactions of alkenes. Acidic catalys. Markovnikov's rule.
- 13. Electrophilic substitution reactions of aromatic hydrocarbons. Substituent effects in the aromatic ring on the reactivity of aromatic hydrocarbons. Alkylation reactions of aromatic compounds.
- 14. Electronic and spatial structure of the carbonyl group. Comparative reactivity of aldehydes and ketones.
- 15. Oxidation and reduction reactions of carbonyl compounds. Visual tests on the aldehyde group (silver mirror test, Trommer test). Reduction reactions *in vivo*, NADH as a hydride ion donor.
  - 16. Nucleophilic addition reactions of aldehydes and ketones; addition of water and alcohols.
  - 17. Addition of amines to carbonyl compounds, mechanism. Schiff's bases.
- 18. Electronic and spatial structure of the carboxylic group. Acidic properties of the carboxylic acids: mono-, dicarboxylic, aliphatic saturated, aliphatic unsaturated, aromatic carboxylic acids.
- 19. Nucleophilic substitution at sp<sup>2</sup>-hybridized carbon atom in the carboxylic group: esterification reaction. Properties of esters, hydrolysis.

## LABWORK № 8 HETEROFUNCTIONAL COMPOUNDS OF ALIPHATIC, BENZENE AND HETEROCYCLIC SERIES, METABOLITES AND BIOREGULATORS

**Objective:** to develop skills to predict chemical properties biologically important heterofunctional compounds taking into account a structure and interference of various functional groups.

#### **Recommended literature:**

- 1. Ryneiskaya, O.N. Bioorganic chemistry / O.N. Ryneiskaya [et al.]. 2020. P. 76-86.
- 2. Ryneiskaya, O.N. Bioorganic chemistry / O.N. Ryneiskaya [et al.]. 2018. P. 76-86.
- 3. Zurabyan, S. E. Fundamentals of Bioorganic Chemistry / S. E. Zurabyan. 2012. P. 163–172.

#### **Problems for discussion:**

- 1. Polyfunctional compounds: classification, chemical properties.
- 2. Heterofunctional compounds: classification, a role in biological processes.
- 3. Amino alcohols: their biological role.
- 4. Hydroxy acids. A structure, typical and specific properties of  $\alpha$ -,  $\beta$ -,  $\gamma$ -hydroxy and amino acids.
  - 5. A citric acid: a structure, properties. Citrates.
  - 6. Oxoacids. Acid properties and reactivity. Ketone bodies.
  - 7. Keto-enol tautomerism.
  - 8. Amides of carbonic acid. Urea.
  - 9. Salicylic acid, its derivatives.
  - 10. Para-aminobenzoic acid, its derivatives.
  - 11. Sulfanylamides.

#### **Exercises**

1. Write the structural formulas of the following polyfunctional compounds:

glycerol	ethylene glycol		inositol
catechol	hydroquinone		resorcinol
oxalic acid		malonic acid	
salts —		salts —	
succinic acid		glutaric acid	
salts —		salts —	

fumaric acid	maleic acid
salts —	salts —

2. Write the structural formulas of the amino alkohols:

2-aminoethanol	choline

3. Write the structural formulas of the hydroxy acids:

lactic acid	malic acid	citric acid
	1	
salts —	salts —	salts —

4. Write the structural formulas of the oxo acids:

pyruvic acid	oxaloacetic acid	α-oxoglutaric acid
salts —	salts —	salts —

5. Indicate the acidic and basic centers in the following molecules and write its ionic forms:

$$\begin{array}{c|c} & \text{NH}_2 \\ \text{O} & \text{CH}_2 & \text{CH} \\ \text{C} & \text{CH}_2 & \text{C} \\ \text{OH} & \text{OH} \end{array}$$

6. Fill in the scheme of the  $\alpha$ -glycerophosphate formation:

7. Show the catechol at the catecholamine molecules and its precursor DOPA (3,4-dihydro-xyphenylalanine). Write the name of the reactions occurring during the synthesis of catecholamines *in vivo* (alkylation, decarboxylation, hydroxylation). Mark the chiral centers in molecules.

? HO 
$$CH_2$$
 PHO  $CH_2$  PHO  $CH_2$  PHO  $CH_2$   $CH_2$ 

8. Complete the scheme of the reactions *in vivo*:

- 9. Write scheme of the oxidation reaction in vivo of malic acid.
- 10. Write scheme of the reduction reaction in vivo of pyruvic acid.
- 11. Write down the tautomeric forms of oxaloacetic acid:

12. Write the names of the ketone bodies formation according to the following scheme:

13. Fill in the scheme of the acetylsalicylic acid formation reaction.

salicylic acid

acetylsalicylic acid

14. Fill in the scheme of the *p*-aminobenzoic acid derivatives formation reaction:

benzocaine

p-aminobenzoic acid

procaine

15. Explain the structure peculiarities of the modern anesthetic remedies such as lidocaine.

$$\begin{array}{c|c} CH_3 & H_2 & C_2H_3 \\ \hline & N & C & N \\ C & N & C_2H_5 \\ CH_3 & C_2H_5 \end{array}$$

lidocaine

#### **TEST CONTROL**

1. Indicate the product of malic acid oxidation in vivo:

$$0 \\ 0 \\ C \\ COOH_2) \\ HOOC \\ CH_2 \\ COOH_3) \\ HOOC \\ CH_2 \\ COOH_4 \\ COOH_4 \\ CH_2 \\ COOH_4 \\ COOH_4$$

- 2. Salicylic acid is stronger than benzoic acid because of:
- 1) both functional groups are acidic;
- 2) mesomeric effect of phenol OH-group decrease anion stability;
- 3) formation of intermolecular hydrogen bond between ionized carboxyl group and phenol hydroxyl group;
- 4) mesomeric effect of phenol OH-group increase anion stability.
- 3. Novocain possess less long-term anesthetic action in comparison with ultracaine because of:
- 1) it has ethers bonds;
- 2) it is Shiff's base which hydrolyzes easy;
- 3) it has esters bond which hydrolyze easier then amide bond;
- 4) it has glycoside bond.

## 4. As a result of decarboxylation of 2-amino-3-hydroxypropanoic acid decarboxylation forms CO<sub>2</sub> and:

- 1) propanon;
- 2) 2-aminoethanol;
- 3) ethanoic acid;
- 4) methanoic acid.

#### 5. Indicate correct statements about oxaloacetic acid:

- 1) refer to ketoacids; 3) exist in toutomeric forms in solution;
- 2) posseses optical activity; 4) undergo in nucleophilic substitution reaction.

#### 6. Choose the carbonic acid derivatives:

1) carbamic acid; 2) carbamide; 3) uric acid; 4) urea.

# 7. As result of interaction of salicylic acid and acetic anhydride forms:

- 1) acetylsalicylic acid; 3) methyl salicylate;
- 2) phenyl salicylate; 4) ethyl salicylate.

#### 8. Indicate correct statements about urea:

- 1) gives acidic properties of medium; 4) oxygen is protonated after interaction with acid;
- 2) possess basic properties; 5) nitrogen is protonated after interaction with acid.
- 3) is the final product of nitrogen metabolism in human body;

# 9. Which acids undergo elimination reaction:

- 1) 4-hydroxypentanoic acid; 3) 3-hydroxybutanoic acid;
- 2) 2-hydroxy-3-methylbutanoic acid; 4) 3-aminopentanoic acid.

# 10. Which one of the following compounds forms gamma-lactone under heating:

- 1) 4-hydroxy-2-methylbutanoic acid; 3) 3-hydroxybutanoic acid;
- 2) 2-hydroxybutanoic acid; 4) 5-hydroxypentanoic acid.

## PRACTICAL PART

#### 1. Evidense of two carboxyl groups in tartaric acid structure

Tartaric acid as dioic forms two salts — acid salt and neutral [normal] salt which differ with water solubility.

**Accomplishment:** to 3 drops of tartaric acid (50) add 2–3 drops of KOH solution (51), intensively intermix rubbing with glass rod against walls of a test tube. There is a crystal deposit. Add 2–3 drops of NaOH solution into a test tube to form the solution of **segnetic salt** (sodium and potassium tartrate). Save this solution for next experiment.

Observed cha	anges:	 	 
Conclusion:			

#### 2. Evidense of two hydroxyl groups in tartaric acid structure

Qualitative test on polyols is used. Tartaric acid reacts with Cu(OH)<sub>2</sub> and forms copper (II) alcoholate (chelate).

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

Copper alcoholate of sodium and potassium tartrate is called the Fehling's reagent and is used for qualitative and quantitative definition of carbohydrates.

**Accomplishment:** Pour 2 drops of 5 % solution of CuSO<sub>4</sub> (26) and 2 drops of 10 % solution of NaOH (21) in the test tube. Then to the formed mixture add the solution of segnetic salt received at the last experiment.

Observed cha	anges:			
Conclusion:				

# 3. Test on the high quality of aspirin

At hydrolysis of aspirin o-hydroxybenzoic acid is formed which with Fe (III) chloride forms complex compound.

COOH
$$C = O$$

$$CH_3$$

$$COOH$$

$$OH$$

$$HO$$

$$CH_3$$

$$CH_3$$

**Accomplishment:** place some grains of aspirin\* and 5–6 drops of water in a test tube, shake it. Divide the test tube contents into 2 parts. To one part add 1 drop of FeCl<sub>3</sub> (8), another part boil for half a minute and then add 1 drop of FeCl<sub>3</sub>.

Observed ch	anges:	 	 
Conclusion:		 	 

Signature of teacher:

# LABWORK № 9 POLYMER MATERIALS USING IN DENTISTRY

**Objective:** to develop knowledge about composition and properties of polymer materials using in stomatology.

#### **Recommended literature:**

- 1. Ryneiskaya, O.N. Bioorganic chemistry / O.N. Ryneiskaya [et al.]. 2020. P. 97–115.
- 2. Ryneiskaya, O.N. Bioorganic chemistry / O.N. Ryneiskaya [et al.]. 2018. P. 97–115.
- 3. Solomons, T. W. Fundamentals of Organic Chemistry / T. W. Solomons. 1994. P. 951–961.

#### **Problems for discussion:**

- 1. General characteristic of high-molecular compounds (AMC): monomer elementary groups, degree of polymerisation. Oligo- and polymers, subpolymers, compositional polymers.
  - 2. Classification of polymers.
  - 3. Ways of receipt polymers.
  - 4. Mechanism of free radical polymerization of acrylic acid ester's.
- 5. Generation of free radicals. Initiators of process polymerization. Activators. Inhibitors of free radical reaction.
  - 6. Modern restore materials photo- and chemical hardening.
- 7. Main components of composite materials. Reaction of bilding Bis-GMa (bis-phenol-A-glyc-idylmethacrylate). TEG-GMA (triethylene glycoldimethacrylate).
- 8. Low-molecular components, using in the adhesive systems for improvement for stiking of material filling to tissue of tooth.

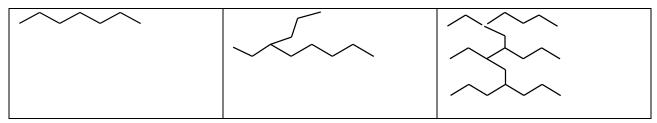
#### **Exercises**

1. Classify the polymers:

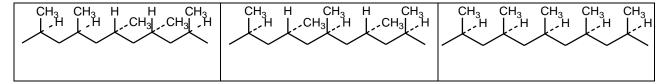
according to the origin (natural or synthetic)

polysterene	starch	polyethylene	polyethyleneglycol

#### according to the structure of macromolecule (linear, branched, spatial)



#### according to the spatial isomerism chain (isotactic, syndiotactic, atactic)



- 2. The main methods of polymer formation: ...
- 3. Radical polymerization may be initiated with...

39

4.	<b>Initiators</b>			
	TITUTE OF S	٠	•	•

Activators ...

Inhibitors...

Select initiators, activators and inhibitors:

FeSO <sub>4</sub>	OH	H <sub>3</sub> C CH <sub>3</sub> CH <sub>3</sub> H <sub>3</sub> C CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub>	$H_3C$ $\sim$	0,00,00
-------------------	----	---	--	---------

- 5. Write schemes of the formation reactions of....
- a) polymethylmethacrylate
- b) polyethylmethacrylate

6. Describe the mechanism of free radical polymerization of ethylmethacrylate with participation of initiator (benzoyl peroxide).

7. Modern restore materials photo- and chemical cured contain Bis-GMA (bis-phenol-A-glyc-idylmethacrylate). Analyze compounds, from which Bis-GMA forms and complete the scheme.

$$\begin{array}{c} \text{H}_2\text{C} \\ \text{C} \\ \text{C$$

.....

8. Triethylene glycoldimethacrylate add to composition materials to reduce viscosity. Select familiar fragments at the molecule of triethylene glycoldimethacrylate.

$$\begin{array}{c} O \\ II \\ H_2C \\ C \\ C \\ C \\ CH_2 \\ CH$$

triethylene glycoldimethacrylate

9. Dimethacrylate of glycerophosphate acid uses as component of adhesive systems. Write down the formula of dimethacrylate of glycerophosphate acid.

#### **TEST CONTROL**

1. Indicate structural formula of polymethacrylate monomer:

2. Indicate structural formula of free radical reaction activator:

3. Indicate structural formula of free radical reaction inhibitor:

4. Indicate compound which may provide a tooth tissue bi	nding witl	, roctoration	n matarial:
			$H_3C_{\searrow}CH_3$
CH <sub>3</sub> CH <sub>3</sub> H <sub>2</sub> H <sub>2</sub> C C C	H <sub>2</sub>	$H_2$	
$1)  H_{3}C - \overset{CH_{3}}{\overset{-}{C}} - O - O - \overset{-}{\overset{-}{C}} - CH_{3}  2)  \overset{CH_{3}}{\overset{-}{C}}  \overset{H_{2}}{\overset{-}{C}}  \overset{H_{2}}{\overset{-}{C}}  \overset{H_{2}}{\overset{-}{C}}  \overset{O}{\overset{-}{C}}  3)  H_{3}C$	C H <sub>2</sub>	H C	4)       CH <sub>3</sub>
<b>5. Gutta-percha represented by:</b> 1) <i>cis</i> -polybutadiene; 2) <i>trans</i> -polybutadiene; 3) <i>cis</i> -polyisoprene; 4) <i>trans</i> -polyisoprene.			3
6. Find the reasons of including gypsum in alginate impress 1) to decrease thermal stability; 2) to increase elasticity and rigidity of material; 4) using	as a preser	ving agent;	
<ul><li>7. Polyethylene glycol is polymer:</li><li>1) carbo chained; 2) hetero chained; 3) linear;</li></ul>	4) bran	ched.	
8. Natural rubber represented by: 1) cis-polybutadiene; 2) trans-polybutadiene; 3) cis-polyisoprene; 4) trans-polyisoprene.			
<ul><li>9. To slow down the aging processes of polymer are used:</li><li>1) peroxides;</li><li>2) aromatic amines;</li><li>3) phenols;</li><li>4)</li></ul>	carboxylic	acid.	
<ul> <li>10. Find the reasons of using dimethacrylate of glyceropho</li> <li>1) presence of double bonds in hydrophobic part;</li> <li>2) capability to undergo nucleophilic addition reactions;</li> <li>3) presence of free phosphoric acid residual;</li> <li>4) it has biphilic properties.</li> </ul>	osphic acio	l in adhesive	e systems:
PRACTICAL PART			
1. Prepare and consolidation (hardening) forming filling.  Accomplishment: In a porcelain cup ½ spoon of pow 2-3 drops of liquid from the kit. Mix using a glass stick duri form tooth filling during 1,5-2 min. If you follow all rules you Conclusion:	der (Acryi ng 40-50 s ı observe h	oxide or Act sec. Mass mu	rodent) and add ust be plastic to er 8-10 min.
Conclusion.			
2. Depolymerisation of polymethylmethacrilate and of Accomplishment: in the test tube put small pieces of polymethylmethacrilate and the accomplishment: in the test tube put small pieces of polymethylmethacrilate and the accomplishment: in the test tube put small pieces of polymethylmethacrilate and the accomplishment: in the test tube put small pieces of polymethylmethacrilate and the accomplishment: in the test tube put small pieces of polymethylmethacrilate and the accomplishment: in the test tube put small pieces of polymethylmethacrilate and the accomplishment: in the test tube put small pieces of polymethylmethacrilate and the accomplishment: in the test tube put small pieces of polymethylmethacrilate and the accomplishment: in the test tube put small pieces of polymethylmethacrilate and the accomplishment: in the test tube put small pieces of polymethylmethacrilate and the accomplishment in the accomplin	olymer, fix	the tube alm	ost horizontally
Observed changes:			
Conclusion:			

Signature of teacher:

# LABWORK № 10 CARBOHYDRATES. MONOSACCHARIDES

**Objective:** to develop knowledge of a stereochemical structure, consider important properties of monosaccharides and gain skills to carry out qualitative reactions on monosaccharides.

#### **Recommended literature:**

- 1. Ryneiskaya, O.N. Bioorganic chemistry / O.N. Ryneiskaya [et al.]. 2020. P. 116-126.
- 2. Ryneiskaya, O.N. Bioorganic chemistry / O.N. Ryneiskaya [et al.]. 2018. P. 116-126.
- 3. Zurabyan, S. E. Fundamentals of Bioorganic Chemistry / S. E. Zurabyan. 2012. P. 195–207.

#### **Problems for discussion:**

- 1. Carbohydrates: definition, biological role.
- 2. Monosaccharides, definition, classification, stereoisomerism. Epimers.
- 3. Monosaccharide tautomerism. Anomers. Tautomeric forms of D-glucose, D-galactose, D-fructose, D-ribose, 2-deoxy-D-ribose. Fisher and Haworth formulas. Conformations of cyclic forms.
  - 4. Chemical properties of monosaccharides. Glycosides (O- and N-glycosides).
  - 5. Monosaccharide esters. A biological role of monosaccharide phosphates.
  - 6. Monosaccharide oxidation: aldonic, aldaric and uronic acids.
  - 7. Monosaccharide reduction. Xylitol and sorbitol.
  - 8. Amino sugars. Their structure, properties and a biological role.
  - 9. Ascorbic acid (vitamin C) as water-soluble antioxidant.

#### **Exercises**

1. Classify the following monoses according to the type of carbonyl group and the number of carbon atoms. Show the chiral centers.

2. Write the all tautomeric forms of D-glucose (according to Fisher and Haworth).

3. Write the formulas of  $\beta$ -D-ribofuranose and  $\beta$ -D-deoxyribofuranose (according to Fisher and Haworth).

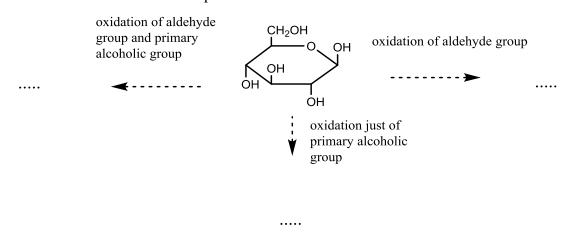
4. Write the all tautomeric forms of D-fructose.

5. Call the pairs of isomers (epymers, anomers, functional isomers, enantiomers).

1	(1)	,	, <b>J</b>	•	,
H—OH HO— H—OH HO—	CHO CHO H OH OH HO H OH H OH CH2OH CH2OH	CHO HO—H HO—H H—OH CH <sub>2</sub> OH	н—он	$CH_2OH$ $C=O$ $HO \longrightarrow H$ $H \longrightarrow OH$ $CH_2OH$	н он

6. Complete the scheme of the reaction:

7. Write down the formulas of product reactions.



8. Write down the formulas of reduction products of monoses.

D-xylose

D-glucose

9. From the formulas raw select the following compounds: 2-deoxy-2-amino- $\beta$ -D-glucopyranose, 2-deoxy-2-amino- $\alpha$ -D-galactopyranose, N-acetylgalactosamine, N-acetylglucosamine, glucuronic acid, galacturonic acid, reduce form of ascorbic acid, oxidizedform of ascorbic acid.

10. Phosphorylation is the way of formation of metabolic active forms of compound. Write down the products of phosphorylation reactions.

6 - phosphate-D - glucopyranose

1,6 - diphosphate-D - fructofuranose

#### TEST CONTROL

1. Select monosaccharaides which refer to aldohexoses:

1) mannose;

2) galactose;

3) xylose;

4) glucose;

5) fructose.

2. Find characteristics for D-glucose:

1) refer to hexose;

2) isaldose;

3) refer to pentose;

4) is ketoses.

3. Choose a type of glucose fermentation where hydrogen liberate?

1) lactic-acid;

2) alcoholic;

3) butyric-acid;

4) citric-acid.

4. How many chiral carbon atoms in cyclic glucose form?

1) 4.

2) 5;

3) 3;

4) 6;

5) 2

5. Give the name of the following compound:

1) α-D-galactopyranose;

3)  $\alpha$ -D-fructofuranose;

2) α-D-glucofuranose;

4) β-D-glucopyranose.

6. D-glucose and D-mannose are stereoisomers which are called:

1) enantiomers;

2) epimers;

3) functional isomers;

4) anomers.

7. Find β-D-galactopyranose:

$$1)_{HO} \underbrace{\begin{array}{c} H \text{ OH} \\ H \text{$$

8. Point out the product of interaction between  $\alpha$ -D-glucopyranose and methanol (with HCl presence):

1) 2,3,4,6-tetramethyl-D-pyranose;

3) methyl-α-D-glucopyranoside;

2) 2,3,4,6-tetramethyl-O-methyl-D-glucopyranoside;

4) methyl-β-D-glucopyranoside.

#### 9. Point out glucuronic acid:

# 10. Select correct statements about transformation acyclic form of monosaccharide in cyclic form:

- 1) acetal is cyclic form of monosaccharide;
- 2) carbon atom pass into sp<sup>3</sup>-hybridization from sp<sup>2</sup>-hybridization and becomes asymmetric;
- 3) anomer forms of monosaccharide are created;
- 4) acetal is acyclic form of monosaccharide.

#### PRACTICAL PART

# 1. A qualitative test on the hydroxyl groups in the glucose molecule.

Definition of some hydroxyl groups in the monosaccharide composition is carried out with  $Cu(OH)_2$ . This reaction is the same that on the polyatomic alcohols.

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

First forming sediment Cu(OH)<sub>2</sub> is dissolved when polyatomic alcohol is added.

This is the evidence of some hydroxyl group presence in the compound.

**Accomplishment:** to 5 drops of glucose (54) solution add 2 drops of NaOH (21) and 2 drops of CuSO<sub>4</sub> (26).

Observed cha	anges:	 	 
Conclusion:			

## 2. A qualitative test on the aldehyde group in the glucose molecule.

This reaction is carried out with the Fehling's reagent which is an alkaline solution of Cu<sup>2+</sup> alcoholate with K-, Na-tartrates. Obtained chelate is stable and when heated the color doesn't change. However if it is heated at the aldose presence alcoholate will be hydrolyzed. And obtained Cu(OH)<sub>2</sub>oxidizes glucose.

47

$$2Cu(OH)_2 \longrightarrow [O] + H_2O + 2CuOH$$
 
$$2CuOH \longrightarrow H_2O + Cu_2O$$

Oxygen molecule oxidizes glucose and monosaccharide molecules are completely broken up into acids and oxoacids. The first intermediate of glucose oxidation is gluconic acid.

The Fehling's reaction is used to discover glucose in urine.

**Accomplishment:** pour 10–12 drops of glucose (54) solution in the test-tube and add 3 drops of the Fehling's reagent (55) and heat up.

Observed changes: _	 	 
Conclusion:		 

## 3. Comparison of reactions of glucose and formalin with Shiff's reagent.

This qualitative test is negative for monosaccharides because of cyclic hemiacetal structure that hasn't aldehyde group.

**Accomplishment:** in one test tube pour 5–7 drops of formalin (32), in another as much a solution of glucose (54) and add in everyone on 2 drops Shiff's reagent (33). In a test tube with formalin — red violet color with glucose this reaction is negative.

Observed char	nges:	 	 
Conclusion:		 	 

#### 4. The qualitative test on ketohexoses (the Selivanov's test).

The test is predicated on the oxymethylfurfural formation which is condensed with resorcinol forming complex compound of characteristic color.

$$\begin{array}{c} \text{CH}_2\text{OH} \\ \text{C}=\text{O} \\ \text{HO}-\text{C}-\text{H} \\ \text{H}-\text{C}-\text{OH} \\ \text{H}-\text{C}-\text{OH} \\ \text{CH}_2\text{OH} \\ \end{array}$$

**Accomplishment:** to 10 drops of fructose (56) solution add 2 drops of HCl\* concentrated solution and 1 spatula of resorcinol\* crystals. Heat up.

Observed cha	anges:	 	 	
Conclusion:				

Signature of teacher:

#### **LABWORK № 11**

#### **OLIGO- AND POLYSACCHARIDES**

**Objective:** to develop knowledge of a structure, consider important chemical properties of homo- and heteropolysaccharides in view of their biological properties.

#### **Recommended literature:**

- 1. Ryneiskaya, O.N. Bioorganic chemistry / O.N. Ryneiskaya [et al.]. 2020. P. 127-135.
- 2. Ryneiskaya, O.N. Bioorganic chemistry / O.N. Ryneiskaya [et al.]. 2018. P. 127-135.
- 3. Zurabyan, S. E. Fundamentals of Bioorganic Chemistry / S. E. Zurabyan. 2012. P. 207–216.

#### **Problems for discussion:**

- 1. Classification of polysaccharides.
- 2. Disaccharides: maltose, cellobiose, lactose, lactulose, sucrose. Their structures and properties.
  - 3. Starch: structure, biological role. Glycogen.
  - 4. Cellulose: structure, biological role.
  - 5. Dextrane as a source to obtain plasma substitutes.
  - 6. Heteropolysaccharides. Impressional materials on the basis of alginate acids.

#### Exercises

1. Classify the polysaccharides (reducing disaccharide, non-reducing disaccharide, homopoly-saccharide, heteropolysaccharide):

sucrose	cellulose	starch	maltose		lactose
dextrane		chondroitin sulfate		hyaluı	onic acid

2. Indicate the monosaccharide residuals of disaccharide. Call this disaccharide and type of glycoside bond.

49

3. Write the reaction of lactose formation.

4. Complete the reaction of sucrose hydrolysis:

5. Starch consists of the following fractions:

At the amylose and amylopectine fragments, indicate monomer, bond types between monosaccharide residuals.

The end hydrolysis product of starch is ...

6. Call mentioned below fragment of polysaccharide. Indicate monomer and bond types between monosaccharide residuals.

50

7. Write the fragment of hyaluronic acid (min. 4 monosaccharide residuals) consisting of disaccharide fragment — D-glucuronic acid and N-acetyl-D-glucosamine bonded  $\beta$  (1-3) glycoside linkage. Between disaccharide fragments —  $\beta$  (1-4) glycoside bond.

8. Call the residuals of monosaccharide at the chondroitin sulfate structure.

9. Mark the residuals of monosaccharide derivatives at the alginic acid fragment and indicate the type of glycosidic bond.

#### **TEST CONTROL**

- 1. Point out functional groups participated in bond formation between monosaccharide residues in nonreducing disaccharide:
- 1) two alcoholic OH-groups;

3) two hemiacetal OH-groups;

2) hemiacetal and alcoholic OH-groups;

- 4) aldehyde and alcoholic OH-group.
- 2. Which disaccharides could undergo mutarotation?
- 1) lactulose;
- 2) cellobiose;
- 3) sucrose:
- 4) lactose.
- 3. As a result of sucrose hydrolyses forms:
- 1) glucose and mannose;
- 3) galactose and fructose;
- 2) galactose and glucose;
- 4) glucose and fructose.
- 4. Point out characteristics and properties of dextran:
- 1) main type of glycoside bond between monosaccharide residue is  $\alpha$  (1 $\rightarrow$ 6);
- 2) hydrolysis yield glucose;
- 3) bacterial metabolic product;
- 4) has plant origin.
- 5. Choose disaccharide(s) acid-catalyzed hydrolysis of which yields only glucose
- 1) lactose;
- 2) lactulose;
- 3) maltose;
- 4) cellobiose;
- 5) sucrose.

# 6. Select sugar which refer to homopolysuccharides:

- 1) heparin;
- 2) starch;
- 3) dextran;
- 4) cellulose;
- 5) hyaluronic acid.

### 7. Invert sugar is hydrolysis product of:

- 1) cellobiose;
- 2) maltose;
- 3) lactose;
- 4) sucrose.

# 8. Chose the type of glycoside bond in lactose:

- 1)  $\alpha$  (1-4);
- 2)  $\alpha,\beta$  (1-2);
- 3)  $\beta$  (1-4);
- 4)  $\alpha$  (1-3).

# 9. Chose the type of glycoside bond in lactulose:

- 1)  $\alpha,\beta$  (1-2);
- 2)  $\alpha$  (1-4);
- 3)  $\beta$  (1-4);
- 4) α (1-6).

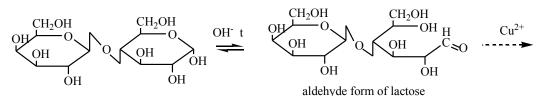
# 10. Find characteristics and properties of cellulose:

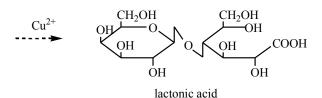
- 1) monosuccharide residues link by  $\alpha$  (1-4) glycoside bond;
- 2) hydrolysis yield glucose molecules;
- 3) monosuccharide residues link by  $\beta$  (1-4) glycoside bond;
- 4) produced by plants.

#### PRACTICAL PART

#### 1. The Fehling's reaction with sucrose and lactose.

Lactose has free hemiacetal hydroxyl group and in alkaline medium when heated it can turn into tautomeric forms containing aldehyde groups that possess reducing properties. Unlike lactose (and maltose) sucrose hasn't free hemiacetal hydroxyl group and belong to unreducing disaccharides.





**Accomplishment:** take 2 test tubes. In the one test-tube pour 10 drops of sucrose solution (57), in another pour the same quantity of the lactose solution (58), add to each test-tube 3–4 drops of the Fehling's reagent (55) and carefully heat up.

Observed changes: \_\_\_\_\_\_
Conclusion: \_\_\_\_\_

## 2. The qualitative test on the starch.

**Accomplishment:** to 10–12 drops of gelatinized starch add 1 drop of the Lugol's solution (47). Fix the color change, heat up the solution and fix the changes.

Observed ch	anges:	 	 	
<b>Conclusion:</b>		 	 	

Signature of teacher:

# LABWORK № 12 STRUCTURE AND REACTIVITY OF AMINO ACIDS ACTING AS HETEROFUNCTIONAL COMPOUNDS

**Objective:** to discuss characteristics of amino acids as heterofunctional compounds acting as structural components of peptides and proteins; to form skills for carrying out qualitative reactions on the amino acids.

#### **Recommended literature:**

- 1. Ryneiskaya, O.N. Bioorganic chemistry / O.N. Ryneiskaya [et al.]. 2020. P. 136-144.
- 2. Ryneiskaya, O.N. Bioorganic chemistry / O.N. Ryneiskaya [et al.]. 2018. P. 136-144.
- 3. Zurabyan, S. E. Fundamentals of Bioorganic Chemistry / S. E. Zurabyan. 2012. P. 217–224.

#### **Problems for discussion:**

- 1. Biogenic amino acids. Proteinogenic amino acids: classification, structures, stereochemistry.
- 2. Amphoteric properties of amino acids.
- 3. Reactions of amino acids on the carboxylic group.
- 4. Reactions of amino acids on the amino group.
- 5. Biologically important reactions of amino acids: deamination, transamination, decarboxylation, hydroxylation reactions.

#### **Exercises**

1. Write down proteinogenic amino acids at the mentioned below table with three letter code.

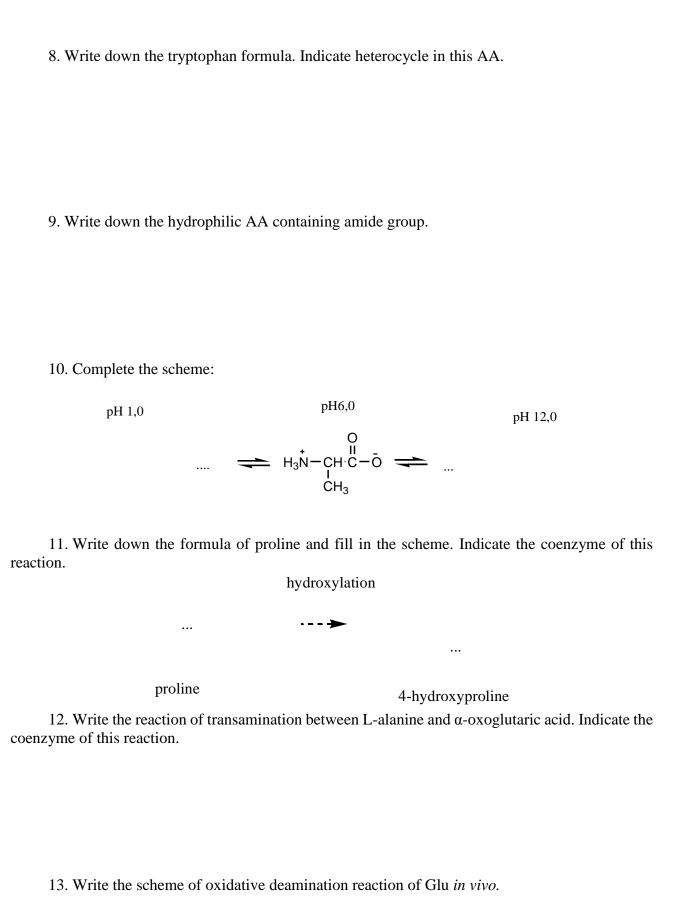
Uvdnonhobio A A	Hydrophilic AA					
Hydrophobic AA	With inionized radi-	With negative ionized	With positive ionized			
(8)	cal (7)	radical(2)	radical(3)			

Aliphatic AA (5)	
Hydroxy amino acids (2)	
Dicarbonic (acidic) AA (2)	
Amides of dicarbonic AA (2)	
Diaminomonocarbonic acids (2)	
S-containing AA (2)	
Aromatic AA (2)	
Heterocyclic AA (3)	

Designate(\*) essential AA at the table.

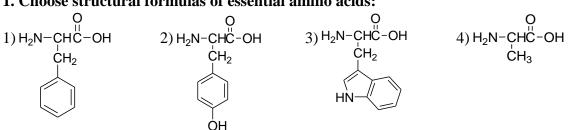
proje	2. Write down the formulas of aliphatic amino acids, designate chiral centers. ection of L-valine.	Write Fischer
	3. Write down the formulas of aromatic amino acids.	
	Complete the scheme.	
	··· decarboxylation	
Tyr	3,4-dihydroxyphenylalanine (DOPA)	dopamine
	4. Write the structures of hydroxyl containing amino acids.	
as co	Write down the serine decarboxylation reaction. Call vitamin, which participates a penzyme.	nt that reaction

5. Write the structures of S-containing amino acids.
Write the oxidation reaction of cysteine <i>in vivo</i> .
6. Write down the hydrophilic amino acids with negative ionized radical.
Write down the reaction of decarboxylation of Glu. Indicate the biological role of reaction product.
7. Write down the hydrophilic AA with positive ionized radical.
Write down the reaction of decarboxylation of His. Indicate the biological role of reaction product.

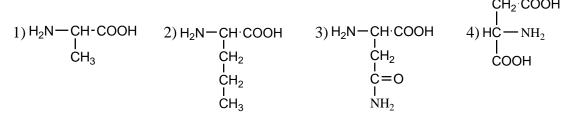


# TEST CONTROL

1. Choose structural formulas of essential amino acids:



2. Choose structural formulas of proteinogenic amino acids:



3. Choose aromatic cycle containing amino acids:

1) Tyr; 2) Pro; 3) Thr; 4) His; 5) Trp.

4. Point out amino acids with ionogenic radical:

1) Asn; 2) Asp; 3) Arg; 4) Glu; 5) His.

5. Choose amino acids which exist in the form of four stereoisomers:

1) isoleucine; 2) threonine; 3) 4-hydroxyproline; 4) arginine.

6. Choose amino acids with two carboxylic group:

1) Gln; 2) Ala; 3) Glu; 4) Asn; 5) Asp.

7. Which vitamin participate in reactions of prolin and lysine hydroxylation for connective tissue synthesis:

1) B<sub>6</sub>; 2) C; 3) PP; 4) D.

8. As a result of posttranslational modification is formed:

1) cysteine; 2) 4-hydroxyproline; 3) 5-hydroxylysine; 4) threonine.

9. Choose amino acids structures in following sequence: leucine, asparagine, cysteine, glycine:

a) 
$$H_2N-CH-C-OH$$
 b)  $H_2N-CH-C-OH$  c)  $H_2N-CH-C-OH$  d)  $H_2N-CH_2-C-OH$  C $H_2$  C $H_2$  C $H_2$  C $H_3$  C $H_3$  1) c, a, b, d; 2) a, c, d, b; 3) a, b, c, d; 4) d, a, b, c.

10. Select transamination reaction products of pyruvic acid and Glu:

- 1) Ala and 2-oxobutanedioic acid; 3) Ala and 2-oxopentanedioic;
- 2) Gly and 2-oxopentanedioic; 4) Asp and 2-oxopentanedioic.

#### PRACTICAL PART

## 1. Reactions of amino acids with copper salts

Amino acids as the amphoteric compounds form water soluble chelated compounds with copper ions.

$$\begin{array}{c|c} O & H_2N & R \\ \hline C & Cu & CH \\ \hline R & NH_2 & O & C \end{array}$$

**Accomplishment:** add 1 copper (II) sulfate crystal (3) and 1 sodium acetate crystal (42) to 10 drops of 1 % glycine (6) solution. Shake the test-tube.

Observed char	nges:	 	 
Conclusion:			

# 2. Glycine has neutral medium

**Accomplishment:** add 1 drop of 0.2 % methyl red indicator\* solution to 5 drops of 1 % glycine (6) solution.

Observed changes: \_\_\_\_\_\_
Conclusion: \_\_\_\_\_

#### 3. Reactions of amino acid with formaldehyde

Formaldehyde is able to react in the  $A_N$  reaction (nucleophilic addition with the following water elimination) with amines and amino acids. At the same time the amino group of amino acid transforms into the methylenamino group (substituted imine). A free carboxylic group of the methylenamino acid causes pH medium change (the medium becomes acidic). It may be proved by the indicator color change.

$$H_2N$$
— $CH$ — $COOH$   $+$   $H_2C$ = $N$ — $CH$ — $COOH$   $R$ 

This reaction is the basis of amino acid quantitative detection in the biological substrates (formalin titration with alkali according to the Serensen method).

**Accomplishment:** add 1 drop of 0.2 % methyl red indicator\* solution to 5 drops of 40 % formaldehyde solution (32). Carefully add (with glass stick) NaOH solution (21) to neutral medium of solution (fix color change). Then add 3 drops of 1 % glycine (6) solution (fix color change again).

Observed chai	nges:	 	 
Conclusion:			

#### 4. Ninhydrin reaction

This reaction is characterized for amino groups of free amino acids and  $\alpha$ -amino groups of amino acids that are the part of peptide and protein structure. A ninhydrin reaction is used for  $\alpha$ -amino acid detection in the biological liquids under consideration.

**Accomplishment:** add 2 drop of 0.1 % ninhydrin\* solution to 5 drops of 1 % glycine (6) solution. Heat the mixture to boil.

Observed changes:	 	 	
Conclusion:	 		

Signature of teacher:

# LABWORK № 13 PEPTIDES. THE LEVELS OF PROTEIN ORGANIZATION

**Objective:** to form knowledge about organization levels of protein molecules, stereochemical features of peptide bond and types of interactions in protein molecule formation.

#### **Recommended literature:**

- 1. Ryneiskaya, O.N. Bioorganic chemistry / O.N. Ryneiskaya [et al.]. 2020. P. 145-149.
- 2. Ryneiskaya, O.N. Bioorganic chemistry / O.N. Ryneiskaya [et al.]. 2018. P. 145-149.
- 3. Zurabyan, S. E. Fundamentals of Bioorganic Chemistry / S. E. Zurabyan. 2012. P. 224–228.

#### **Problems for discussion:**

- 1. Peptides: structure and functions. Glutathione, aspartam, insulin.
- 2. Peptide bond.
- 3. Proteins. Primary structure of peptides and proteins.
- 4. Artificial peptide synthesis.
- 5. Secondary structure of proteins.
- 6. Tertiary and quaternary structures of proteins. Hemoglobin.
- 7. Denaturation of proteins.

#### **Exercises**

1. Write down the reaction of dipeptide formation.

a) Ala-Thr
b) Glu-His
c) Asp-Tyr-Met
d) aspartyl asparaginyl leucine
3. Write down the formula of glutathione.

5. Tertiary structur	e is stabilized with		
Indicate the type of	f interaction between AA	at the polypeptide chair	n.
Phe and Ala	Arg and Glu	Ile and Val	Cys and Cys
Ser and Gln	Tyr and Thr	Asp and Lys	His and Ser
Trp and Leu	Glu and His	Asn and Ser	Met and Ala
6. <b>Denaturation</b> is			
	TEST CO	ONTROL	
1. Indicate amino acids tein:	which participate in io	n bonds formation in	tertiary structure of pro-
1) Asn; 2) Arg; 3	) Cys; 4) Asp; 5)	Glu.	
protein:	which participate in hy ine; 3) phenylalanine;	_	as in tertiary structure of  asparaginic acid.

4. Call the type of the secondary protein structure:

Complete the pictures with bonds stabilizing secondary protein structure.

They are stabilized with ...

#### 3. Choose correct statements:

- 1) proteins are polymers of proteinogenic amino acids;
- 2) secondary protein structure is stabilized by ionic bonds;
- 3) N-end and C-end presents in polypeptide chains;
- 4) proteins-shaperones participates in tertiary protein structure formation.

# 4. Indicate amino acids which participate in hydrogen bonds formation in tertiary structure of protein:

- 1) glutamine; 2) phenylalanine; 3) tyrosine; 4) proline; 5) serine.
- 5. In physiological conditionals positive charge has:
- 1) His-Val; 2) Thr-Lys; 3) Arg-Ser; 4) Ile-Tyr; 5) Cys-Arg.
- 6. Aspartameis dipeptide consisting of asparaginic acid and residue of methyl ether of:
- 1) glycine; 2) phenylalanine; 3) glutamine; 4) tyrosine.

#### 7. Point out correct statement(s) about peptide bond:

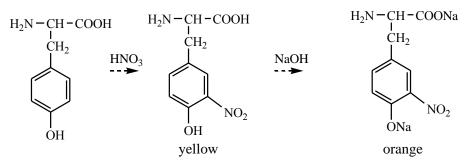
- 1) carbon, nitrogen and oxygen atoms are in sp<sup>2</sup>-hybridisation;
- 2) a lone pair of electrons enter in conjugation with p-electrons of double bond;
- 3) rotation is capable around peptide bind;
- 4) carbon, nitrogen and oxygen atoms are in the same plane.

# 8. Peptide bonds in proteins and peptides are detected by reaction:

- 1) biuretic; 2) xanthoproteinic; 3) decarboxylation; 4) deamination.
- 9. In physiological conditionals negative charge has:
- 1) Asp-Phe; 2) Gln-Trp; 3) Glu-Thr; 4) Ile-Asp; 5) Asn-Pro.
- 10. C-end amino acid of glutathione is:
- 1) Glu; 2) Gly; 3) Cys; 4) Gln; 5) Ser.

# PRACTICAL PART

1. Xantoproteinic reaction proves the presence of aromatic and heterocyclic  $\alpha$ -amino acids such as tryptophane, phenylalanine, tyrosine, histidine in protein structure. When reacted HNO<sub>3</sub> concentrated solution with protein solution nitro-compound is formed. When alkali is added to protein solution the ionization of phenol OH-group occurs.



**Accomplishment:** to 10 drops of protein solution\* add drop by drop concentrated solution of HNO<sub>3</sub>\* to form sediment (of what color?). Then heat carefully this test-tube (fix the change of color). Add some NaOH (21) solution (fix the change of color again).

Observed cha	anges:	 	 
Conclusion:			
_			

**2. Biuretic reaction** determines the peptide bond in the solution of analysed compound. Complex compound of Cu with protein peptide group is formed as a result of biuretic reaction. Commonly peptide bond is presented in amide (or keto-form) in peptides and protein, but in alkaline medium it turns to iminol (enol) form.

Biuretic reaction proceeds in such way:

**Accomplishment:** to 5 drops of protein solution\* add 5 drops of NaOH (21) concentrated solution and then by degrees on the test-tube side pour 2–3 drops of 2 % solution of CuSO<sub>4</sub> (26).

Observed cha	anges:	 	 
Conclusion:		 	 

# 3. Precipitation of proteins with sulfosalicylic acid.

It is the example of in reversible protein precipitation. Proteins can not be soluble in the same solvent. In reversible reactions are protein precipitation reactions with heavy metals, mineral (inorganic) and organic acids, alkaloid reagents and when boiled.

**Accomplishment:** pour 5 drops of 20 % sulfosalicylic acid\* solution to 10 drops of protein solution\*. Solution turbidity occurs.

Observed ch	anges:	 	 
Conclusion:			

# 4. Precipitation of proteins with dehydrating agents (alcohol or acetone).

It is the example of reversible protein precipitation. It's called graining that means precipitation process with the concentrated salt solutions (NaCl, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, MgSO<sub>4</sub>) or denaturants (alcohol, acetone). Hydration of protein polar group decreases and charge disappearance leads to aggregation and precipitation of proteins. Obtained precipitate can be dissolved with dilution or dialysis that's why it is the reversible precepitation.

**Accomplishment:** to 10 drops of protein\* solution pour 5 drop of acetone\*. Solution turbidity occurs.

Observed cha	anges:	 	 
Conclusion:		 	

Signature of teacher:

# LABWORK № 14 NUCLEOSIDES. NUCLEIC ACIDS

**Objective:** to form knowledge about structure and properties of purine and pyrimidine bases, nucleosides and nucleotides, nucleic acids; to develop skills to carreing out of qualititative reactions on structural components of nucleotides.

#### **Recommended literature:**

- 1. Ryneiskaya, O.N. Bioorganic chemistry / O.N. Ryneiskaya [et al.]. 2020. P. 150-156.
- 2. Ryneiskaya, O.N. Bioorganic chemistry / O.N. Ryneiskaya [et al.]. 2018. P. 150-156.
- 3. Zurabyan, S. E. Fundamentals of Bioorganic Chemistry / S. E. Zurabyan. 2012. P. 246–256.

#### **Problems for discussion:**

- 1. Structural components of nucleic acids.
- 2. Heterocyclic bases: pyrimidine bases and purine bases.
- 3. Tautomeric forms of heterocyclic bases.
- 4. Pentoses of nucleic bases.
- 5. Nucleosides.
- 6. Nucleotides.
- 7. Primary structure of DNA and RNA.
- 8. Secondary structure of DNA.
- 9. Nucleotide derivatives: cyclic AMP, cyclic GMP, ATP. NAD<sup>+</sup> coenzyme.

#### **Exercises:**

1. Complete the table.

2. Write down the pyrimidine, number its atoms. Then write uracil, thymine and cytosine at the lactam and lactim tautomeric forms.

pyrimidine	uracil
thymine	cytosine

	Write down the automeric forms		Then write	adenine and guanine at the lactam and
	purine	adenine		guanine
	Write the struct	tural formulas showing the	e hydrogen	bonds in complementary base pairs of
DNA:	thymine – aden	nine		b)cytosine – guanine
a)	guanosine	ulas of the following nucle	b)	thymidine
	adenosine- 5'-	-monophosphate	dec	oxycytidine-5'-monophosphate

7. Draw ATP molecule, indicate the bond types. Indicate its biological role.

8. Analyze the formula of NAD $^+$ . Mark the structural components of this molecule. Indicate its biological role.

# TEST CONTROL

1. Point out types of tautomerism which characterize cytosine:

1) lactim-lactam; 3) amino-imine; 2) keto-enol; 4) cyclo-oxo.

2. Select products of deoxyadenosine-5'-monophosphate alkaline hydrolysis:

deoxyribose;
 phosphate;
 deoxyadenosine.

3. Choose nitrogen bases included in RNA:

1) 2-amino-6-hydroxypurine; 4) 4-amino-2-hydroxypyrimidine; 2) 2,4-dihydroxy-5-methylpyrimidine; 5) 2,4-dihydroxypyrimidine.

3) 6-aminopurine;

4. Which type of I NAD+:	bond take	place between amide	of nicotine acid and ribose residue in coenz	zyme
	1) anhydride bond; 3) O- 2) N-glycoside bond; 4) am			
_	s of thymic 2) ribose;	dine-5'-monophospha 3) deoxyribose;	ate acidic hydrolyses (pH 1): 4) thymidine; 5) phosphoric acid	
_		adenosine-3',5'-cycl		
,	2) 2;	3) 3;	4) 4.	
1) keto-enol;	2) cyclo-ox <b>bonds pre</b> s	erism which characte to; 3) amino-imine; sents in nucleotide str 3) anhydride an	; 4) lactim-lactam. ructure:	
· · · · · · · · · · · · · · · · · · ·		4) phosphodiest		
	<b>h-energy</b> b 2) 2;	oonds in adenosine-5' 3) 1;	-triphosphate: 4) 4.	
	f bonds pr	resents in GTP molec	ule between second and third phosphoric	acid
residues: 1) anhydride;	2) ester;	3) thioester;	4) hydrogen.	
		PRACTICA	AL PART	
_	ment: add	_	f nucleoprotein hydrolysis (hydrolyzates). c reagent* to 3–5 drops of yeast hydrolyzate	* and
$H_3PO_4 + 12$	2 (NH <sub>4</sub> ) <sub>2</sub> M <sub>6</sub>	$OO_4 + 21 \text{ HNO}_3 \rightarrow (NI_3)$	$H_4)_3PO_4 \cdot 12MoO_3 + 21NH_4NO_3 + 12H_2O$	
Observed change	es:			
Conclusion:				
	ed with H <sub>2</sub> S condensed v	SO <sub>4</sub> concentrated soluti with orcinol.	protein hydrolysis (the Bial's test). ion or dilute HCl pentoses are dehydrated to  HC—CH  HC—CH  HC  C—C  H  HC  HC  HC	form
	НО	OH OH		
pentose furfural				
_		10 drops of the Bial's e* and boil 1–2 minute	s reagent* (orcinol solution in HCl with FeC es.	l <sub>3</sub> ) to
Observed change	es:			

# 3. Purine base detection in products of nucleoprotein hydrolysis

$$\begin{array}{c} O \\ N \\ N \\ N \\ N \\ NH_2 \end{array} + AgNO_3 + NH_4OH \\ \longrightarrow \begin{array}{c} N \\ N \\ N \\ N \\ NH_2 \end{array} + NH_4NO_3 + H_2O \\ \\ Ag \\ \end{array}$$
guanine

**Accomplishment:** add 1 drop of concentrated solution of ammonia and 5 drops of 1 % solution of AgNO<sub>3</sub>\* to 5 drops of yeast hydrolyzate\*. Leave the test-tube for 3–5 minutes without mixing.

Observed changes:	 	 	
Conclusion:	 		
,			

Signature of teacher:

# LABWORK № 15 LIPIDS. LIPID PEROXIDATION

**Objective:** to develop knowledge about the saponifiable lipids.

#### **Recommended literature:**

- 1. *Bioorganic* chemistry: учебное пособие для иностранных студентов / О. Н. Ринейская [и др.] 2020. Р. 157-166.
- 2. *Bioorganic* chemistry: учебное пособие для иностранных студентов / О.Н. Ринейская [и др.] 2018. Р. 157-166.
- 3. Zurabyan, S. E. Fundamentals of Bioorganic Chemistry / S. E. Zurabyan. 2012. P. 173–182.

#### **Problems for discussion:**

- 1. Classification of lipids, their biological role.
- 2. Fatty acids, their structure, properties and nomenclature. Alcohols which form fats and lipids.
- 3. Waxes, their composition and role.
- 4. Triacylglycerols, their structure, nomenclature, properties.
- 5. Phospholipids, their structure, nomenclature, physicochemical properties.
- 6. Sphingolipids, biological role.
- 7. The lipid peroxidation of cell membranes. Antioxidants.

#### **Exercises**

1. Write the molecular and stick formulas of fatty acids. Give their names according to ω-nomenclature.

Stearic acid		
D-1		
Palmitic acid		

Oleic acid	
Linoleic acid	
Linolenic acid	
Arachidonic acid	

2. Write the formulas of the following hydroxyl containing compounds.

ethanolamine
choline

3. Analyze the mentioned below formulas of waxes.

$$CH_{3}(CH_{2})_{14} - C \longrightarrow CH_{2}(CH_{2})_{14}CH_{3}$$

$$CH_{3}(CH_{2})_{14} - C \longrightarrow CH_{2}(CH_{2})_{28}CH_{3}$$

$$CH_{3}(CH_{2})_{14} - C \longrightarrow CH_{2}(CH_{2})_{28}CH_{3}$$

4. Write a structural formulas of the following triacylglycerol:

1-linoleoyl 2-palmitoyl 3-stearoylglycerol

1,3-dioleoyl-2-linoleoylglycerol

5. Write the hydrolysis reactions of fat. What is the soaps?

- 6. Draw the structural formulas of the following compounds. Mark the hydrophobic tails and hydrophilic head.
  - a) 1-stearoyl-2-oleoylphosphatidylserine

b) 1-stearoyl-2-linoleoylphosphatidylcholine

c) 1-palmitoyl-2-arachidonoylphosphatidylethanolamine

7. Analyse the mentioned below scheme peroxidation of linolenic acid.

# TEST CONTROL

1. Indicate name of the following structure: CH 1) linoleic acid; 3) oleic acid; 2) arachidonic acid; 4) stearic acid.	I <sub>3</sub> \\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\			
2. Choose simple lipid: 1) myricylpalmitate; 2) trioleoylglycerol; 3) 1-palmytoil-2-oleoy 4) dipalmitoylphospha				
, , , , , , , , , , , , , , , , , , , ,	d fatty acids including in lipids structure: nched carbon chain; ally cis-isomeres.			
<b>4. ω-Nomenclature name of linoleic acid is:</b> 1) 20:4 ω 6; 2) 18:3 ω 3; 3) 18:1 ω 9;	4) 18:2 ω 6.			
<ul><li>5. Choose complex lipid:</li><li>1) myricylpalmitate;</li><li>2) 1-srearoyl-2-oleoylphosphatidylinositol;</li></ul>	<ul><li>3) 1-palmitoyl-2-oleoylphosphatidylcholine;</li><li>4) tristearoylglycerol.</li></ul>			
6. Select alcohols which are a part of lipids comp 1) propantriol-1,2,3; 2) ethanol; 3) 2-aminooctadecen-4 4) inositol.				
7. Vitamin E is native antioxidant because of pre 1) amino group; 3) phenol hydroxyl; 2) alcoholic hydroxyl; 4) thiol group.	sence in its structure			
8. ω-Nomenclature name of arachidonic acidis: 1) 20:4 ω6; 2) 20:4 ω 3; 3) 18:1 ω 6;	4) 18:2 ω 6.			
<ul><li>9. Choose reserve lipids:</li><li>1) 1,2-dioleoyl-3-linolenoylglycerol;</li><li>2) 1-oleoyl-2-steariylphosphatidylcholine;</li></ul>	<ul><li>3) 1-oleoyl-2-stearoylphosphatidylinositol;</li><li>4) 1,3- dioleoyl-2-stearoylglycerol.</li></ul>			
10. Point out type of chemical bond in phosphatid 1) ester bond; 2) anhydride bond; 3) O-glyco	ylserine between phospatidic acid and serine? oside bond; 4) amid bond.			
PRACTICAL PART				
1. Qualitative reactions on the unsaturated acids which form fats.				
$+$ $Br_2 \longrightarrow Br$				
unsaturated fragment of fatty acid	product of addition reaction			
<b>Accomplishment:</b> to 1 drop of fat* add some	drops of bromine water*. Shake the test-tube.			
Observed changes:				
Conclusion:				

#### 2. Oxidation reaction with potassium permanganate.

Oxidation occurs in the double bond location.

**Accomplishment:** to 1 drop of fat\* pour 10 drops of KMnO<sub>4</sub> solution\* and 2 drops of Na<sub>2</sub>CO<sub>3</sub> (43). Shake the test-tube.

Observed cha	anges:	 	 
Conclusion: _			

#### 3. Malonic dialdehyde detection in the vegetable oil peroxidation products.

The model of lipid peroxidation is rancidification. One of the lipid peroxidation products is malonic dialdehyde which can be formed from  $\omega$ -3 unsaturated fatty acid hydroperoxides. To detect the malonic dialdehyde the reaction with thiobarbituric acid is used which goes according to the nucleofilic addition mechanism.

trimethin complex

**Accomplishment:** in a test-tube № 1 pour 10 drops of a fresh sunflower-seed oil\* solution, in a test-tube № 2 pour 10 drops long time stored on the light (in conditions of oxygen access) sunflower-seed oil, in a test-tube № 3 pour 10 drops of margarine\* solution (oils and margarine are dissolved in heptane-chloroform mixture in the volume ratio 1:1). Then in each of the test-tubes add on 10 drops of the TBA-reagent (0.8 % solution of thiobarbituric acid in an ice acetic acid)\*. Test-tubes with a reaction mixture shake up, close with foil, place into boiling water bath. In 15 minutes take out the test-tubes and visually estimate color intensity of solutions.

Observed cha	anges:	 	 
Conclusion:			

Signature of teacher:

### LABWORK № 16 STEROIDS. ALKALOIDS

**Objective:** to develop knowledge of a stereochemical structure, consider important properties of steroids and alkaloids and develop skills to carry out qualitative reactions on steroids.

#### **Recommended literature:**

- 1. Ryneiskaya, O.N. Bioorganic chemistry / O.N. Ryneiskaya [et al.]. 2020. P. 136-144.
- 2. Ryneiskaya, O.N. Bioorganic chemistry / O.N. Ryneiskaya [et al.]. 2018. P. 136-144.
- 3. Zurabyan, S. E. Fundamentals of Bioorganic Chemistry / S. E. Zurabyan. 2012. P. 167-173.

#### **Problems for discussion:**

- 1. Steroids: their structure, nomenclature and classification.
- 2. Stereochemistry of steroids.  $5\alpha$  and  $5\beta$  series of steroids.
- 3. Sex hormones: estrane and androstane derivatives.
- 4. Pregnane derivatives: corticosteroids and progestins.
- 5. Cholic acid. Bile acids.
- 6. Cholesterol. Biological importance.
- 7. Vitamins  $D_2$  and  $D_3$ .
- 8. Alkaloids.

#### **Exercises**

1. Number carbon atom of gonane.

2. Draw the conformations of  $5\alpha$  and  $5\beta$  steroids.

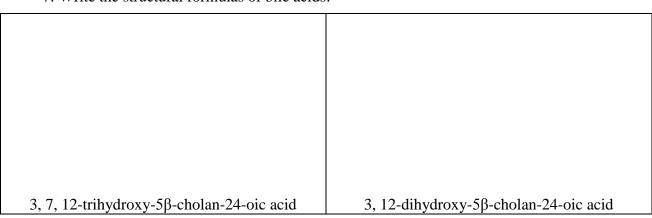
3. Draw the basic classes of steroids:

estrane	androstane	pregnane

cholane	cholestane
4. Write the structural formulas of estrogens	:
estr-1,3,5(10)- triene-3,17-diol (estradiol)	3-hydroxyestr-1,3,5(10)- trien-17-one (estrone)
 5. Write the structural formulas of androgen	s:
17-hydroxyandrost-4-ene-3-one (testosteron)	3-hydroxy-5α-androstan-17-one (androsterone)
6. Write the structural formulas of pregnane	derivatives:
17, 21-dihydroxypregn-4-ene-3,11,20-trione (cortisone)	17, 11, 21-trihydroxypregn-4-ene-3,20-dione (cortisol)

11, 21-dihydroxy-3,20-dioxopregn-4-ene-18-al	
(aldosterone)	pregn-4-ene-3,20-dione (progesterone)
(aluosterolle)	pregn-4-ene-5,20-drone (progesterone)

7. Write the structural formulas of bile acids:



8. Write the formula of cholesterol (cholest-5-en-3 $\beta$ -ol).

9. Vitamine  $D_3$  is formed from 7-dehydrocholesterol in skin with ultraviolet. Explain the peculiarity of this reaction.

$$\begin{array}{c} H_3C \\ CH_3 \\ CH_2 \\ CH_2 \\ CH_2 \\ CH_2 \\ CH_3 \\ CH_3 \\ CH_4 \\ CH_5 \\ CH$$

76

10. Define the group of the following steroids (according to structural classification — estrange, androstane, pregnane, cholane, cholestane).

11. Define the trivial names of the following alkaloids:

#### **TEST CONTROL**

#### 1. Structural base of steroids is:

- 1) phenanthrene;
- 2) gonane;
- 3) perhydrophenanthrene cyclopentane;
- 4) pyrrole.

#### 2. Structure of steroids is characterized:

- 1) plane structure;
- 2) non-plane structure;
- 3) gonane has chiral centers;
- 4) gonane has no chiral centers.

#### 3. The parent structures of the sex hormones are:

- 1) androstane; 2) pregnane; 3) cholane; 4) estrange.
- 4. Bile acids contain:
- 1) androstane; 2) pregnane; 3) cholestane; 4) cholane.

#### 5. Select the correct statements about estradiol:

- 1) it contains oxo group at 3 carbon atom;
- 2) it contains hydroxyl group at 3 carbon atom;
- 3) it has basic properties;
- 4) it has acidic properties.

#### 6. Select the correct statements about cholesterol:

- 1) it has oxo-group at 3 carbon atom;
- 2) it is base to form sex hormone;
- 3) it is base to form bile acids;
- 4) it is a component of biological membranes.

#### 7. Select the correct statements about bile acids:

- 1) they are cholestane derivatives;
- 2) they are formed by liver;
- 3) they are cholane derivatives;
- 4) it is a components of biological membranes.

#### 8. Select the correct statements about steroids:

- 1) they have hydrophilic properties;
- 2) they have hydrophobic properties;
- 3) purine is the base of steroids;
- 4) gonane is the base of steroids.

#### 9. Select the correct statements about alkaloids:

- 1) they are formed by plants;
- 2) alkaloids have basic properties;
- 3) alkaloids have acidic properties;
- 4) they are formed by animals.

#### 10. Caffeine contains the following cycle:

1) isoquinoline; 2) xanthine; 3) phenanthrene; 4) indole.

#### PRACTICAL PART

## 1. Color reaction on the cholesterol.

**Accomplishment:** in the dry test-tube pour 1 drop of FeCl<sub>3</sub> solution in acetic acid\* and 5-8 drops of concentrated solution of  $H_2SO_4*$ . Carefully shake the test-tube and add 5 drops of cholesterol solution in acetic acid\*.

Observed changes:
Conclusion:
2. Reactions to discover alkaloids.  Accomplishment: on an object-plate add 3 drops of investigated solution* at distance of 2 cm from each other. To the first drop add 1 drop of the Lugol's solution (47), to the second add 1 drop of 1 % picric acid solution*, to the third add 1 drop of a phosphomolybdic acid.
Observed changes:
Conclusion:

Signature of teacher:

# LABWORK m M 17 CONCLUDING TEST «BIOPOLYMERS AND THEIR STRUCTURAL COMPONENTS»

**Objective:** form a holistic view of the structure of biopolymers, their structural components, lipids.

## Remind the program material from the theme $N_2$ 1 to $N_2$ 16.

#### **Recommended literature:**

Study the literature from the theme  $N_2$  1 to  $N_2$  16.

#### Questions to the test control:

- 1. Conformations. Newman projections. Types of strains. Energetic characteristic of eclipsed, gauche and staggered conformations (butane). Conformational structure of hydrocarbon radicals of fatty acids (palmitic and stearic acids). Cyclohexane conformations.
- 2. Configuration of organic compounds. Stereoisomerism. Fischer projections. Relative configuration and D, L-convention. Glyceraldehyde as the configurational standart. Stereoisomerism of molecules with one chiral centre (lactic acid as an example). Enantiomers. Optic activity. Racemic mixtures. Absolute configuration of stereoisomers. R, S-convention. Relationship of spatial structure with biological activity.
- 3. Electronic effects in organic molecules (inductive and mesomeric), their role in the reactivity centers in the molecule. Electron donors and withdrawers.
- 4. Conjugation ( $\pi$ , $\pi$  and p, $\pi$ -conjugations). Conjugated systems with open chain (butadiene-1,3).
- 5. Conjugated systems with close chain. Aromaticity, criteries of aromaticity, Huchel's rule (benzene, naphtaline, phenantrene).
  - 6. Acidity and basicity of organic compounds; Brensted and Lewis theories.
- 7. Acidic properties of organic compounds (alcohols, phenols, thiols, carboxylic acids, amides). Factors of anion stability.
- 8. Basic properties of organic compounds (alcohols, ethers, thioesters, amines). Comparing of basic properties of aliphatic and aromatic amines; salt formation.
- 9. Classification of organic reactions (substitution, addition, elimination, isomerisation, red-ox, acid-basic interaction). Classification of organic reactions on the mechanism of covalent bond cleavage (radical and ionic).
- 10. Oxidation reactions of organic compounds (alcohols, thiols). Antioxidants (2,3-dimercapto-propanol, ascorbic acid, phenols and others).
- 11. Radical substitution reactions. Propane chlorination as an example of free radical substitution. Initiators of radical reactions. Antioxidants.
  - 12. Electrophilic addition reactions of alkenes. Hydration reactions of alkenes.
  - 13. Electrophilic substitution reactions of aromatic hydrocarbons.
- 14. Oxidation and reduction reactions of carbonyl compounds. Visual tests on the aldehyde group (silver mirror test, Trommer test). Reduction reactions *in vivo*.
  - 15. Nucleophilic addition reactions of aldehydes and ketones; addition of water and alcohols.
  - 16. Addition of amines to carbonyl compounds, mechanism. Schiff's bases.
- 17. Electronic and spatial structure of the carboxylic group. Acidic properties of the carboxylic acids: mono-, dicarboxylic, aliphatic saturated, aliphatic unsaturated, aromatic carboxylic acids.
- 18. Nucleophilic substitution at sp<sup>2</sup>-hybridized carbon atom in the carboxylic group: esterification reaction. Properties of esters, hydrolysis.
- 19. Polyfunctional compounds and their characteristics. Polyols: ethylene glycol, glycerol, inositol, xylitol, sorbitol. Visual test on the diol fragment. Dicarboxylic acids and their properties. Decarboxylation reactions and anhydride formation. Diatomic phenols: hydroquinone, resorcinol, catechol. Oxidation of diatomic phenols. Phenols as antioxidants. Adrenaline.

- 20. Heterofunctional compounds and their characteristics. Intramolecular and intermolecular reactions of nucleophilic substitution in the amino acids and hydroxy acids. Elimination reactions.
  - 21. Citric acid (2-hydroxypropane-1,2,3-tricarboxylic acid). Decomposition reactions. Citrates.
- 22. Oxo acids (pyruvic acid, acetoacetic acid, oxaloacetic acid,  $\alpha$ -ketoglutaric acid). Transamination reactions of  $\alpha$ -oxo acids.
  - 23. Keto-enol tautomerism. Reactions on the enol fragment.
- 24.  $\beta$ -Hydroxy butyric acid,  $\beta$ -oxo butyric acid, acetone as representatives of *ketone bodies*, their biological and diagnostic significance (visual tests on the acetone).
- 25. Anesthesin and novocain as ester of p-aminobenzoic acid. Novocain chloride. Modern anesthetics: lidocaine, ultracaine.
  - 26. Salicylic acid, acetylsalicylic acid.
  - 27. Properties of fatty acids. Saturated and unsaturated fatty acids.
  - 28. Lipids. Properties. Triacylglycerols: structures, biological role.
  - 29. Phospholipids as amphiphilic molecules.
- 30. Carbohydrates. Classification, biological properties. Monosaccharides. D, L-stereochemical rows.
- 31. Tautomeric forms of monosaccharides: open chain and cyclic forms. The Fischer projection formulas and Haworth formulas of glucose and galactose. Conformations of cyclic forms of glucose. Ring-chain tautomerism of fructose. Furanoses and pyranoses;  $\alpha$  and  $\beta$ -anomers. Structure and tautomeric forms of important representatives of pentoses (ribose and deoxyribose). Their biological role.
- 32. Nucleophilic substitution at the anomeric centre in the cyclic forms of monosaccharides. O-and

N-glycosides. Hydrolysis of glycosides.

- 33. Oxidation of monosaccharides. Biological role of glycuronic acids.
- 34. Ascorbic acid as water soluble antioxidant.
- 35. Reducing disaccharides (maltose, lactose, cellobiose). Structure, ring-chain tautomerism.
- 36. Lactose: structure, ring-chain tautomerism. Reducing properties. Hydrolysis. Role of oligo-saccharides of lactose group in the nonpathogenic intestinal flora necessary for normal digestion. Lactulose.
- 37. Sucrose as representative of nonreducing disaccharides (the Haworth formula). Hydrolysis of sucrose. Invert sugar.
- 38. Starch. Structure (amylose and amylopectin), properties, hydrolysis reactions. Biological role.
  - 39. Cellulose. Structure, properties, application, role in nutrition.
- 40. Glycogen is reserve homopolysaccharide of animals and human (the Haworth structure). Biological significance of branched structure of glycogen.
- 41. Dextran as representative of bacterial origin homopolysaccharides. The Haworth structure. Partial hydrolysis products of dextranand their medical application.
- 42. Proteinogenic amino acids. Structure, nomenclature, acid-basic properties, bipolar structure. Stereoisomerism of natural  $\alpha$ -amino acids with one and two chiral centers.
- 43. Biologically important reactions of  $\alpha$ -amino acids. Deamination reactions (oxidative and non-oxidative). Hydroxylation reactions (phenylalanine tyrosine, tryptophane 5-hydroxytryptophane).
- 44. Decarboxylation reaction of  $\alpha$ -amino acids way to formation of biogenic amines and bioregulators (colamine, histamine,  $\gamma$ -amino butyric acid).
  - 45. Peptides. Electronic and spatial structure of peptide bond.
- 46. Representatives of peptides and their biological significance (glutathione, neuropeptides, insulin).
- 47. Proteins. Organization levels of protein molecules and types of interactions in the stabilization. Primary, secondary ( $\alpha$ -helix and  $\beta$ -conformation) and tertiary protein structures.
  - 48. Pyridine and purine heterocyclicbases, their aromaticity as reason of high stability.

- 49. Nucleotides. Structure of mononucleotides forming nucleic acids. Nomenclature. Hydrolysis of nucleotides.
- 50. Primary structure of nucleic acids. Ribonucleic and deoxyribonucleic acid. Nucleotide composition of RNA and DNA. Hydrolysis of nucleic acids.
- 51. General characteristic high-molecular compounds: monomer, elementary groups, degree of polymerisation. Oligo- and polymers, compositional polymers.
- 52. Classification of polymers. Ways of receipt polymers (polymerization, polycondensation, chemical modification of natural polymers). Mechanism free radicae polymerization of acrylic acid ester's.
- 53. Generation of free radicals. Initiators of process polymerization. Activators. Inhibitors of free radical reaction.
- 54. Modern restore materials photo- and chemical hardening. Main components compositions materials. Reaction of bilding Bis-GMa. TEG-GMA (triethylene glycoldimethacrylate).
- 55. Low-molecular components, using in adhesive systems for improvement for stiking of material filling to tissue of tooth.
  - 56. Impressional materials on the basis of alginate acids.

#### LABWORK № 18 CONCLUDING SESSION «BIOORGANIC CHEMISTRY»

**Objective:** form a holistic view of the structure of biopolymers, their structural components, lipids.

**Remind the program material** from the theme  $N_2$  1 to  $N_2$  17.

#### **Recommended literature:**

Study the literature from the theme  $N_0 = 1$  to  $N_0 = 17$ .

## MUST KNOW STRUCTURAL FORMULAS

Formaldehyde	Acetaldehyde	Acrolein
O H C H	$H_3C$ $H$	$H_2C$ $C$ $H$
Malonic aldehyde	Glutaric aldehyde	Acetone
$\begin{array}{cccc} O & O \\ \parallel & \parallel \\ C & C \\ H & CH_2 & H \end{array}$	$\begin{bmatrix} O & O & O \\ \parallel & \parallel & \parallel \\ C & CH_2 & CH_2 & H \end{bmatrix}$	$H_3C$ $CH_3$
Methanoic (formic) acid	Ethanoic (acetic) acid	Propanoic (propionic) acid
О Н С ОН	$H_3C$ OH	$H_3C$ $C$ $C$ $C$ $C$ $C$ $C$ $C$
Butyric acid	Valeric acid	Caproic acid
$H_3C$ $CH_2$ $CH_2$ $CH_2$ $OH$	$H_3C$ $CH_2$ $CH_2$ $CH_2$ $OH$	ОН
Acrylic acid	Benzoic acid	Acetyl coenzyme A
$H_2C$ $C$ $OH$	ОН	O     C  SCoA
Metacrylic acid  O  H <sub>2</sub> C  C  OH  CH <sub>3</sub>	Urea $\begin{matrix} O \\ \parallel \\ H_2N \end{matrix} \qquad NH_2$	Carbamic acid  O  H <sub>2</sub> N  OH
Creatine	Creatine phosphate	Creatinine
$\begin{array}{c c} CH_3 & O \\ & \parallel \\ H_2N & N & C \\ & \parallel \\ NH & \end{array}$	HO H N OH O NH	$HN$ $N$ $H_3C$
Ethylene glycol	Glycerol	Inositol
HO CH <sub>2</sub> OH	СН <sub>2</sub> —ОН   СН—ОН   СН <sub>2</sub> —ОН	OH HO OH OH

Xylitol	Sorbitol	Catechol
CH <sub>2</sub> OH	CH₂OH	ОН
Н—ОН	Н—ОН	OH
НО—Н	НО——Н	
Н—ОН	Н—ОН	
ĊH <sub>2</sub> OH	Н—ОН	
	ĊН <sub>2</sub> ОН	
Resorcinol	Hydroquinone	Oxalic acid
OH	но—ОН	O OH
ОН		О ОН
Malonic acid	Succinic acid	Glutaric acid
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{c c} O \\ \parallel \\ C \\ CH_2 \\ CH_2 \\ O \\ \end{array} O \\ O \\$	$\begin{array}{c} O & O \\ \parallel & \parallel \\ C & CH_2 & CH_2 \\ \end{array}$
Fumaric acid	Maleic acid	Ethanolamine
C = C H COOH	Н Н Н Н Н Н СООН	H <sub>2</sub> N CH <sub>2</sub> OH
Choline	Acetylcholine	Dopamine
$H_3C$ $CH_3$ $CH_2$ $CH_2$ $CH_2$ $CH_3$	$\begin{array}{c c} CH_3 \\ H_3C & CH_2 \\ N \oplus \\ CH_3 \end{array}  \begin{array}{c} CH_2 \\ CH_2 \end{array}  \begin{array}{c} CH_3 \\ CH_3 \end{array}$	HO CH <sub>2</sub> NH <sub>2</sub> HO
Adrenaline (epinephrine)	Noradrenaline	Lactic acid (lactate)
OH	(norepinephrine) OH	H <sub>3</sub> C COOH
HO CH <sub>2</sub> CH <sub>3</sub>	$HO$ $CH$ $CH_2$ $NH_2$	CH   OH
НО	но	
Malic acid (malate)	Citric acid (citrate)	Cis aconitic acid
СН2 СООН	СООН	COOH 
HOOC CH OH	HOOC CH <sub>2</sub> COOH OH	HOOC CH <sub>2</sub> COOH

Isocitric acid (isocitrate)	Pyruvic acid (pyruvate)	Oxaloacetic acid	
СООН	H <sub>3</sub> C COOH	(oxaloacetate) CH <sub>2</sub> COOH	
HOOC CH COOH	0	HOOC C	
ÓН			
α-keto glutaric acid	Acetoacetic acid	β-hydroxy butyric acid	
HOOC CH <sub>2</sub> COOH	(β-keto butyric acid) O	OH 	
	HOOC CH <sub>2</sub> CCH <sub>3</sub>	HOOC CH CH <sub>3</sub>	
Salicylic acid	Methyl salicylate	Phenyl salicylate	
ОН	OH CH3	ОН	
Acetylsalicylic acid	Para aminobenzoic acid	Anaesthesin	
COOH OCH3	H <sub>2</sub> N COOH	$O$ $C_2H_5$ $H_2N$	
Novocaine		,	
$\begin{array}{c c} O & C_2H_5 \\ \hline \\ C & CH_2 & C\\ \hline \\ H_2N & C_2H_5 \end{array}$			
Sulfanilic acid	General formula of sulfa drags		
$H_2N$ $\longrightarrow$ $S$ $O$ $S$ $O$ $S$ $O$ $O$ $S$ $O$	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	R	
Uric acid	Xanthine	Hypoxanthine	
O HN N H N H	O N N H N H	HN N N H	

Nicotinic acid		Nicotinamide	
ОН		O C NH <sub>2</sub>	
Glycine (Gly)		Alanine (Ala)	
O    		$\begin{array}{c} O \\ \parallel \\ H_2N-CH-C-OH \\ CH_3 \end{array}$	
Valine (Val)	Leucine (Leu)		Isoleucine (Ile)
O    	O H <sub>2</sub> N—CH—C—OH   CH <sub>2</sub>   CH—CH <sub>3</sub>   CH <sub>3</sub>		H <sub>2</sub> N—CH—C—OH    CH—CH <sub>3</sub>   CH <sub>2</sub>   CH <sub>3</sub>
Phenylalanine (Phe)	Tryptophane (T	rp)	Methionine (Met)
H <sub>2</sub> N—CH—C—OH CH <sub>2</sub>	H <sub>2</sub> N—CH—C CH <sub>2</sub> N H	—ОН	H <sub>2</sub> N—CH—C—OH (CH <sub>2</sub> ) <sub>2</sub>   S   CH <sub>3</sub>
Serine (Ser) Proline (Pro)			Threonine (Thr)
О    		DН	H <sub>2</sub> N—CH—C—OH     CH—OH     CH <sub>3</sub>
Cysteine (Cys)  Tyrosine (Tyr)			Glutamine (Gln)
H <sub>2</sub> N—CH—C—OH     CH <sub>2</sub>   SH	H <sub>2</sub> N—CH—C·	—ОН	$H_2N$ — $CH$ — $C$ — $OH$ $CH_2$ $CH_2$ $C$

Asparagine (Asn)	Aspartic acid (Asp)	Glutamic acid (Glu)
O	O	0
$H_2N$ — $CH$ — $C$ — $OH$	$H_2N$ — $CH$ — $C$ — $OH$	$H_2N$ — $CH$ — $C$ — $OH$
CH <sub>2</sub>	CH <sub>2</sub>	ĊH <sub>2</sub>
c=o	ĊH <sub>2</sub>     C <b>=</b> O	CH <sub>2</sub>
NH <sub>2</sub>	OH	c=0
		OH
Lysine (Lys)	Arginine (Arg)	Histidine (His)
0     U.N.—C.H.—C.—O.H.		0
H <sub>2</sub> N—CH—C—OH	H <sub>2</sub> N—CH—C—OH	H <sub>2</sub> N—CH—C—OH
CH <sub>2</sub>	CH <sub>2</sub>	ĊH <sub>2</sub>
CH <sub>2</sub>	CH <sub>2</sub>	N
ĊH <sub>2</sub>	CH <sub>2</sub>	HN—
CH <sub>2</sub>	NH 	
NH <sub>2</sub>	Č=NH	
	NH <sub>2</sub>	
Selenomethionine	Selenocysteine	Taurine
	0	
$H_2N$ — $CH$ — $C$ — $OH$ $(CH_2)_2$	H <sub>2</sub> N—CH—COH	$H_2N$ $CH_2$ $N$ $OH$
	CH <sub>2</sub>	o o
Se 	ŠеН	
ĊH <sub>3</sub>		
3,4-dioxyphenylalanine (DOPA)	γ-aminobutyric acid (GABA)	Histamine
0	$H_2N$ $CH_2$ $C$	H <sub>2</sub> N—CH <sub>2</sub>
HO CH <sub>2</sub> CH C OH	$CH_2$ $CH_2$ $OH$	ĊH <sub>2</sub>
NH <sub>2</sub>		N
HO MII2		HN—
Serotonine	Tryptamine	
$H_2N-CH_2$	$H_2N$ — $CH_2$	
CH <sub>2</sub>	$CH_2$	
OH		
H	N H	

Oxidized glutathione

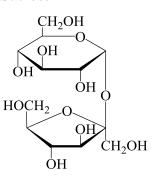
D-glucose	D-mannose	D-galactose	D-fructose
СНО	СНО	СНО	CH₂OH
Н—ОН	НО——Н	Н—ОН	<b>=</b> 0
НО—Н	НО——Н	НО——Н	НО——Н
Н—ОН	Н—ОН	НО——Н	Н—ОН
Н—ОН	Н—ОН	Н—ОН	Н—ОН
CH <sub>2</sub> OH	CH <sub>2</sub> OH	CH <sub>2</sub> OH	CH <sub>2</sub> OH
D-ribose	2-deoxy-D-ribose	Gluconic acid	Glucaric acid
СНО	СНО	СООН	СООН
Н—ОН	Н——Н	Н—ОН	Н—ОН
Н—ОН	Н—ОН	НО——Н	НО——Н
Н—ОН	Н—ОН	Н—ОН	Н—ОН
CH <sub>2</sub> OH	CH <sub>2</sub> OH	Н—ОН	Н—ОН
		ĊН <sub>2</sub> ОН	СООН
Glucuronic acid	Galacturonic acid	2-deoxy-2-amino-α-	2-deoxy-2-amino-α-
СООН	СООН	D-glucopiranose (glucosamine)	D-galactopiranose (galactosamine)
0	OH O	ÇH <sub>2</sub> OH	CH <sub>2</sub> OH
ОН	ОН	0	OH O
ÓН ÓН	ОН	OH OH	OH
		NH <sub>2</sub>	NH <sub>2</sub>

N-acetyl-D-glucosamine	N-acetyl-D-gala	actosamine	α-D-galactopyranose		
CH <sub>2</sub> OH OH OH OH CCCH <sub>3</sub>	CH <sub>2</sub> OH OH	OH —CH <sub>3</sub>	HO OH HO OH HO OH		
β-D-galactopyranose  HO OH HO OH HO OH H OH	Methyl-α-D-gal CH <sub>2</sub> OH OH OH	actopyranoside	Methyl-β-D-galactopyranoside  CH <sub>2</sub> OH  OH  OH  OH  OH		
α-D-glucopyranose	β-D-glucopyran	iose	Ethyl-α-D-glucopyranoside		
HO HO HO OH	HO HO H	ОН	CH <sub>2</sub> OH OH OH OC <sub>2</sub> H <sub>5</sub>		
Ascorbic acid (reduced form)  CH <sub>2</sub> OH  HO  OH		Ascorbic acid (oxidized form)  CH <sub>2</sub> OH  O			
6-phosphate-D-glucopyranose (gphate)  HO HO HO HO OH OH	glucose-6-phos-	1,6-diphosphate	ОНОНООН		
Maltose  CH <sub>2</sub> OH OH OH OH OH	ОН	Cellobiose  HO OH OH OH OH			

#### Lactose

## Lactulose

#### Sucrose

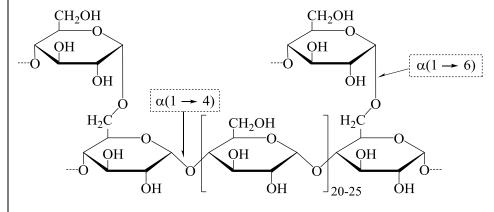


## fragment of cellulose

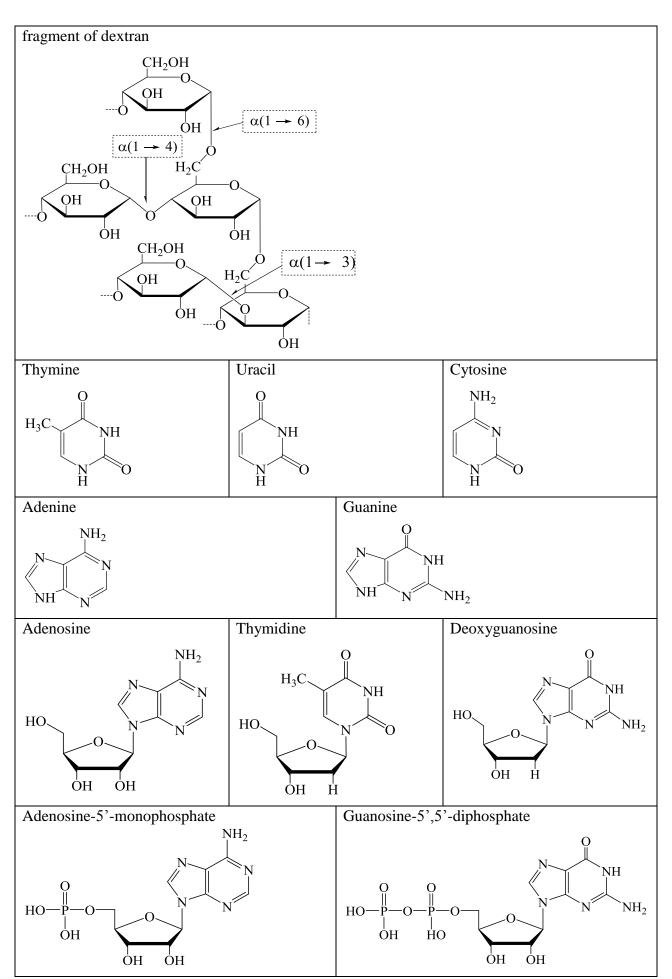
#### fragment of amylose

$$\begin{array}{c|c} CH_2OH & CH_2OH \\ OH & OH \\ OH & OH \\ \end{array}$$

## fragment of amylopectin



## fragment of glycogen



## Adenosine-5',5'-diphosphate

## Uridine-3'-monophosphate

ATP

## GTP

## Cytidine-5',5'-diphosphate

## Cyclic adenosine-3',5'-phosphate

## Coenzyme NAD<sup>+</sup> (oxidized form)

## Coenzyme NADH (reduced form)

Palmitic acid C <sub>15</sub> H <sub>31</sub> COOH	(C <sub>16·0</sub> )				
	O				
	\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\	ОН			
Stearic acid C <sub>17</sub> H <sub>35</sub> COC	OH (C10.0)	ОП			
Stearie acid C1/1135COC	711 (C18:0)	0			
	^^^	C			
Oleje sejd C. H. COO	)	OH Uinglaig a sid	C II COOII		
Oleic acid C <sub>17</sub> H <sub>33</sub> COC 18:1 ω 9	Л	Linoleic acid 18:2 ω 6	C <sub>17</sub> H <sub>31</sub> COOH		
18.1 @ 9	0	18.2 @ 0	0		
	C				
	OH		A A A OH		
Linolenic acid C <sub>17</sub> H <sub>29</sub> CC	ЮН	Arachidonic ac	id C <sub>19</sub> H <sub>31</sub> COOH		
18:3 ω 3		20:4 ω 6			
C	)		СООН		
	ОН				
		lycerols			
1-stearoyl-2,3- dioleoylglycerol	1-oleoyl-2-paln stearoylglycero		1,2,3-trioleoylglycerol		
			О		
$H_{2}C-O-C-C_{17}H_{35}$	$H_2C-O-\overset{\circ}{C}-C_1$		$H_{2}C-O-C-C_{17}H_{33}$		
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	$\begin{array}{c c} & O \\ & HC-O-C-C \end{array}$	<sub>15</sub> H <sub>31</sub>	O   HC-O-C-C <sub>17</sub> H <sub>33</sub>		
$ \begin{array}{c c}  & O \\  & HC-O-\overset{"}{C}-C_{17}H_{33} \\  & \downarrow \\  & H_2C-O-\overset{"}{C}-C_{17}H_{33} \\  & \overset{"}{O} \end{array} $	$H_2C-O-C-C$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			
U		xes	0		
Cetyl palmitate (spermaceti com		Myricyl palmitate (beeswax component)			
		0			
$C_{15}H_{31}$ $O^{-}C_{16}H_{31}$		$C_{15}H_{31}$ $O^{-}C_{31}H_{63}$			

## Glycerophospholipids 1-stearoyl-2-oleoyl-phosphati-1-palmitoyl-2-linolenoyl-1-stearoyl-2-arachidonoyldylserine phosphatidylethanolamine phosphatidylcholine $R_3$ Gonane $R_2$ 17\ D 19 C $R_1$ 10 В Pregnane Estrane Androstane <sup>18</sup>CH<sub>3</sub> <sup>18</sup>CH<sub>3</sub> $^{18}$ CH<sub>3</sub> $\sqrt{^{20}}$ <sup>19</sup>CH<sub>3</sub> <sup>19</sup>CH<sub>3</sub> Cholane Cholestane

# LIST OF COMPOUNDS THAT STUDENT MUST RECOGNISE AND ANALYSE AT THE FINAL EXAMINATION

Folic acid

$$\begin{array}{c|c} O & COOH \\ \hline \\ HN & N \\ \end{array}$$

Vitamin E (α-tocopherol)

β-carotene

Vitamin A (retinol)

## Inositoltriphosphate

## Sphingolipids

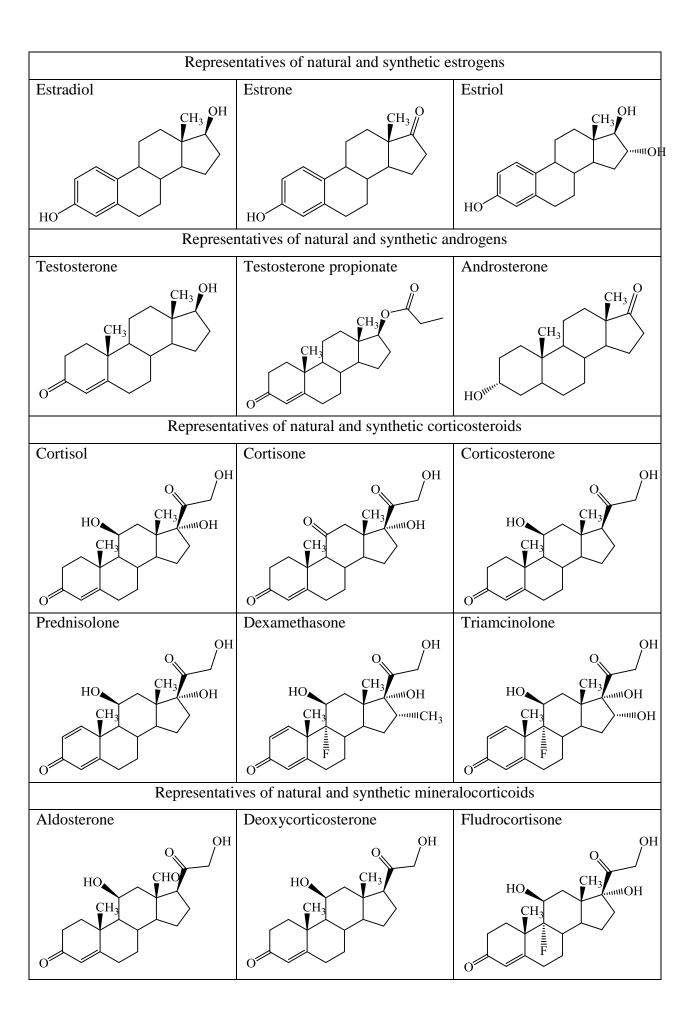
## Sphingomyelin

$$\begin{array}{c|c} C_{17}H_{29} \\ H_3C \\ N + \\ CH_3 \\ O \end{array} \begin{array}{c} O \\ P \\ O \\ OH \end{array} (CH_2)_{12}CH_3$$

## Glycolipids

## Cerebroside

## Ganglioside



## Representatives of natural and synthetic progestogens and progestins Progesterone Levonorgestrel ОН ..... $CH_3$ Н $\underline{C}H_3$ Cholesterol and its derivatives 7-dehydrocholesterol Cholesterol $\underline{CH_3}$ $\underline{CH_3}$ CH<sub>3</sub> $\underline{C}H_3$ HO Group D vitamins and its precursors Ergosterol Vitamin D<sub>2</sub> CH<sub>3</sub> $CH_3$ $CH_3$ $CH_2$ Ю 1α,25-dihydroxycholecflciferol Vitamin D<sub>3</sub> (cholecalciferol) (calcitriol – activated form of vitamin D<sub>3</sub>) CH<sub>3</sub> $\underline{\mathrm{CH}}_3$ $CH_2$ $CH_2$

## Bile acids Cholic acid Deoxycholic acid -СООН -СООН $\underline{C}H_3$ $CH_3$ $\underline{C}H_3$ $CH_3$ $HO^{\mu \nu \nu}$ '′⁄⁄//ОН $HO_{lllll}$ Glycocholic acid Taurocholic acid QH $\underline{C}H_3$ $\underline{C}H_3$ ΝH NH CH<sub>3</sub> CH<sub>3</sub> HOOC HO<sub>3</sub>S "///OH НО ′′′′′/ОН Ħ Porpins Protoporphyrin Heme соон ноос соон ноос Anesthetics Lidocaine Ultracaine OCH<sub>3</sub> NH o =

## Polymers in dentistry

## Spiroorthocarbonate (SOC)

$$\begin{array}{c|c}
 & O & O \\
\hline
R_1 & C & R_2 \\
\hline
O & O & O \\
\hline
O &$$

## Epoxy resin

## Polyurethanes

$$\begin{bmatrix} H & H & H & H & C & CH_2 &$$

## Polysiloxanes

$$\begin{bmatrix} R \\ | \\ Si - O \end{bmatrix}_n$$

$$CH_3$$

$$Si$$

$$H_3C$$

$$OC_2H_5$$

$$CH_3$$

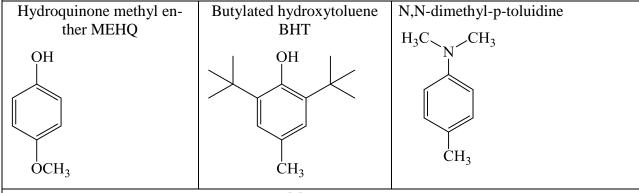
$$OC_2H_5$$

$$CH_3$$

$$OC_2H_5$$

$$OC_2H_5$$

## Free-radical polymerization inhibitors



## Monomers

$$\begin{array}{c} CH_{3} \\ C \\ C \\ C \\ C \\ CH_{2} \\ CH_{2} \\ CH_{2} \\ CH_{3} \\ CH_{4} \\ CH_{4} \\ CH_{5} \\ CH_{5}$$

## Ethoxy-Bis-GMA

## Photoinitiators

## Camphoroquinone (CQ)

 $CH_3$ 

N,N-dimethylaminoethyl methacrylate (DMAEMA)

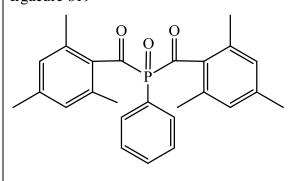
$$H_3C$$
 $CH_2$ 
 $CH_2$ 
 $CH_3$ 
 $CH_3$ 

## LucirinTPO-L

CH<sub>3</sub>  $H_3C$ 

## Benzil BZ

Irgacure 819



## Phenyl propanedione (PPD)

$$O$$
  $CH_3$ 

## Ivocerin

## Silane (coupling agent)

3-methylacryloxypropyltrimetoxysilane

## Components of adhesive systems

Dimethacrylate of glycerophosphoric acid

2-hydroxyethyl methacrylate (HEMA)

$$\begin{array}{c} O \\ \parallel \\ C \\ C \\ C \\ CH_{3} \end{array}$$
 CH<sub>2</sub> CH<sub>2</sub> OH

## NTG-GMA

$$\begin{array}{c|c} O & O & O \\ HO & C - CH_2 - N - CH_2 - CH - CH_2 \\ \hline OH & CH_3 \\ \hline \end{array}$$

Anhydride 4-acrylic hydroxyethyl of pyromellitic acid (4-AETA)

Anhydride 4-methacrylic hydroxyethyl of pyromellitic acid (4-META)

#### **ANSWERS TO TESTS**

## Labwork № 1. Classification and nomenclature of organic compounds

Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8	Test 9	Test 10
2	2	4	4	1	1	3	2	1, 3, 4	3

#### Labwork № 2. Chemical bond structure and atom effects in the organic molecules

Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8	Test 9	Test 10
2, 3, 4	2, 4	3, 4	3	2	2, 3, 4	3	4	1, 2	A3 B2
									C3 D4

## Labwork № 3. Stereoisomerism, its role for biological activity demonstration

Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8	Test 9	Test 10
4	1, 3, 4	4	2	1, 3	4	1, 2	1, 3	A2 B1	2
								C4 D3	

## Labwork No 4. Hydrocarbons

Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8	Test 9	Test 10
1, 2, 3, 5	2, 4	1, 2	3	1, 4	2	1, 4	2	3, 5	2

#### Labwork № 5. Monofunctional hydrocarbon derivatives

Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8	Test 9	Test 10
2	4	1, 3, 4	1,3	3, 4, 1, 2	2	2, 4	4	2	A3 B2
									C1 D4

#### Labwork № 6. Biologically important reactions of aldehydes and ketones

Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8	Test 9	Test 10
2, 3	A2 B4	2	3	1, 3	1, 2	1, 3, 4	4	2	2
	C1 D3								

#### Labwork № 7. Carboxylic acid and their derivatives

Ī	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8	Test 9	Test 10
ſ	1, 4, 3, 2	A4 B2	1	1, 2, 4	1, 3, 4, 5	2	1, 2, 4	2, 3	3, 4	1, 4
		C3 D1								

#### Labwork № 9. Poly- and heterofunctional compounds

Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8	Test 9	Test 10
4	3	3	2	1, 3, 4	1, 2, 4	1	2, 3, 4	3, 4	1

## Labwork № 10. Organic compounds using in stomatology

Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8	Test 9	Test 10
2	3	4	2	4	2	2, 3	3	2, 3	1, 3, 4

#### Labwork № 11. Carbohydrates. Monosaccharides

Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8	Test 9	Test 10
1, 2, 4	1, 2	3	2	2	2	4	3, 4	1	1, 2, 3

## Labwork № 12. Oligo- and polysaccharides

Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8	Test 9	Test 10
3	1, 2, 4	4	1, 2, 3	3, 4	2, 3, 4	4	3	3	2, 3, 4

## Labwork № 13. Structure and reactivity of amino acids

Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8	Test 9	Test 10
1, 3	1, 3, 4	1, 4, 5	2, 3, 4, 5	1, 2, 3	3, 5	2	2, 3, 4	1	3

## Labwork № 14. Peptides. The levels of protein organization

Ī	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8	Test 9	Test 10
ĺ	2, 4, 5	2, 3, 4	1, 3, 4	1, 3, 5	1, 2, 3, 5	2	1, 2, 4	1	1, 3, 4	2

## Labwork № 15. Nucleosides. Nucleotides. Nucleic acids

Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8	Test 9	Test 10
1, 3	3, 4	1, 3, 4	2	1, 3, 5	2	3	2	2	1

## Labwork № 16. Lipids. Structure, properties. Lipid peroxidation

Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8	Test 9	Test 10
3	1, 2	2, 3, 5	4	2, 3	1, 3, 4	3	1	1, 4	1

#### Учебное издание

Ринейская Ольга Николаевна Ермоленко Елена Михайловна Глинник Станислава Владимировна

# БИООРГАНИЧЕСКАЯ ХИМИЯ BIOORGANIC CHEMISTRY

Практикум для студентов-стоматологов На английском языке

3-е издание, исправленное

Ответственная за выпуск О. Н. Ринейская Переводчики О. Н. Ринейская, Е. М. Ермоленко, С. В. Глинник Компьютерная вёрстка А. В. Янушкевич

Подписано в печать 01.06.22. Формат 60×84/8. Бумага «Discovery». Ризография. Гарнитура «Times». Усл. печ. л. 12,55. Уч.-изд. л. 4,61. Тираж 54 экз. Заказ 204.

Издатель и полиграфическое исполнение: учреждение образования «Белорусский государственный медицинский университет». Свидетельство о государственной регистрации издателя, изготовителя, распространителя печатных изданий № 1/187 от 18.02.2014. Ул. Ленинградская, 6,220006, Минск.