MINISTRY OF PUBLIC HEALTH
ZAPOROZHYE STATE MEDICAL UNIVERSITY
DEPARTMENT OF ORGANIC AND BIOORGANIC CHEMISTRY

GUIDELINES AND LABORATORY PROTOCOLS OF BIOORGANIC CHEMISTRY

for medical students
specialty "Medicine"

1st-year student of ___ group

_____

surname, name

Zaporozhye
2016

GUIDELINES AND LABORATORY PROTOCOLS OF BIOORGANIC CHEMISTRY was approved by Zaporozhye State Medical University Methodical Council (Protocol № 1 from 29.09.2016) and recommended for medical students of specialty "Medicine".

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THEMATIC PLANS OF LESSONS

№	Theme	Hours
1	Classification. Principles of nomenclature. The spatial structure of organic molecules. Isomerism.	2
2	Electronic structure of chemical bonds and mutual influence of atoms in organic molecules. Acidic and basic properties. Chemical reactions mechanisms.	2
3	Aromatic and aliphatic hydrocarbons. Structure, nomenclature, chemical properties.	2
4	Halogen and hydroxy hydrocarbons, their thio analogues. Amines. Structure, nomenclature, chemical properties.	2
5	***Final submodule control I: «The theoretical basis of the structure and reactivity of organic compounds, aliphatic and aromatic, hydroxy and halogeno hydrocarbons, their thio analogues and amines."***	**2**
6	Investigation of the aldehydes and ketones' chemical properties. Biologically important reactions of carbonyl compounds.	2
7	Structure, properties and biological significance of carboxylic acids. Heterofunctional carboxylic acids' (hydroxy, oxo, phenolic) derivatives.	2
8	Polyfunctional derivatives of aliphatic and aromatic compounds.	2
9	Saponificated lipids: fats, oils, phospholipids, waxes. Structure, nomenclature, chemical properties.	2
10	Non-saponificated lipids: prostaglandins, terpenes, steroids. Structure, nomenclature, chemical properties.	2
11	***Final submodule control II: «Heterofunctional organic compounds - metabolites and basis of the most important***	**2**

	groups of drugs. Carbonyl compounds. Carboxylic acids and their functional derivatives".	
12	α-Amino acids. Peptides. Structure, nomenclature, chemical properties.	2
13	Structural organization, physical and chemical properties of proteins. Synthesis and analysis.	2
14	Carbohydrates. The structure, classification and chemical properties of monosaccharides.	2
15	The structure and functions of di- and polysaccharides.	2
16	Classification, structure, nomenclature, chemical properties and biological value of heterocyclic compounds.	2
17	The structure and biochemical function of nucleosides, nucleotides and nucleic acids.	2
18	***Final submodule control III: "Biologically important classes of bioorganic compounds. Heterocyclic. Biopolymers and their structural components".***	**2**
	Together	**36**
19	***FINAL MODULE CONTROL "Biologically important classes of bioorganic compounds. Biopolymers and their structural components".***	**2**
	Together	**38**

EVALUATION CRITERIA OF STUDENT ACADEMIC PROGRESS

Every lesson student gets mark: "excellent" - 5 points, "good" - 4 points, "satisfactory" - 3 points, "unsatisfactory" - 0 points.

The student is allowed to take the final module control if he scores no less than 54 mark points (18 × 3 = 54) for 18 lessons, which corresponds to 60 rate points.

The final module is counted finished if the student scores no less than 50 rate points.

Characteristics	The minimum score	The maximum score
Total score for submodules.	**60**	**110**
Individual student self-work: Preparation the scientific literature review on the selected topic.	**–**	**10**
The score for final module test.	**50**	**80**
TOTAL	**110**	**200**

AT THE FINAL MODULE EACH STUDENT MUST BE ABLE TO:

1. name compounds by IUPAC rules;
2. determine the electronic influence of substituents (inductive and mesomeric effects) and to predict the effect of substituents on the distribution of electron density in the molecule;
3. compare the acid-base properties of compounds;
4. know the structural formulas of the following list of compounds: methane, ethane, propane, butane, pentane, ethylene, propene, butene-1, butene-2, penten-1 penten-2, acetylene, propyne, 2-methylbut-1,3-diyne, pent-2-yn, benzene, toluene, methanol, ethanol, propan-1-ol, propan-2-ol, 2-metylpropanol, 2-metylpropan-2-ol, phenol, methyl iodide, formaldehyde, ethanal (acetaldehyde) propan-2-one (acetone), pentan-3-on, benzaldehyde, formic acid, acetic acid, propionic acid, butyric acid, oxalic acid, malonic acid, succinic acid, glutaric acid, benzoic acid, stearic acid, palmitic acid, oleic acid, linoleic acid, linolenic acid, salicylic acid, acetoacetic ester, acetic anhydride, pyrrole, furan, thiophene, pyridine, pyrazole, imidazole, purine, xanthine, barbituric acid, uric acid, aspirin (acetylsalicylic acid), paracetamol, benzocaine, novocaine, sulfonamides, nicotinic acid, methyl salicylate, ethyl salitsylate, ribose, glucose, galactose, fructose, lactose, maltose, celobioze, sucrose, trehalose, adenine, thymine, uracil, cytosine, guanine and structure of proteinogenic amino acids.

CHEMISTRY LABORATORY SAFETY RULES

One often forgets that chemistry is a potentially dangerous enterprise; a careless attitude often results in disastrous consequences. Therefore, extreme caution should be exercised at all time, especially when one handles chemical reactions that are exothermic or when dealing with toxic, reactive chemicals, carcinogens using any glassware.

You are expected to learn and adhere to the following general safety guidelines to ensure a safe laboratory environment both for yourself and people you are working with. Additional safety precautions will be announced in class prior to experiments if there is potential danger. Students who are failed to follow all the safety rules have to leave the laboratory and obtain 0 points for the lesson.

PERSONAL PROTECTION

- Laboratory coats and caps provide an important barrier for your clothes and, more important, your skin from chemicals. The laboratory coat should fit comfortably, have long sleeves, and should be clean.
- Laboratory gloves are an essential part of safe laboratory practice and must be worn while handling chemicals.
- Closed toe shoes and long pants must be worn in the lab. Sandals and shorts are not allowed.
- The coats, backpacks, etc., should not be left on the lab benches and table. Beware that lab chemicals can destroy personal possessions.
- Eating, drinking, and smoking are strictly prohibited in the laboratory.
- The most common forms of eye protection include safety glasses (with side shields), goggles, and face shields. Prescription eye glasses are acceptable provided that the lenses are impact resistant and they are equipped with side shields. Contact lenses are not allowed. Even when worn under the safety goggles, various fumes may accumulate under the lens and cause serious injuries or blindness.
- Long hair must be tied back when using open flames.
- Learn where the safety and first-aid equipment is located. This includes fire extinguishers, fire blankets, and eye-wash stations.
- Always wash your hands before leaving the lab.
- Inform the teacher immediately in case of an accident.

PROPER HANDLING OF CHEMICALS AND EQUIPMENT

- Consider all chemicals to be hazardous unless you are instructed otherwise. Material Safety Data Sheets (MSDS) are available in lab for all chemicals in

use. These will inform you of any hazards and precautions of which you should be aware.

- Know what chemicals you are use. Carefully read the label twice before taking anything from a bottle. Learn how to interpret hazardous materials labels.
- Never taste chemicals.
- No unauthorized experiments are to be performed. Every experimental procedure must be consulted with your teacher.
- Never directly smell the source of any vapor or gas. You should waft a small sample of scent air to your nose with cupped hand. Do not inhale these vapors but detect if the odor is observed.
- The excess of reagents are never to be returned to their bottles. If you take too much, dispose of the excess.
- Many common reagents, for example, alcohols and acetone, are highly flammable. Do not use them near working burner.
- Never leave the burners unattended. Turn them off whenever you leave your workstation. Be sure that the gas is shut off at the bench rack when you leave the lab.
- Never point a test tube or any vessel that you are heating at yourself or your neighbor - it may erupt like a geyser.
- Always pour acids into water. If you pour water into acid, the appearing exothermic reaction causes water transformation into steam with powerful acid splattering.
- Clean up all broken glassware immediately and dispose of it properly.
- Contact the stockroom for special bottle for mercury spills.

FIRST AID IN THE LABORATORY

THE OCCURRENCE OF AN ACCIDENT OF ANY KIND IN THE LABORATORY SHOULD BE REPORTED IMMEDIATELY TO YOUR TEACHER, EVEN IF IT SEEMS RELATIVELY MINOR!

Thermal burns. In the case of a burn, apply cold water and/or ice immediately to the burned area until the pain subsides. Wrap the burned area to protect from infection. It is best to avoid oils and ointments in first aid treatment since these frequently complicate the physician's job.

Chemical burns. Areas of the skin with which corrosive chemicals have come in contact should be immediately and thoroughly washed with soap and warm

water. Acid or minor bromine burns may then be treated with 5% sodium carbonate solution. Alkali burns can be washed with 5% acetic acid solution or saturated boric acid solution. If the burns are minor, apply burn ointment; for treatment of more serious burns, see a physician. If chemicals, in particular corrosive or hot reagents, come in contact with the eyes, immediately flood the eyes with water from the nearest outlet. A specially designed eyewash fountain is useful if available in the laboratory. Do not touch the eye. The eyelid as well as the eyeball should be washed with water for several minutes. In all instances where sensitive eye tissue is involved in such an accident, consult an ophthalmologist as soon as possible.

Fire. Your first consideration is to remove yourself from any danger, not to extinguish the fire. If *it is possible to do so without endangering yourself*, turn off any burners and remove containers of flammable solvents from the immediate area to prevent the fire from spreading. For the most effective use of a fire extinguisher, direct its nozzle toward the base of the flames. If your clothing is on fire, DO NOT RUN; rapid movement will only fan the flames. Roll on the floor to smother the fire and to help keep the flames away from your head. Your neighbors can help to extinguish the flames by using fire blankets, laboratory coats, or other items that are immediately available. Do not hestitate to aid your neighbor if he or she is involved in such an emergency; a few seconds delay may result in serious injury. If burns are minor, apply a burn ointment. In the case of serious burns, do not apply any ointment; seek professional medical treatment at once.

Minor bleeding. Allow the blood to flow a few moments. Flush the wound thoroughly with water. Apply an antiseptic and bandage to the wound to prevent contamination. Minor cuts may be treated by ordinary first-aid procedures; seek professional medical attention for serious cuts. If severe bleeding indicates that an artery has been severed, attempt to stop the bleeding with compresses and pressure; a tourniquet should be applied only by those who have received first-aid training. Arrange for emergency room treatment at once. A person who is injured severely enough to require a physician's treatment should be accompanied to the doctor's office, or infirmary, even if he or she claims to be all right. Persons in shock, particularly after suffering burns, are often more seriously injured than they appear to be.

Toxic fumes. If there are complaints of a headache or dizziness in the laboratory in which the odors of such toxic gases are, you should go immediately to a fresh air outside.

Read and Agree with the Safety Rules _____

Name Signature

Lesson №1

Subject: CLASSIFICATION. PRINCIPLES OF NOMENCLATURE. THE SPATIAL STRUCTURE OF ORGANIC MOLECULES. ISOMERISM.

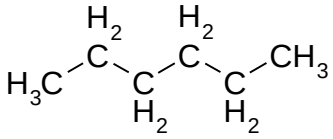
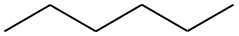
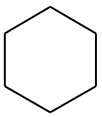
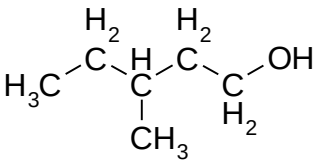
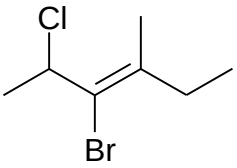
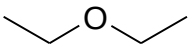
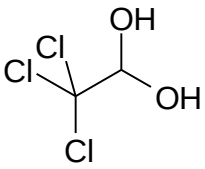
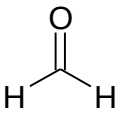
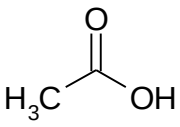
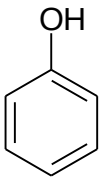
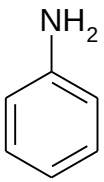
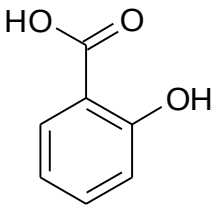
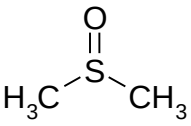
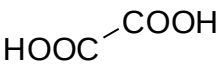
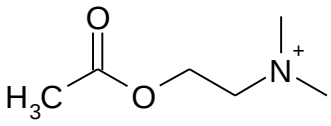
Subject motivation: The rapid development of Pure and Applied Organic Chemistry has created serious problems for the development of the huge flow of new information and theoretical understanding of factual material. In this regard, the assimilation of chemical language, nomenclature rules, the formation of ideas about the unity of structure, configuration, conformation of organic molecules are of much importance for the successful study and exchange of chemical information, understanding the link "structure - biological activity".

Learning goal: To study the basic principles of chemical nomenclature, classification, the spatial structure of organic compounds, and to determine the class of drugs by the main functional group.

THEORETICAL QUESTIONS

1. The theory of the chemical structure of organic compounds by A.M. Butlerov. The functional groups of organic compounds.
2. The International Union of Pure and Applied Chemistry (IUPAC) nomenclature of organic compounds.
3. The spatial structure of methane, ethylene, acetylene. Representation of the structure in three-dimensional, ball-and-stick or space-filling model, and expanded structural formulas.
4. The conformations of ethane and their potential energies. The Newman projections: eclipsed (30°) and staggered (60°, anti and gauche).
5. The cyclohexane and methylcyclohexane conformations.
6. Chiral molecules. Optical activity. Relative and absolute configurations. The D and L system: relative configuration. The R-S system of absolute configuration.
7. Stereochemistry of chemical reactions, which produce chiral centers.
8. Constitutional (structural) isomerism of alkanes. Substituted cyclohexanes: axial and equatorial hydrogen atoms Distributed cyclohexanes: cis-trans isomerism.
9. *Cis-trans* isomerism of alkenes.

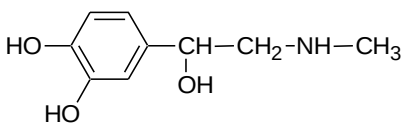
Give the IUPAC name for each of the following substances:

ADDITIONAL PROBLEMS

1. Indicate which class of organic compounds aniline can be referred:
   A. primary
   B. aliphatic amine
   C. primary aromatic amine
   D. secondary aromatic amine
   E. tertiary aromatic amine

2. Specify the functional group which is absent in the molecule of adrenaline:



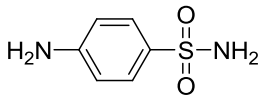
   A. the primary alcoholic hydroxyl

B. secondary alcoholic hydroxyl
C. secondary amine
D. phenolic hydroxyl
E. aromatic ring

3. Specify the number of asymmetric carbon atoms in the molecule of noradrenaline:

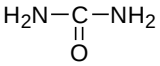
A. 0
B. 1
C. 2
D. 3
E. 4

4. Determine which class of organic compounds streptocid is referred to:



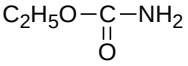
A. aromatic amine
B. carbocyclic amine
C. aromatic acid
D. aromatic sulfonic acid
E. amide of the aromatic sulfonic acid

5. Indicate which class of organic compounds urea can be referred:



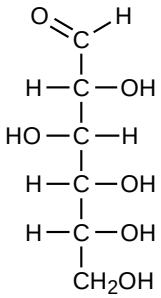
A. amino acid
B. diamide of the carboxylic acid
C. ketone
D. aldehyde
E. diamino carboxylic acid

6. Specify the senior functional group in the molecule of urethane:



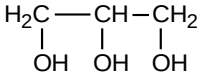
A. amino group
B. ketone group
C. amide group
D. ester group
E. ether group

7. Specify the number of asymmetric carbon atoms in the aldehyde form of glucose:



A. 1
B. 2
C. 3
D. 4
E. 5

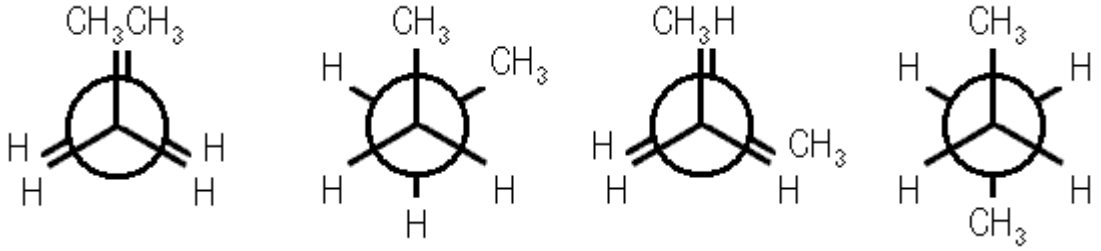
8. Glycerin is triatomic alcohol, which is the part of fats. Specify it's number of asymmetric carbon atoms (chiral centers):



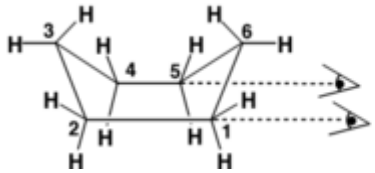
A. 0
B. 1
C. 2
D. 3
E. 4

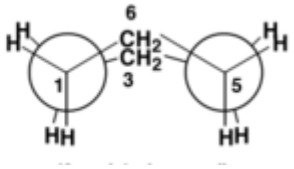
CHALLENGE QUESTIONS

1. How is the tetrahedral shape maintained in a molecule with two carbon atoms?
2. Name the Newman projections of the butane.



3. Name and choose the most preferred conformation of the cyclohexane.





Literature

1. Organic Chemistry / J. McMurry. – 8th ed. Brooks/Cole. 2012; 1262 p.
2. Principles of general, organic, and biological chemistry / J.G. Smith. – 1st ed. McGraw-Hill. 2012; 596 p.
3. Organic Chemistry / W.H. Brown, Ch.S. Foote, B.L. Iverson, E.V. Anslyn. – 5th ed. Brooks/Cole. 2011; 1146 p.
4. Organic Chemistry / I. Blei, G. Odian – 2nd ed. W. H. Freeman and Company. 2006; 787 p.
5. General, Organic, and Biological Chemistry: An Integrated Approach / K.W. Raymond. – 2nd ed. John Wiley & Sons, Inc. 2008; 541 p.
6. Lectures.

Lesson №2

Subject: ELECTRONIC STRUCTURE OF CHEMICAL BONDS AND MUTUAL INFLUENCE OF ATOMS IN ORGANIC MOLECULES. ACIDIC AND BASIC PROPERTIES. CHEMICAL REACTIONS MECHANISMS.

Subject motivation: The knowledge about electronic structure of atomic orbitals and their hybridization, the covalent bond, the conjugation, the electronic effects, their mutual influence is very important part of the organic chemistry study, that helps to understand reactivity of the biologically important organic compounds, qualitatively compare thermodynamic stability of the compounds, to interpret the mechanisms of biochemical reactions. The acidity and basicity of organic compounds are among the fundamental concepts, which are necessary for understanding bioorganic chemistry as well as other subjects. Knowledge of these properties are used to correctly predict the reaction mechanism, to understand the acid and base catalysis, to assess the compatibility of drugs, etc.

Learning goal: To form knowledge about the structure of chemical bonds, electron effects of substituents; the structure of molecules with conjugated bonds

as a thermodynamically stable systems, which are used in the construction of biologically important compounds. To form the knowledge of organic compounds acidity and basicity, their relation to oxidation as the most important properties that lead to the many important chemical reactions in living organisms.

THEORETICAL QUESTIONS

1. The bonding in organic chemistry. The sp^3, sp^2, sp hybrid orbitals.
2. The hydrogen-bonding. Polar covalent bonds.
3. Bronsted-Lowry acids and bases. Nucleophilicity of the substances.
4. Inductive and resonance effects. Substituent's effects in aromatic rings.
5. Radical substitution reactions (S_R) of alkanes and cycloalkanes.
6. Electrophilic addition reactions (A_E) of alkenes, alkadienes and alkynes.
7. Electrophilic substitution reactions (S_E) of arenes and heteroaromatic compounds.
8. The nucleophilic substitution reactions (S_N) at the saturated carbon atom.
9. Elimination reactions (E).
10. Oxidation of hydrocarbons.

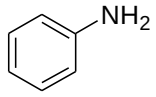
ADDITIONAL PROBLEMS

1. Determine the influence of the chlorine atom in the molecule of vinyl chloride:

$H_2C{=}CH{-}Cl$

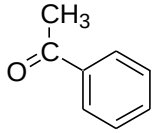
A. σ-electrons acceptor
B. π-electrons acceptor
C. σ- and π-electrons acceptor
D. σ- and π-electrons donor
E. σ-electrons donor and π-electrons acceptor

2. Specify the type and charge of the electronic effects of the nitrogen atom in the molecule of the aniline



A. -I
B. -I; -M
C. -I; +M
D. +I
E. +I; +M

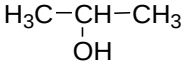
3. Specify the type and charge of the electronic effects of the oxygen atom of the carbonyl group in the molecule of acetophenone:



A. -I
B. -I; -M
C. -I; +M

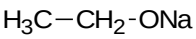
D. +I
E. +I; +M

4. Specify the type and charge of the electronic effect of the oxygen in the molecule of 2-propanol:



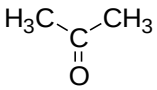
A. -I
B. +I
C. -M
D. +M
E. -I; +M

5. Specify the type and charge of the electronic effect of the oxygen atom in a molecule of sodium ethoxide:



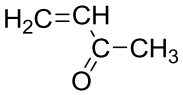
A. -I
B. +I
C. -M
D. +M
E. -I; +M

6. Specify the type and charge of the electronic effect of the oxygen atom in a molecule of acetone:



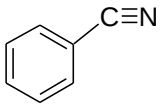
A. -I
B. -M
C. +I
D. +M
E. -I; -M

7. Specify the type and charge of the electronic effects of the oxygen atom in the molecule butenone:



A. +I
B. +M
C. -I
D. -I; +M
E. -I; -M

8. Specify the type and charge of the electronic effect of the nitrogen atom in the molecule of benzonitrile:



A. -I; -M
B. -I
C. -I; +M
D. -M
E. +M

LABORATORY PRACTICE

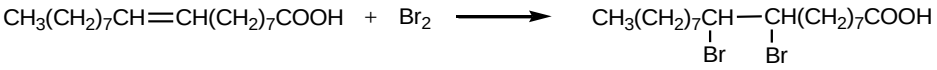
Protocol № 2 Date _____

Experiment № 1

Bromination of unsaturated compounds

Place 3-4 drops of oleic acid in the test tube, and dissolve it in 1 ml of carbon tetrachloride (CCl_4). Then add 4-5 drops of 5% solution of bromine in carbon tetrachloride. Note the observed changes.

The chemistry of the reaction:



Observations:

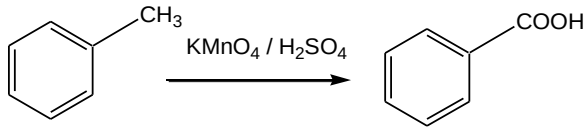
Conclusions:

Experiment № 2

Oxidation of the side chains of benzene homologues.

Place 5 drops of water, 3 drops of 2% potassium permanganate solution, and 1 drop of 10% sulfuric acid solution in the test tube. Add 1-2 drops of toluene and vigorously shake the tube. Then heat the mixture in the burner flame. Note how the solution changes its color. Regardless of its length, each side chain of benzene eventually forms a carboxyl group in the result of oxidation. Thus, using the oxidation reaction, it is possible to establish the presence of side chains in aromatic hydrocarbons.

The chemistry of the reaction:



Observations:

Conclusions:

CHALLENGE QUESTIONS

1. Write the reaction of acetylene hydration (Kucherov's reaction). Name the product of the reaction.

2. Determine the hybridization of carbon atoms in the molecule of the following compounds: pent-1-en-3-yne, penta-2,3-diene, naphthalene, pyrrole, furan, pyridine.

Literature

1. Organic Chemistry / J. McMurry. – 8th ed. Brooks/Cole. 2012; 1262 p.
2. Principles of general, organic, and biological chemistry / J.G. Smith. – 1st ed. McGraw-Hill. 2012; 596 p.
3. Organic Chemistry / W.H. Brown, Ch.S. Foote, B.L. Iverson, E.V. Anslyn. – 5th ed. Brooks/Cole. 2011; 1146 p.
4. Organic Chemistry / I. Blei, G. Odian – 2nd ed. W. H. Freeman and Company. 2006; 787 p.
5. General, Organic, and Biological Chemistry: An Integrated Approach / K.W. Raymond. – 2nd ed. John Wiley & Sons, Inc. 2008; 541 p.
6. Lectures.

Lesson №3

Subject: AROMATIC AND ALIPHATIC HYDROCARBONS. STRUCTURE, NOMENCLATURE, CHEMICAL PROPERTIES.

Subject motivation: The hydrocarbons are the most broadly used organic known compounds. The greatest amounts of hydrocarbons are used as fuel for combustion, particularly in heating and motor fuel applications. In medicine the mineral hydrocarbons used as adjutants for vaccines, bases for ointments, emollients, ingredients in antiparasiticides, and slow release devices.

Learning goal: To gain skills to predict the ability of hydrocarbons to polar or nonpolar reactions due to electronic structure of the carbon atoms and electronic effects of the substituents or heteroatoms introduced into the aromatic ring.

THEORETICAL QUESTIONS

1. Saturated hydrocarbons: alkanes (paraffins). Petroleum and petróleum refining. Physical properties of alkanes. Conformations of alkanes. Constitutional (structural) isomerism of alkanes.

2. Combustion of alkanes. Halogenation of alkanes. Chlorination of methane Cycloalkanes.
3. Conformations of cyclohexane. Substituted cyclohexanes: axial and equatorial hydrogen atoms. Bicyclic alkanes.
4. Unsaturated hydrocarbons: alkenes and alkynes. Nomenclature and structure of alkenes.
5. *Cis-trans* isomerism of alkenes. 1,3-Butadiene: electron delocalization.
6. The stability and light absorption of conjugated polyenes.
7. Addition reactions of alkenes. Activation of the π-bond.
8. Addition of hydrogén halides to alkenes. Acid-catalyzed hydration of alkenes.
9. Addition of halogens to alkenes. Catalytic hydrogenation of alkenes.
10. Polymerization of alkenes.
11. The Kekulé structure fór benzene. Aromaticity and Hückel's rule.
12. Conjugated compounds, conjugation energy, π – π and π-p conjugation.
13. Nomenclature of aromatic compounds. Properties of aromatic hydrocarbons.
14. Benzene and its derivatives. Polycyclic aromatic hydrocarbons.
15. Chemical reactions of aromatic compounds.
16. Effect of substituents: reactivity and orientation.
17. Reactivity of polycyclic and heterocyclic aromatic compounds. Oxidation.

LABORATORY PRACTICE

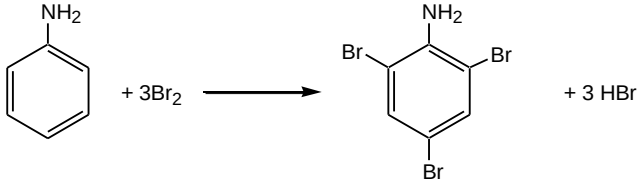
Protocol № 3 Date_____

Experiment № 1

The formation of tribromaniline

Place one drop of aniline and 5-6 drops of water in the test tube, shake well and add a few drops of bromine water until a white precipitate of 2,4,6-tribromaniline is formed. The bromination proceeds quantitatively. And this reaction is used in pharmaceutical analysis for the discovery of aniline and some of its derivatives.

The chemistry of the reaction:



Observations:

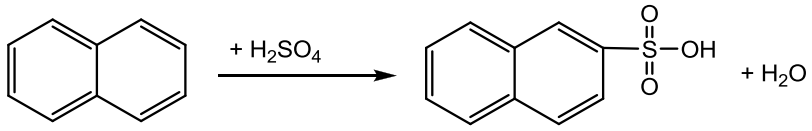
Conclusions:

Experiment № 2

Sulfonation of naphthalene.

Place a bit of naphthalene in a dry test tube. Heat the tube till the naphthalene is melt. Then let it cool and add 10 drops of concentrated sulfuric acid (**you should add it in a fume hood**!). Gently heat the test tube in the burner flame, shaking constantly until formation of the completely homogeneous mixture. Then let the mixture cool, and add 10 drops of water. Heat the mixture slightly again. Crystals obtained after the cooling are the *β*-naphthalenesulfonic acid.

The chemistry of the reaction:

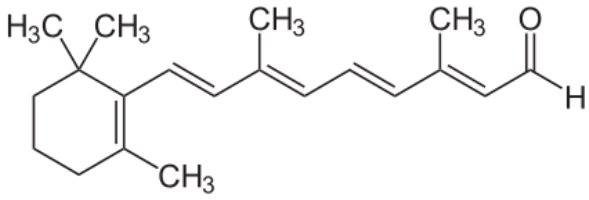


Observations:

Conclusions:

CHALLENGE QUESTIONS

1. When ethylbenzene is brominated the substitution could happen as in the aromatic ring so in the side chain. Write the bromination of ethylbenzene in each of these directions and name the reaction products. Specify the conditions and mechanisms of these reactions.
2. Write the formulas of furan, thiophene, pyrrol, pyrazole, imidazole, pyridine, pyrimidine, purine. Number the atoms in molecules. Determine the criteria of aromaticity of these compounds.
3. Compare the electron density in the molecule of heptadiene-2,4-oic acid and butadiene-1,3.
4. Retinal, also called retinaldehyde or vitamin A aldehyde, is one of the many forms of vitamin A., is a polyene chromophore, and bound to proteins called opsins, is the chemical basis of animal vision. Mark the conjugate chain, and specify the form and sign the electronic effects of the aldehyde group.



Literature

1. Organic Chemistry / J. McMurry. – 8th ed. Brooks/Cole. 2012; 1262 p.
2. Principles of general, organic, and biological chemistry / J.G. Smith. – 1st ed. McGraw-Hill. 2012; 596 p.
3. Organic Chemistry / W.H. Brown, Ch.S. Foote, B.L. Iverson, E.V. Anslyn. – 5th ed. Brooks/Cole. 2011; 1146 p.
4. Organic Chemistry / I. Blei, G. Odian – 2nd ed. W. H. Freeman and Company. 2006; 787 p.
5. General, Organic, and Biological Chemistry: An Integrated Approach / K.W. Raymond. – 2nd ed. John Wiley & Sons, Inc. 2008; 541 p.
6. Lectures.

Lesson 4

Subject: HALOGEN AND HYDROXY HYDROCARBONS, THEIR THIO ANALOGUES. AMINES. STRUCTURE, NOMENCLATURE, CHEMICAL PROPERTIES.

Subject motivation: The halogenated hydrocarbon is a volatile liquid used as an inhalation anesthetic, administered in combination with oxygen and/or nitrous oxide. The first widely used inhalation anesthetic was diethyl ether, which is a non-substituted (non-halogenated) ether. Diethyl ether was initially replaced by non-flammable (but more toxic) halogenated hydrocarbons such as chloroform and trichloroethylene. The only halogenated hydrocarbon used for anesthesia is halothane. Many drugs are designed to mimic or to interfere with the action of natural amine neurotransmitters, exemplified by the amine drugs: Chlorpheniramine is an antihistamine that helps to relieve allergic disorders due to cold, hay fever, itchy skin, insect bites and stings; Chlorpromazine is a tranquilizer that sedates without inducing sleep. It is used to relieve anxiety, excitement, restlessness or even mental disorder; Ephedrine and phenylephrine, as amine hydrochlorides, are used as decongestants; Amphetamine, methamphetamine, and methcathinone are psychostimulant amines that are

listed as controlled substances by the US DEA; Amitriptyline, imipramine, lofepramine and clomipramine are tricyclic antidepressants and tertiary amines; Nortriptyline, desipramine, and amoxapine are tricyclic antidepressants and secondary amines; Substituted tryptamines and phenethylamines are key basic structures for a large variety of psychedelic drugs; Opiate analgesics such as morphine, codeine, and heroin are tertiary amines.

Learning goal: To gain skills to predict the ability of halogenated hydrocarbons to polar reactions due to electronic effects of the substituents. To predict basic properties of amines and acidic – of alcohols and phenols. To know the main biologically active substances of the above mentioned compounds classes.

THEORETICAL QUESTIONS

1. Chemical reactions of halogén compounds. Nucleophilic substitution. Elimination reactions.
2. Important halogenated compounds.
3. Classification of alcohols and phenols. Physical properties of alcohols and phenols.
4. Synthesis of alcohols and phenols. The acidity of alcohols and phenols.
5. Preparation of ethers. Dehydration of alcohols. Formation of esters.
6. Biological oxidation of alcohols. Oxidation of phenols.
7. Important alcohols and phenols. Derivatives of alcohols and phenols.
8. Thiols (mercaptans). Thioethers.
9. Physical properties of amines.
10. Preparation of amines. Chemical properties of amines.
11. Amines as bases. Ammonium salts. Quaternary ammonium salts.
12. Reactions of amines. Schiff's base formation. Acylation reaction. Reactions of amines with nitrous acid.
13. Biologically important amines. Amines as neurotransmitters. Pyrimidine and purine bases.

LABORATORY PRACTICE

Protocol № 4 Date _____

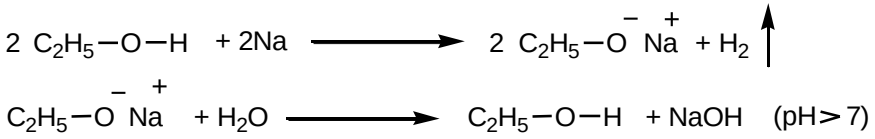
Experiment № 1

Preparation of sodium ethoxide and its hydrolysis

Place 3 drops of absolute ethanol in a dry test tube. Squeeze out kerosene from a little piece of sodium (about the size of a match head) with the filter

paper. Put sodium in the tube with ethanol. Collect the released hydrogen, closing the tube with a stopper. Then remove the stopper and carefully bring the tube to the burner flame. A mixture of hydrogen and air burns with a characteristic "barking" sound. Dissolve the white precipitate of sodium ethoxide in 2-4 drops of ethanol and add 1 drop of 1% alcoholic solution of phenolphthalein. Add to the tube 1-2 drops of water. Explain the appearance of the crimson color.

The chemistry of the reaction:



Observations:

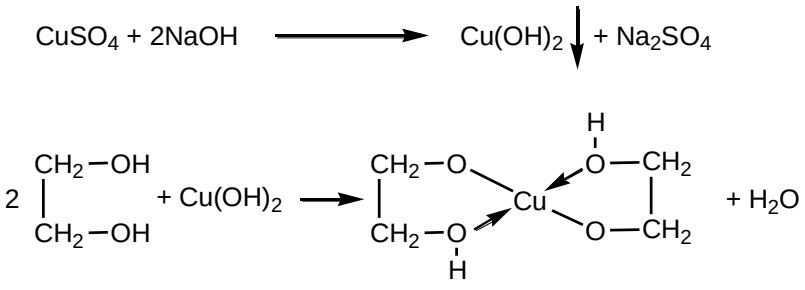
Conclusions:

Experiment № 2

Preparation of the copper(II)-ethyleneglycol

Add 2 drops of 2% solution of copper(II) sulphate ($CuSO_4$) and 2 drops of 10% solution of sodium hydroxide in the test tube. Note the color of the precipitant. Add to the latter tube a drop of ethylene glycol and shake it. Note the color of the solution. This reaction is used to detect the organic compounds containing the diol fragment (two hydroxyl groups on adjacent carbon atoms) in its structure.

The chemistry of the reaction:



Observations:

Conclusions:

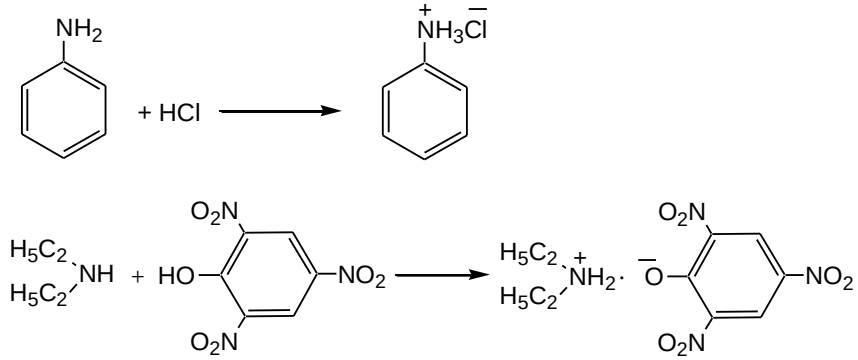
Experiment № 3

Basicity of aliphatic and aromatic amines

1. Add 2 drops of water in the two test tubes. Then in the first test tube place 1 drop of aniline ($C_6H_5NH_2$), and in the second - a drop of diethylamine $(C_2H_5)_2NH$ and shake it. Compare the solubility of these amines in water. Put 1 drop of these mixtures on a strip of universal indicator paper. Determine its pH.

2. Add 1 drop of 10% solution of hydrochloric acid to the emulsion of aniline in water. A clear solution is formed. Add 3 drops of a saturated aqueous solution of picric acid to a solution of diethylamine and mix. Put the tube into a glass of cold water. The precipitate of diethylamine picrate is formed in a few minutes.

The chemistry of the reaction:



Observations:

Conclusions:

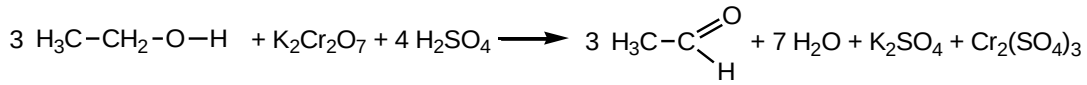
Experiment № 4

The oxidation of ethyl alcohol by chromic mixture

Place 2 drops of ethanol, 1 drop of 10% solution of sulfuric acid (H_2SO_4) and 2 drops of 10% solution of potassium dichromate ($K_2Cr_2O_7$) in the test tube. Heat the resulting orange solution in the burner flame till the color changes. Note the change of the color. After a few seconds, the solution becomes blue-green (the color of the resulting chromium (III) sulphate, $Cr_2(SO_4)_3$). At the

same time one can smell characteristic odor of acetaldehyde (the smell of rotten apples).

The chemistry of the reaction:



Observations:

Conclusions:

Literature

1. Organic Chemistry / J. McMurry. – 8th ed. Brooks/Cole. 2012; 1262 p.
2. Principles of general, organic, and biological chemistry / J.G. Smith. – 1st ed. McGraw-Hill. 2012; 596 p.
3. Organic Chemistry / W.H. Brown, Ch.S. Foote, B.L. Iverson, E.V. Anslyn. – 5th ed. Brooks/Cole. 2011; 1146 p.
4. Organic Chemistry / I. Blei, G. Odian – 2nd ed. W. H. Freeman and Company. 2006; 787 p.
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6. Lectures.

Lesson №5

FINAL SUBMODULE CONTROL I

«The theoretical basis of the structure and reactivity of organic compounds, aliphatic and aromatic, hydroxy and halogeno hydrocarbons, their thio analogues and amines"

Subject motivation: Knowledge of the nomenclature of organic compounds and their conformational features and configuration, the mutual influence of atoms in the molecules is critical in predicting organic substances physico-chemical properties and reactivity. It contributes the understanding of the radical, electrophilic mechanisms of reactions *in vivo* and *in vitro*, as well as to form the conception about the pharmacological properties of drugs.

Learning goal: To develop knowledge about the chemical behavior of the major classes of organic compounds depending on their chemical structure.

QUESTIONS AND PROBLEMS

1. Give the definition of "conformers". Draw a Newman projections of the conformations of ethane, ethyl chloride, ethanol, and compare their energy rate. Draw the possible conformations of the open hexagonal chain. What is the reason for the formation of five- and six-membered rings?
2. Draw the "chair" conformation of cyclohexane. Mark the axial and equatorial bonds.
3. What type of stereoisomerism is characteristic for alkenes and cycloalkanes? What π-diastereomers are? Write the *cis* and *trans* isomers for fumaric and cyclohexane-1,4-dicarboxylic acids.
4. Give the electronic structure of C-C bonds in alkanes. What types of reaction mechanism are typical for alkanes? Give the scheme of polar and nonpolar covalent bond breaking. Show the electronic structure of the methyl radical.
5. What are the three steps of a radical reaction? Write bromination of propane, cyclohexane, and describe its mechanism (S_R).
6. Give the electronic structure of ethylene and butadiene-1,3. What types of reaction mechanism are typical for alkenes? What electrophilic reagents are? Write the reaction of electrophilic addition (A_E) of halogen, halides and water (with acid catalyst) to ethylene, propylene, butene-2, and butandiene-1,3. Describe the reaction mechanism.
7. Give the definition of "conjugation" and specify the A_E reactions for conjugated dienes. Could the products of the butadiene-1,3 hydrogenation exist as *cis*-or *trans*-isomers? Explain the Markovnikov's rule.

8. Write the reaction of cyclopropane bromination. Specify its mechanism.

9. Show the electronic structure of benzene. Give a definition of "conjugation energy" and "aromaticity". Specify the criteria of aromaticity (Hückel's rule) for pyrrole, furan, thiophene, imidazole, pyridine, pyrimidine, purine. Compare the energy rate for open and closed conjugation chain for 1,3,5-heptatriene and benzene.

10. Write the reactions of halogenation, sulfonation, alkylation of toluene, aniline, phenol, benzoic acid, naphthalene, furan, thiophene, pyrrole, pyridine. Specify its mechanism. Explain the activating or deactivating influence of the substituents and heteroatoms in the aromatic rings.

11. Describe oxidation of alkanes, alkenes and arenes by potassium permanganate. Write this reaction for propylene. Why it is used to identify the double bond?

12. What is “acid” and “base” by Brønsted–Lowry?

13. Explain the amphoteric character of alcohols and phenomenon of their intermolecular association. How this phenomenon affects their boiling point and solubility?

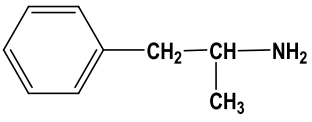
14. Compare the basicity of the next groups of compounds:

A. diethyl ether, diethylsulfide, dimethylalanin;

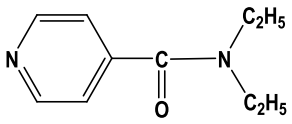
B. diethyl ether, dimethyl sulfide, dimethylalanin,

Write the hydrochloric salt for the most strong bases: What nitrogen atom goes protonation, and why?

C.

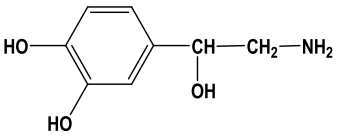


Phemanin

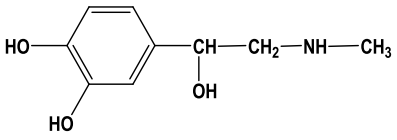


Cordiamin

D.

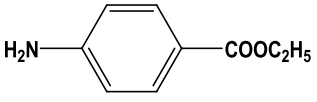


Noradrenalin

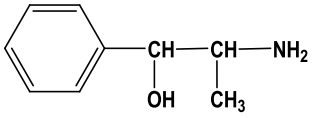


Adrenalin

E.

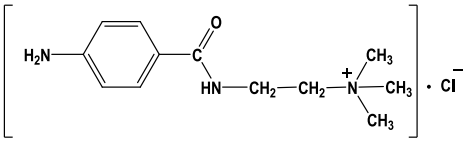


Anaesthesin



Ephedrine

F.



Novocainamide

15. Compare the acidic properties of the next groups of compounds:

A. phenol, *p*-aminophenol;

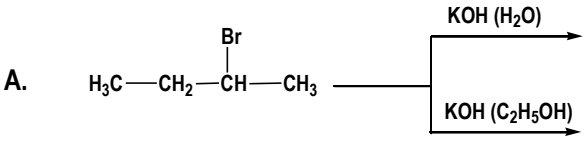
B. phenol, *p*-hydroxyphenol;

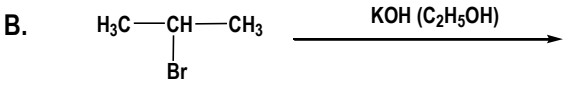
C. *n*-propyl alcohol, 2-chloropropanol-1, 2-mehylpropanol-1;

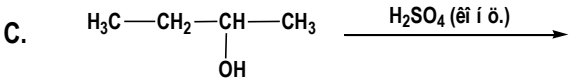
D. ethyl alcohol, ethyl mercaptan, acetic acid;

E. *n*-propyl alcohol, glycerol. What is the qualitative reaction for these alcohols?

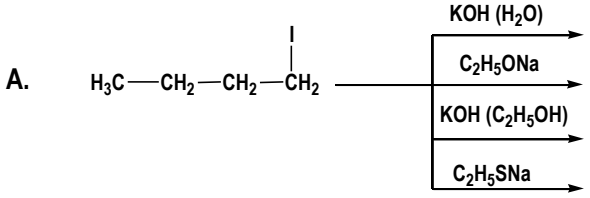
16. Why nucleophilic substitution (S_N) and elimination (E) are possible for alcohols and halogenated compounds? Write chemistry of the next reactions:

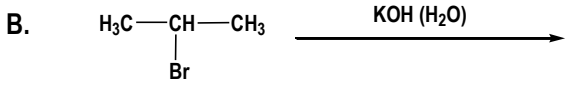


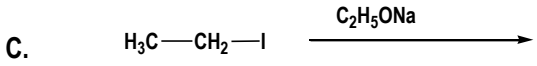




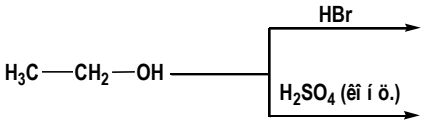
17. Write chemistry of the next reactions. Describe their mechanism. What products could exist as *cis*-, *trans* isomers?







How it is possible to check the quality of the next products?



18. Chlorobutanol, or 1,1,1-trichloro-2-methyl-propan-2-ol, is a chemical preservative, sedative hypnotic and weak local anaesthetic similar in nature to

chloral hydrate. Compare the acidity of chlorobutanol and n-propyl alcohol. Rate the attitude of these alcohols to oxidation. Write the reactions.

What classes of organic compounds are obtained by the interaction of ethyl bromide with the following reagents:

a) NH_3; b) $C_2H_5NH_2$; c) NaCN; d) C_2H_5ONa

19. Determine the structure of compounds A, B, C, D, and name them.

а) $CH_3\text{-}CH_2\text{-}CH{=}CH_2 \xrightarrow{H_2O,\ H^+} A \xrightarrow{H_2SO_4} B \xrightarrow{H_2O,\ O} C \xrightarrow{Cu(OH)_2} D$

б) $CH_3\text{-}CH_2\text{-}CH_2\text{-}Br \xrightarrow{H_2O,\ KOH} A \xrightarrow{H_2SO_4} B \xrightarrow{H_2O,\ H^+} C \xrightarrow{[O]} D$

20. Aminoalcohols: structure, properties. Biomedical significance of ethanolamine (colamin), choline, acetylcholine.

21. Amines: nomenclature, properties. Biomedical significance of biogenic amines (adrenaline, noradrenaline, dopamine, tryptamine, serotonin, histamine) and polyamines (spermidine, spermine, putrescine, cadaverine).

22. Aromatic amines: structure, properties. Aniline as a precursor in the synthesis of pharmaceuticals - sulfanilamide, phenacetin, anaesthesin, novocaine.

23. Thiols (mercaptans), sulfides and disulfides. Structure and chemical properties.

Literature

1. Organic Chemistry / J. McMurry. – 8th ed. Brooks/Cole. 2012; 1262 p.
2. Principles of general, organic, and biological chemistry / J.G. Smith. – 1st ed. McGraw-Hill. 2012; 596 p.
3. Organic Chemistry / W.H. Brown, Ch.S. Foote, B.L. Iverson, E.V. Anslyn. – 5th ed. Brooks/Cole. 2011; 1146 p.
4. Organic Chemistry / I. Blei, G. Odian – 2nd ed. W. H. Freeman and Company. 2006; 787 p.
5. General, Organic, and Biological Chemistry: An Integrated Approach / K.W. Raymond. – 2nd ed. John Wiley & Sons, Inc. 2008; 541 p.
6. Lectures.

Lesson №6

Subject: INVESTIGATION OF THE ALDEHYDES AND KETONES' CHEMICAL PROPERTIES. BIOLOGICALLY IMPORTANT REACTIONS OF CARBONYL COMPOUNDS.

Subject motivation: The carbonyl group is found in many biologically important compounds in plants and animals (vitamins, hormones, steroids, cardiac glycosides, carbohydrates, etc.). The high reactivity of carbonyl compounds is widely used in organic synthesis for obtaining the effective pharmaceuticals. Knowledge of the electronic structure characteristics and chemistry of aldehydes and ketones is the basis for a meaningful understanding and assimilation of biochemical processes, issues of pharmacokinetics, and prediction of the compatibility of drugs.

Learning goal: To generate knowledge about the basic chemical reactions of carbonyl compounds, which are important for biological systems, and be able to conduct qualitative reactions for aldehydes and ketones.

THEORETICAL QUESTIONS

1. The nomenclature of aldehydes and ketones.
2. The structure and reactivity of aldehydes and ketones.
3. The oxidation reaction.
4. Nucleophilic addition reactions (A_N): hydration, cyanohydrin formation, alcohol formation, imine and enamine formation, acetal formation.
5. Biological reduction. Disproportionation, (dismutation, Cannizzaro reaction).
7. Haloform reaction.
8. Keto and enol tautomers.
9. Natural quinones as reversible oxidizing agents.

LABORATORY PRACTICE

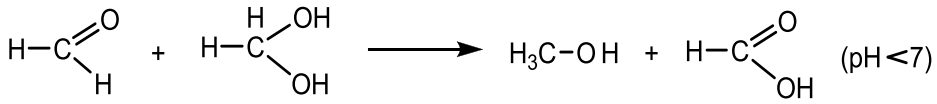
Protocol № 6 Date_____

Experiment 1

Disproportionation of formaldehyde in aqueous solution

Place the tube 2-3 drops of 40% formaldehyde solution. Add 1 drop of 0.2% solution of methyl red indicator. Redness of the solution indicates the acidic medium.

The chemistry of the reaction:



Observations:

Conclusions:

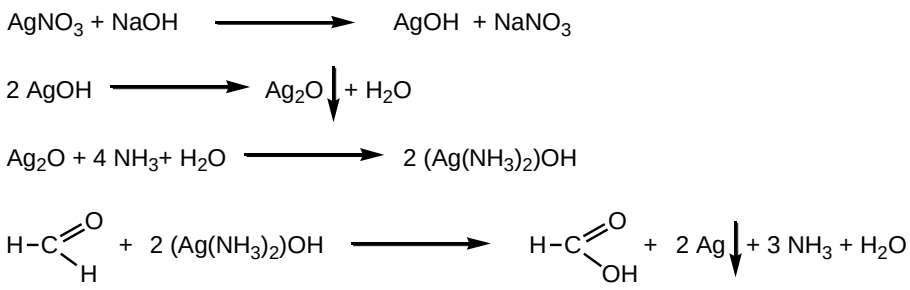
Experiment № 2

Oxidation of the formaldehyde and acetone by alkaline solutions of heavy metal oxides.

1. Oxidation by silver hydroxide (Tollens test, Silver mirror reaction)

Take two test tubes and place in each1 drop of 5% solution of silver nitrate ($AgNO_3$) and 1 drop of 10% solution of sodium hydroxide (NaOH). To the resulting brown precipitate, add dropwisely 10% aqueous ammonia solution to dissolve the precipitate. Then add 2 drops of 40% formaldehyde solution in the first test tube, and in the second - 2 drops of acetone. In the first tube the black precipitate is formed, which after the gentle heating forms the brilliant mirror coating the walls of the tube. There is no precipitate in the second test tube.

The chemistry of the reaction:



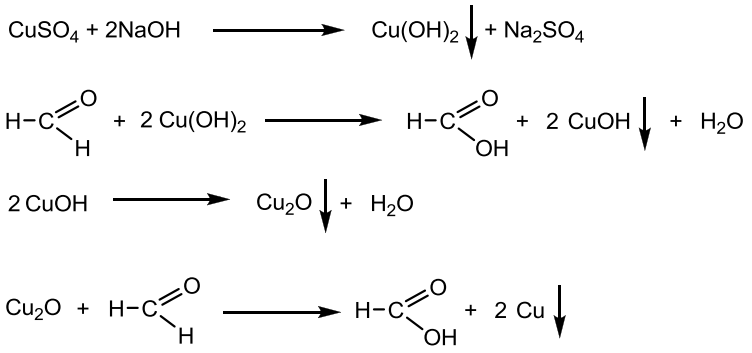
Observations:

Conclusions:

2. Oxidation by copper(II) hydroxide.

Place 5 drops of 10% sodium hydroxide solution and 5 drops of water in a test tube, add 1 drop of 2% solution of copper(II) sulphate ($CuSO_4$). Add 3 drops of 40% formaldehyde solution to the formed copper(II) hydroxide. Gently heat the tube. Firstly the precipitate becomes yellow, then - red and if the tube is clear, metallic copper ("copper mirror") appears on the test tube walls.

The chemistry of the reaction:



Observations:

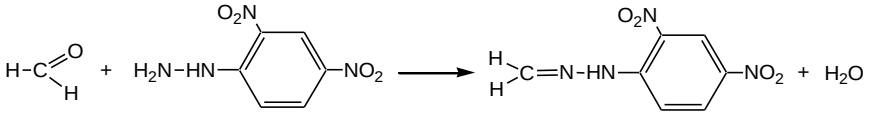
Conclusions:

Experiment № 3

The formation of formaldehyde 2,4-dinitrophenylhydrazone.

Place 5 drops of 2,4-dinitrophenylhydrazine solution in the test tube. Add 1-2 drops of 40% formaldehyde solution until a yellow precipitate of 2,4-dinitrophenylhydrazone is formed.

The chemistry of the reaction:



Observations:

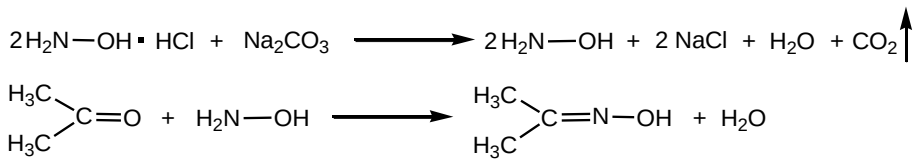
Conclusions:

Experiment № 4

Preparation of acetone's oxime.

Place a bit of hydroxylamine hydrochloride $H_2NOH*HCl$, a bit of crystalline sodium carbonate and 10-25 drops of water in the test tube. After allocating the bulk of carbon dioxide, cool the tube and add, with good stirring, 15 drops of acetone. The mixture is warmed up with formation of white crystals.

The chemistry of the reaction:



Observations:

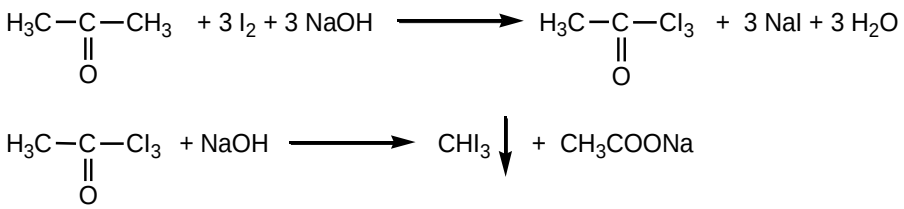
Conclusions:

Experiment № 5

Iodoform test (acetone identifying reaction).

Put 1 drop of iodine solution in potassium iodide and dropwisely 10% sodium hydroxide solution till almost bleaching in the test tube. Then add 1 drop of acetone. At low heat (heat from the hands) the yellowish-white precipitate is formed with a characteristic odor of iodoform. This reaction is used in clinical laboratories and is of practical importance for the diagnosis of diabetes.

The chemistry of the reaction:



Observations:

Conclusions:

CHALLENGE QUESTIONS

1. Describe the mechanism of acetaldehyde transformation in dimethylacetal. What is the role of an acid catalyst in the reaction?

2. The large doses of hydrazine cause the neurological disorders. Describe the chemistry of the interaction of hydrazine (NH_2-NH_2) with coenzyme pyridoxal.

Literature

1. Organic Chemistry / J. McMurry. – 8th ed. Brooks/Cole. 2012; 1262 p.
2. Principles of general, organic, and biological chemistry / J.G. Smith. – 1st ed. McGraw-Hill. 2012; 596 p.
3. Organic Chemistry / W.H. Brown, Ch.S. Foote, B.L. Iverson, E.V. Anslyn. – 5th ed. Brooks/Cole. 2011; 1146 p.
4. Organic Chemistry / I. Blei, G. Odian – 2nd ed. W. H. Freeman and Company. 2006; 787 p.
5. General, Organic, and Biological Chemistry: An Integrated Approach / K.W. Raymond. – 2nd ed. John Wiley & Sons, Inc. 2008; 541 p.
6. Lectures.

Lesson № 7

Subject: STRUCTURE, PROPERTIES AND BIOLOGICAL SIGNIFICANCE OF CARBOXYLIC ACIDS. HETEROFUNCTIONAL CARBOXYLIC ACIDS' (HYDROXY, OXO, PHENOLIC) DERIVATIVES.

Subject motivation: The high reactivity of carboxylic acids and their functional derivatives is widely used in organic synthesis and pharmaceuticals industries. Carboxylic acids play a crucial role in the metabolic processes of plants and

animals. As intermediates in the oxidation of carbohydrates, fats, proteins, they are involved in the biosynthesis of amino acids, steroids, alkaloids, saponines, etc.

Learning goal: To distinguish the peculiarities of the chemical behavior of carboxylic acids and their functional derivatives, taking place in the metabolic processes.

THEORETICAL QUESTIONS

1. The classification and nomenclature of carboxylic acids.
2. Methods of carboxylic acids preparation.
3. Electronic structure of the carboxyl group and the carboxylate anion.
4. Identification reactions of COOH group.
5. Esters of carboxylic acids. Saponification.
6. Decarboxylation. Halogenation. Oxidation.
7. Thioesters. Carboxylic acid anhydrides. Acyl halides. Amides.
8. Derivatives of carbonic acid.
9. Hydroxy acids. Structure and properties of monocarboxylic, dicarboxylic and tricarboxylic hydroxy acids.
10. Phenolic acids. Salicylic acid and its anti-inflammatory derivatives (acetylsalicylic acid, methyl salicylate, sodium salicylate) and antimicrobial (phenyl salicylate) compounds.
11. Paracetamol synthesis.
12. Aniline as a precursor in the synthesis of pharmaceuticals - sulfanilamide, phenacetin, anaesthesin, novocaine.

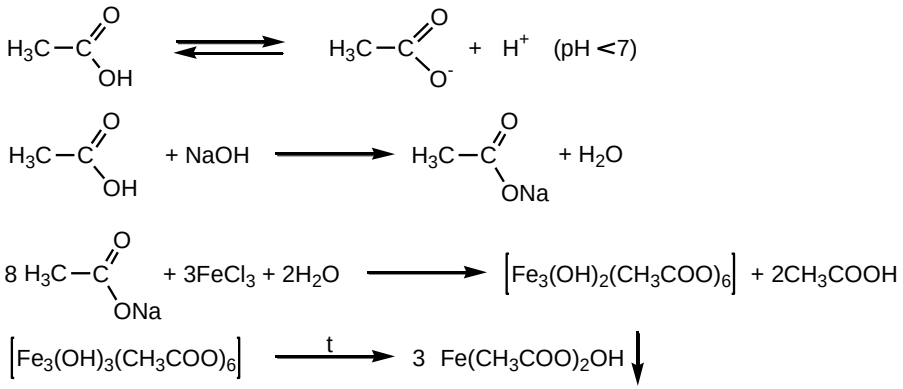
LABORATORY PRACTICE

Protocol № 7 Date_____

Identifying the acetic acid.

Place 3 drops of acetic acid and water in the test tube. Try the pH solution with litmus. Add 2-3 drops of 10% sodium hydroxide solution until complete neutralization of the acetic acid. Then add 2-3 drops of 1% solution of ferric (III) chloride ($FeCl_3$). The iron(III) acetate gives yellowish-red color. Heat the solution. The red-brown precipitate of insoluble in the water hydroxide of the iron diacetate is formed. Solution above the precipitate becomes colorless.

The chemistry of the reaction:



Observations:

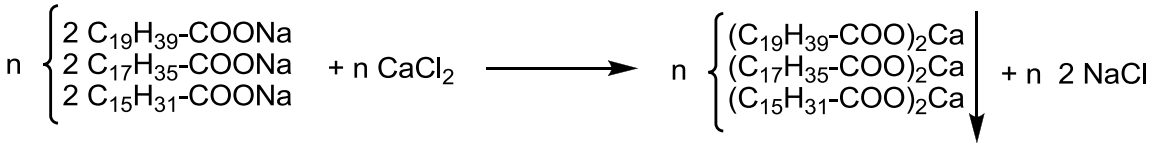
Conclusions:

Experiment № 2

Formation of insoluble fatty acids calcium salts.

Place 5 drops of the soap solution and 1 drop of calcium chloride solution ($CaCl_2$) in the test tube. Shake the tube. A white precipitate is formed.

The chemistry of the reaction:



Observations:

Conclusions:

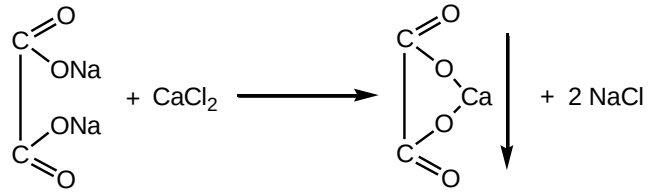
Experiment № 3

Identification calcium salt of oxalic acid.

Place a bit of oxalic acid sodium salt and 4-5 drops of water until salt is dissolved in the test tube. Take one drop of solution with pipette and put on a glass slide. Add a drop of calcium chloride solution. The crystal precipitate is

formed. This reaction is used to determine the oxalates in the urine. The crystals look like envelopes under the microscope.

The chemistry of the reaction:



Observations:

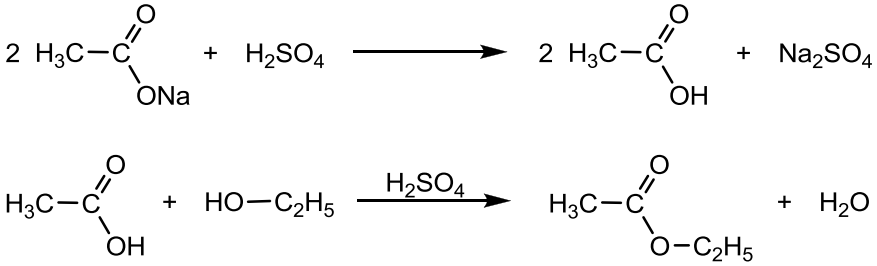
Conclusions:

Experiment № 4

Preparation of ethyl acetate.

Place a powder of anhydrous sodium acetate (height of about 2 mm) and 3 drops of ethyl alcohol in a dry test tube. Add 2 drops of concentrated sulfuric acid (**you should add it in a fume hood**!) and gently heat test tube in a burner flame (**carefully! solution could splash**!). After a few seconds appears the pleasant smell of ethyl acetate. The reaction is used to identify the ethanol.

The chemistry of the reaction:



Observations:

Conclusions:

CHALLENGE QUESTIONS

1. Write the chemistry of reaction to synthesize the ethyl acetate, using as a starting compound malonic acid with subsequent hydrolysis and ammonolysis.
2. Olive oil is used for injection. It is composed of oleic acid (80%) and linoleic (7%) acids. Explain the liquid consistency of olive oil (mp -6 °C). What chemical transformation can change the consistency of this oil to butter?
3. Write the formula of the phospholipid based on phosphatidic acid, esterificated by colamine (2-aminoethanol). Name this phospholipid and describe its relation to hydrolysis

Literature

1. Organic Chemistry / J. McMurry. – 8th ed. Brooks/Cole. 2012; 1262 p.
2. Principles of general, organic, and biological chemistry / J.G. Smith. – 1st ed. McGraw-Hill. 2012; 596 p.
3. Organic Chemistry / W.H. Brown, Ch.S. Foote, B.L. Iverson, E.V. Anslyn. – 5th ed. Brooks/Cole. 2011; 1146 p.
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6. Lectures.

Lesson № 8

Subject: POLYFUNCTIONAL DERIVATIVES OF ALIPHATIC AND AROMATIC COMPOUNDS

Subject motivation: The amino, hydroxy, and keto acids are structural components that play the critical role in life processes of biological systems (proteins, nucleic acids, lipids, etc.). Moreover, many organic heterofunctional compounds and their derivatives are used in medicine as drugs (acetylcholine chloride, diphenhydramine, ephedrine, calcium lactate, etc).

Learning goal: To study the stereochemistry and reactivity of amino alcohols, amino, hydroxy and keto acids, taking into account the mutual influence of different functional groups; to perform and explain their qualitative reactions.

THEORETICAL QUESTIONS

1. The amino and keto acids nomenclature and structural isomerism.
2. The spatial structure of heterofunctional acids.
3. The specific properties of heterofunctional acids (transformations of the α-, *β*-, *γ*-hydroxy and amino acids when heating).
4. The chemical properties of heterofunctional acids and their derivatives.
5. Preparation and chemical properties of biogenic amines.
6. Tautomerism of keto acids.
7. The sulfonamides.
8. Reactions of the tricarboxylic acid cycle.
9. Chemical characterization of *p*-aminophenol.
10. Functional analysis of salicylates.
11. Structure and chemical properties of the *p*-aminobenzoic acid (PABA) and its derivatives.
12. The chemical properties of ureides and ureidoacids.
13. Vitamins A, B5, C, E, K. Structure and properties.

LABORATORY PRACTICE

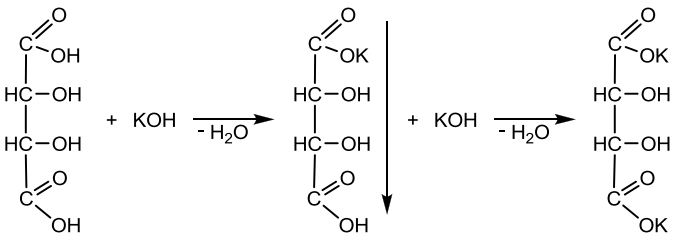
Protocol № 8 Date _____

Experiment №1

The evidence of the two carboxyl groups in tartaric acid

Place a drop of 15% tartaric acid solution, 2 drops of 5% potassium hydroxide solution in the test tube and shake. Then white crystalline precipitate of potassium salt of tartaric acid (potassium hydrotartrate) gradually starts to form. If the precipitate does not appear, cool the tube under the cold running water and rub the inner wall of the tube with a glass rod. Add to the tube 4-5 drops of potassium hydroxide solution. The crystalline precipitate gradually dissolves, because the water-soluble potassium tartrate is formed. The latter solution of potassium tartrate, save for the next experiment.

The chemistry of the reaction:



Observations:

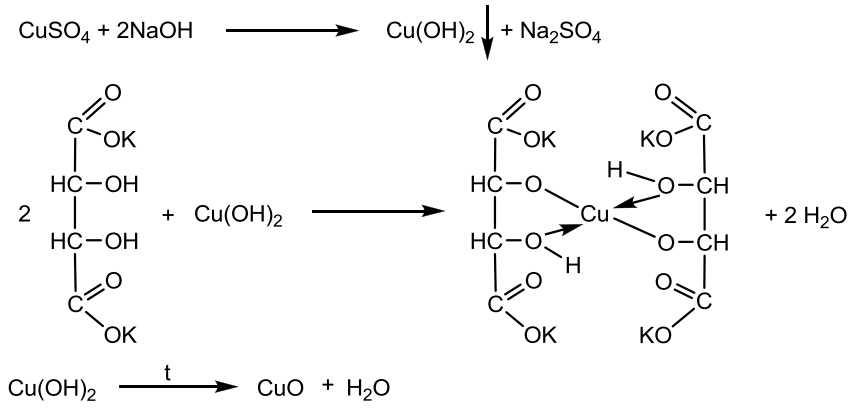
Conclusions:

Experiment № 2

The evidence of the hydroxyl groups in tartaric acid

Place 2 drops of 2% copper(II) sulphate solution ($CuSO_4$) and 10% sodium hydroxide solution in two test tubes. The blue precipitate of copper(II) hydroxide is formed. Add potassium tartrate solution, obtained in previous studies, in the first test tube. The precipitate of copper(II) hydroxide is dissolved forming a blue solution. Heat both tubes over the burner. The color of the solution does not change in the first test tube, and in the second - a blue precipitate of copper(II) hydroxide is converted into red copper(II) oxide. The bistartratocuprate(II) complex in Fehling's solution is an oxidizing agent. In the process the copper(II) ions of the complex are reduced to copper(I) ions the presence of aldehydes and α-hydroxy-ketones. Red copper(I) oxide then precipitates out of the reaction mixture, which indicates a positive result i.e. that redox has taken place. Thus Fehling's reagent is used to detect glucose in urine, detecting diabetes.

The chemistry of the reaction:



Observations:

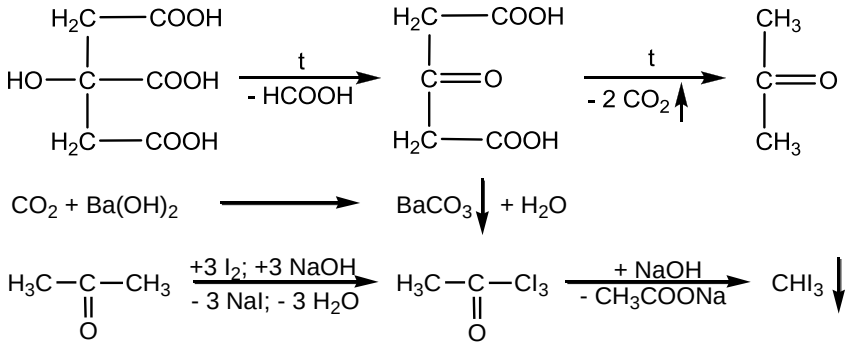
Conclusions:

Experiment № 3

Decomposition of the citric acid

Put a bit of citric acid and 10 drops of concentrated sulfuric acid (**you should add it in a fume hood**!) in a dry test tube equipped with a vapor pipe and heat it. Put the end of vapor tube into the first test tube containing 5 drops of barium hydroxide solution. When the solution turns turbid, put the vapor tube into the second tube containing 2 drops of iodine solution in potassium iodide, previously decolorized by adding a few drops of 10% sodium hydroxide solution. The pale yellow precipitate of iodoform is formed in the second test tube.

The chemistry of the reaction:



Observations:

Conclusions:

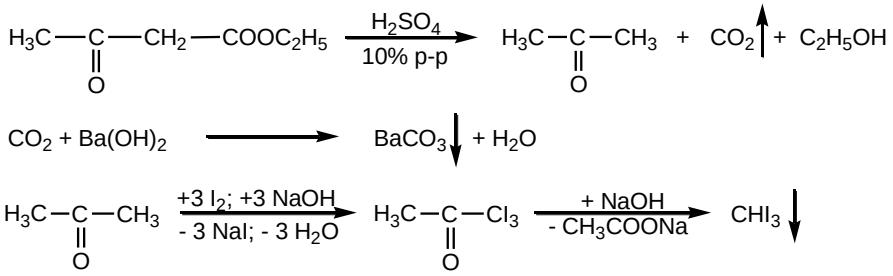
Experiment№ 4

Decarboxylation of acetoacetic ester

Put 5 drops of acetoacetic ester and 10 drops of concentrated sulfuric acid (**you should add it in a fume hood**!) in a dry test tube equipped with a vapor pipe and heat it. Put the end of vapor tube into the first test tube containing 5 drops of barium hydroxide solution. When the solution turns turbid, put the vapor tube into the second tube containing 2 drops of iodine solution in

potassium iodide, previously decolorized by adding a few drops of 10% sodium hydroxide solution. The pale yellow precipitate of iodoform is formed in the second test tube.

The chemistry of the reaction:



Observations:

Conclusions:

CHALLENGE QUESTIONS

1. The lactic acid which is used in medicine is produced in a 4% aqueous solution. Why further concentration by heated evaporation of solution is not advisable?
2. Write all the possible products which are formed when mixture of α-aminopropionic and α-aminoacetic acid is heated.
3. One of the 2-amino-3-methylpentane acid stereoisomers is part of the protein. Write all the possible formulas of acid stereoisomers and name them.

Literature

1. Organic Chemistry / J. McMurry. – 8th ed. Brooks/Cole. 2012; 1262 p.
2. Principles of general, organic, and biological chemistry / J.G. Smith. – 1st ed. McGraw-Hill. 2012; 596 p.
3. Organic Chemistry / W.H. Brown, Ch.S. Foote, B.L. Iverson, E.V. Anslyn. – 5th ed. Brooks/Cole. 2011; 1146 p.
4. Organic Chemistry / I. Blei, G. Odian – 2nd ed. W. H. Freeman and Company. 2006; 787 p.
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6. Lectures.

Lesson 9

Subject: SAPONIFICATED LIPIDS: FATS, OILS, PHOSPHOLIPIDS, WAXES. STRUCTURE, NOMENCLATURE, CHEMICAL PROPERTIES.

Subject motivation: Lipids are one of the major constituents of foods, and are important in our diet for a number of reasons. They are a major source of energy and provide essential lipid nutrients. They are found in cell membranes, insulating layer around nerve cells, etc. Linoleic, linolenic acid and arachidonic acids are important essential fatty acids. Humans don't have the ability to introduce double bonds in fatty acids beyond carbon 9 and 10, because lack desaturase enzymes, required for their production. Waxes on the surface of leaves and insect cuticles, along with oils on feathers and fur, form a water-proof layer which enables the organisms to survive in their environments. Lipid-rich myelin, found wrapped around neurons, provides electrical insulation which makes rapid transmission of impulses possible.

Learning goal: name biological macromolecules and their building blocks, know IUPAC or systematic and common names of a fatty acid, test samples for the presence of lipids.

THEORETICAL QUESTIONS

1. Definitions of lipids, fatty acids.
2. Nomenclature of saturated fatty acids. IUPAC system. Common names.
3. Nomenclature of unsaturated fatty acids. Systematic names. Common names Omega-numbering. Delta-numbering. Shortened form of nomenclature.
4. What are the essential fatty acids?

Physical properties of fatty acids.

5. What are hydrophobic molecules (or hydrophobic molecular regions)? What are hydrophilic molecules? How can they be described in relation to their polarity?
6. What are Lipids? Classification of lipids.
7. Simple lipids (Fats, Oils, Waxes).
8. Complex lipids: Phospholipids, Glycolipids, Glycosphingolipids, Sulfolipids, Aminolipids, Lipolipids.
9. What are saponifiable lipids? Stereospecific numbering system of glycerol.

10. The general structure and properties of phospholipids. Phosphatidic acid, Phosphatidyl-ethanolamine (Cephaline), Phosphatidylcholine (Lecithin), Phosphatidylserine, Phosphatidylinositol, Phosphatidylglycerol.
11. Lysophospholipids, Plasmalogen, Sphingolipids, Ceremides.
12. Why do fats have thermal insulation properties?
13. Saponification number, acidic and iodine number.

LABORATORY PRACTICE

Protocol № 9 Date _____

QUALITATIVE ANALYSIS OF LIPIDS

1. SOLUBILITY TEST

The test is based on the property of solubility of lipids in organic solvents and insolubility in water. The oil will float on water because of lesser specific gravity.

TEST: Take 3 ml of solvents in each test tube and add 5 drops of sample. For water and ethanol, it is insoluble and for chloroform and ether, it is soluble and hence the given sample is lipid.

Observation:

Conclusion:

2. TRANSPARENCY TEST

All the lipids are greasy in nature. Therefore the test may be taken as group test for lipids. The oil does not wet the paper. Take 3 ml of ether in a test tube and dissolve 5 drops of oil in tit. Put a drop of the solution on the filter paper and let it dry. A translucent spot on the filter paper was observed and this indicates the greasy character of the lipid.

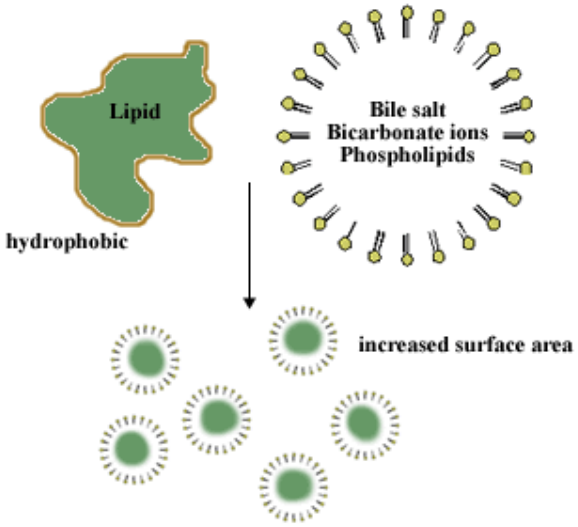
Observation:

Conclusion:

3. **EMULSIFICATION TEST**

When oil and water, which are immiscible, are shaken together, the oil is broken up into very tiny droplets which are dispersed in water. This is known as oil in water emulsion. The water molecule due to the high surface tensions have tendency to come together and form a separate layer. This is why the oil and water emulsion is unstable in the presence of substances that lower the surface tension of water (sodium carbonate, soap, bile salts etc.) The tendency of the water molecule to coalesce is decreased and the emulsion becomes stable. Since bile salts cause the greatest decrease in surface tension they are best emulsifying agents.

TEST: Take 3 ml of water and add 5 drops of sample. In another test tube 10 ml of water is added to ethanol solution of lipid contents and are mixed and two layers of are observed and this confirms the presence of lipids.



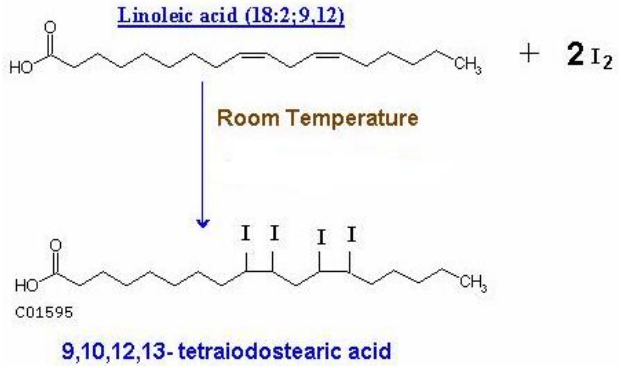
Observation:

Conclusion:

4. TEST FOR UNSATURATION

The amount of iodine required to impart its color to the solution is a measure of the degree of the fatty acids. The unsaturated fatty acids react with iodine at the double bonds until all the double bonds are saturated with iodine.

TEST: Equally into 4 flasks add 10 ml of chloroform, then 10 drops of iodine reagent, the chloroform shows pink color due to the presence of iodine. Add the oil sample to test tube (mustard, coconut, olive oils, saturated fat) drop by drop, shaking the tube vigorously for about 30 seconds after addition of each until the pink color is discharged and count the number of drops. The pink color is discharged owing to the taking up of iodine by the unsaturated fatty acids of the oil. Compare unsaturation, it should be remembered that more the number of drops required to discharge the pink color, the less is the unsaturation.



Observation:

Conclusion:

5. COPPER ACETATE TEST

The copper acetate solution does not react with the oils, while saturated and unsaturated fatty acids react with copper acetate to form copper salt. The unsaturated fatty acids can only be extracted by petroleum ether.

In the case of olive oil notice that petroleum ether upper layer containing the dissolved oil and appears colorless, aqueous solution remains blue in the bottom.

In the case of oleic acid the upper layer of petroleum ether becomes green as a result of copper oleate. The lower layer becomes less in blue.

TEST: Take 1 ml of oil, 1 ml of petroleum ether and 5 drops of 5% copper acetate solution in one test tube; and in other test tube - 1 ml of oleic acid, 1 ml of petroleum ether, and 5 drops of 5% copper acetate solution. Shake vigorously. Compare the colors. Copper oleate petroleum ether layer turns blue-greenish.

Observation:

Conclusion:

Literature

1. Organic Chemistry / J. McMurry. – 8th ed. Brooks/Cole. 2012; 1262 p.
2. Principles of general, organic, and biological chemistry / J.G. Smith. – 1st ed. McGraw-Hill. 2012; 596 p.
3. Organic Chemistry / W.H. Brown, Ch.S. Foote, B.L. Iverson, E.V. Anslyn. – 5th ed. Brooks/Cole. 2011; 1146 p.
4. Organic Chemistry / I. Blei, G. Odian – 2nd ed. W. H. Freeman and Company. 2006; 787 p.
5. General, Organic, and Biological Chemistry: An Integrated Approach / K.W. Raymond. – 2nd ed. John Wiley & Sons, Inc. 2008; 541 p.
6. Lectures.

Lesson №10

Theme: NON-SAPONIFICATED LIPIDS: PROSTAGLANDINS, TERPENES, STEROIDS. STRUCTURE, NOMENCLATURE, CHEMICAL PROPERTIES.

Subject motivation: Investigated substances are among the most important biologically active ones. Prostaglandines functions are regulation of blood pressure and reproductive functions; induce inflammation, fever and pain; inhibit platelet aggregation. Most non-steroidal antiinflammatory drugs (NSAIDS) like aspirin and ibuprofen work by blocking the action of cyclooxygenase, thereby inhibiting prostaglandin production. Thromboxanes also produced from PGH2 but contain a 6-membered “oxane” ring with platelet

aggregation, clotting, constriction of blood vessels functions. Leukotrienes are synthesized directly from arachidonic acid and are about mooth muscle contraction, allergic response, lung constriction and swelling. Terpenes are one of the largest and most varied group of plant chemicals. They have antibacterial properties and wound-healing properties. Squalene is precursor to steroids, etc. Cholesterol main functions are cell membrane structure and fluidity, precursor of steroid hormones and bile acids.

Learning goal: To strengthen knowledge of the structure and chemical properties of the main unsaponificated lipids, taking into account the influence of their characteristic functional groups as the basis of biochemical processes.

THEORETICAL QUESTIONS

1. What are lipids? How are lipids classified according to solubility?
2. What are saponifiable and non-saponifiable lipids? Precursor and derived lipids.
3. Structure and properties of the following compounds. Eicosanoids: Prostanoids (Prostaglandins (PGs), Prostacyclins (PGIs), Thromboxanes (TXs)), Leukotrienes (LTs), Lipoxins (LXs).
4. What are terpenes? Classification.
5. Isoprene rule. Biosynthesis of squalene.
6. Structure and physico-chemical properties and synthesis of limonene, myrcene, linalool, alpha bisabolol, delta-3 carene, borneol, alpha-pinene, beta-pinene, eucalyptol, terpineol, caryophyllene, cineole, camphora, etc.
7. What are steroids? Nomenclature. Their biological function?
8. Examples of cholestanes, cholanes, pregnanes, androstanes and estranes. Reactions of their identification.

LABORATORY PRACTICE

Protocol № 10 Date _____

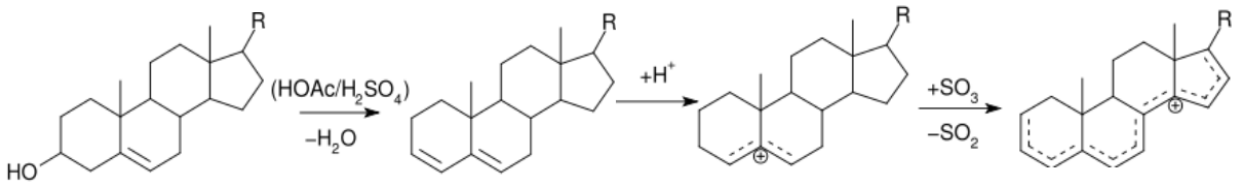
Experiment №1

LIEBERMANN - BURCHARD TEST

The cholesterol reacts as a typical alcohol with a strong concentrated acids and forms colored products. Acetic anhydrides are used as solvent and dehydrating

agents, and the sulfuric acid is used as dehydrating and oxidizing agent. A positive result is observed when the solution becomes red-blue, and finally bluish - green color.

TEST: Dissolve a few crystals of cholesterol in 2 ml of chloroform in a dry test tube. Now add 10 drops of acetic anhydride, add 2 to 3 drops of conc. sulfuric acid.



Observation:

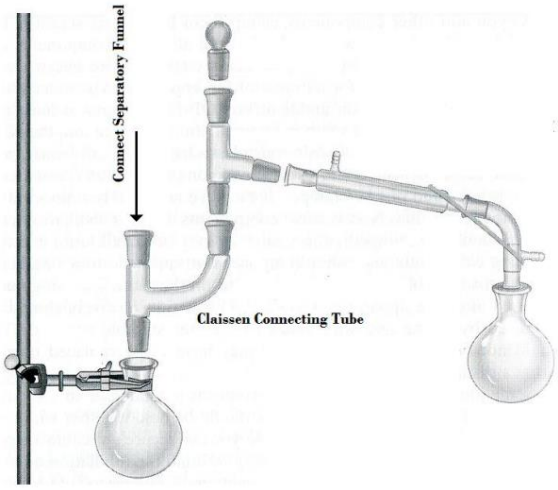
Conclusion:

Experiment №2

STEAM DISTILLATION OF THE OIL OF ORANGE

TEST:

1. Assemble the distillation apparatus as pictured (roughly) below. Because of the large amount of orange peel is required, we will use a 500 mL round bottomed flask as the distilling pot. Use a small hot plate as a heat source. We will be generating the steam directly. Use a 250 mL round bottom flask as a receiver. Use a Claisen connecting tube to connect the distilling pot to the distillation head. Add a separatory funnel filled with water to Claisen tube. This will allow us to easily add water to the system during the distillation, if needed. Wrap the Claisen in some cotton batting and Aluminum foil to keep it hot during the distillation.
2. Peel three medium oranges and measure the mass of the peel. Puree the peel with a minimum of water in a blender. Add the puree to the distilling pot, a 500 mL round bottom flask, using a wide-mouth funnel and a stirring rod. Add enough water so that the distilling pot is about 2/3 full. Add a boiling chip. Turn on the condenser Water and seal the distilling pot.



3. Begin heating the system slowly. Adjust the heat so that the distilling rate equals about 20 drops per minute. As the mixture boils and distills, you will be losing water from the distillation mixture. As the level drops in the flask, add small volumes of water *via* the separator funnel. It is important to watch the water level because of the high concentration of sugar in oranges. If the water level gets too low, the sugar will caramelize and burn. Also, it is better to add small amounts of water so that the temperature doesn't drop drastically. Keep the heat at a low, steady level.

4. Collect about 150 mL of distillate. The presence of the oil in the condensate will cause the drops forming in the condenser to be cloudy. Thus, you can estimate when the condensate no longer contains oil by noting the absence a cloudy appearance.

5. Transfer the distillate to a stopper Erlenmeyer flask.

6. **DO NOT BEGIN THIS PROCESS UNTIL YOU HAVE BEEN GIVEN THE APPROPRIATE INSTRUCTIONS BY YOUR LAB INSTRUCTOR. THERE MUST BE NO FLAME SOURCES OR HOT PLATES ON DURING THE USE OF ETHER. ETHER IS VERY, VERY FLAMMABLE.**

Transfer your distillate to a 250 mL separatory funnel. Add 20 mL of diethyl ether and extract the oil. Your laboratory instructor will demonstrate the correct use of the separatory funnel.

7. Drain the water layer off into a 250 mL Erlenmeyer flask. Drain the ether layer into a small collection flask.

8. Repeat the extraction once more and collect all the ether fractions in the same flask.

9. Dry the ether with a little anhydrous sodium sulfate. This is required because trace amounts of water will dissolve in the ether.

10. Decant the liquid into a small beaker. Add a toothpick to the beaker. (This will act as a nucleation site during the boiling.) Place the beaker on a steam bath in the fume hood. Boil off all the ether. 11. Transfer your oil to a massed and labeled 4-dram vial. Determine the mass of the oil. Calculate the percentage oil in the orange peel.

Observation:

Conclusion:

Literature

1. Organic Chemistry / J. McMurry. – 8th ed. Brooks/Cole. 2012; 1262 p.
2. Principles of general, organic, and biological chemistry / J.G. Smith. – 1st ed. McGraw-Hill. 2012; 596 p.
3. Organic Chemistry / W.H. Brown, Ch.S. Foote, B.L. Iverson, E.V. Anslyn. – 5th ed. Brooks/Cole. 2011; 1146 p.
4. Organic Chemistry / I. Blei, G. Odian – 2nd ed. W. H. Freeman and Company. 2006; 787 p.
5. General, Organic, and Biological Chemistry: An Integrated Approach / K.W. Raymond. – 2nd ed. John Wiley & Sons, Inc. 2008; 541 p.
6. Lectures.

Lesson №11
FINAL SUBMODULE CONTROL II
«Heterofunctional organic compounds - metabolites and basis of the most important groups of drugs. Carbonyl compounds. Carboxylic acids and their functional derivatives".

Subject motivation: The heterofunctional organic compounds are involved in different kinds of tissue, cytosolic and genetic processes, providing a pronounced effect on the vital functions of organism. A lot of them are potent bioregulators of physiological processes and essential medicines. Lipids are essential structural components of cell membranes.

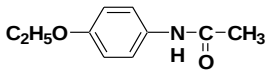
Learning goal: To strengthen knowledge of the structure and chemical properties of the main heterofunctional organic compounds taking into account the mutual influence of their characteristic functional groups as the basis of biochemical processes.

THEORETICAL QUESTIONS

1. Carbonyl compounds. Chemical properties and biomedical significance of aldehydes and ketones.
2. Carboxylic acids. Structure and chemical properties of functional derivatives of carboxylic acids (anhydrides, amides, esters). The reactions of decarboxylation.
3. Structure and properties of dicarboxylic acids: oxalic, malonic, succinic, glutaric, fumaric acid.
4. Structure and properties of carboxylic acid and its derivatives. Urethane, ureido acids, urea.
5. Carboxylic acids esters: nomenclature, preparation, properties.
6. Aromatic amines: structure, properties. Aniline as a precursor in the synthesis of pharmaceuticals - sulfanilamide, phenacetin, anaesthesin, novocaine.
7. Hydroxy acids. Structure and properties of monocarboxylic, dicarboxylic and tricarboxylic hydroxy acids.
8. Structure and properties of the most common oxo acids: pyruvic, acetoacetic, oxaloacetic, α-ketoglutaric. The concept of ketone bodies.
9. Phenolic acids. Salicylic acid and its anti-inflammatory derivatives (acetylsalicylic acid, methyl salicylate, sodium salicylate) and antimicrobial (phenyl salicylate) compounds.
10. Lipids: definition, classification. Fatty acids: palmitic, stearic, oleic, linoleic, linolenic, arachidonic. Lipids. Triacylglycerols (neutral fats): structure, physiologic significance, the hydrolysis.
11. Complex lipids. Phospholipids: phosphatidic acid, phosphatidyl-ethanolamine, phosphatidylcholine, phosphatidylserine. Sphingolipids. Glycolipids. The role of complex lipids in the structure of biological membranes.
12. Steroids as derivatives of sterane. The structure of biologically important representatives of steroids: cholesterol, vitamin D, bile acids, corticosteroids, sex hormones.

ADDITIONAL PROBLEMS

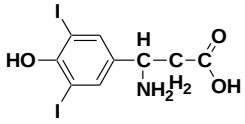
1. Phenacetine is an antipyretic drug.



Determine which class of organic compounds it is referred to:?

A. amine
B. amide
C. aldehyde
D. ester
E. ketone

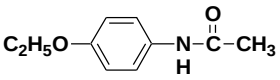
2. Betazine is a synthetic hormone drug:



Specify the senior functional group in the molecule:

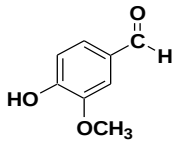
A. –I
B. –OH
C. $–NH_2$
D. –COOH
E. aromatic ring

3. Select the two starting substances for Phenacetin synthesis:



A. *p*-Phenetidin + $(CH_3CO)_2O$
B. Aniline + $(CH_3CO)_2O$
C. *p*-Phenetidin+ C_2H_5OH
D. *p*-Toluidine + $(CH_3CO)_2O$
E. Phenol + CH_3COOH

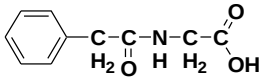
4. Vanilla has a strong smell of aldehyde vanillin:



What is the product of treatment vanillin with $H_2N–NH_2$:

A. the reaction does not go
B. vanillin hydrazine
C. vanillin hydrazone
D. vanillin hydrazide
E. vanillin oxime

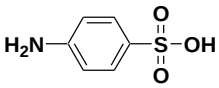
5. Phenaceturic acid is a substance extracted from the urine of animals:



Specify what reagent interacts with phenaceturic acid by COOH-group:

A. C_2H_5Cl ($AlCl_3$)
B. HCl
C. Br_2
D. C_2H_5OH (H^+)
E. $CH_3–O–CH_3$

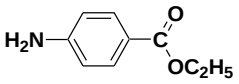
6. Sulfanilic acid is the precursor of sulfanilamides:



Specify the reagent, which interacts only with sulfo-group:

A. CH_3COCl
B. $SOCl_2$
C. Br_2
D. NaOH
E. HCl

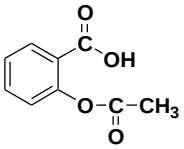
7. Benzocaine is a local anesthetic:



Specify the agent which could qualitatively prove the aromatic amino group in the molecule:

A. $AgNO_3$
B. $NaNO_2$ (HCl)
C. HNO_3 (H_2SO_4)
D. $NaHCO_3$
E. $Cu(OH)_2$

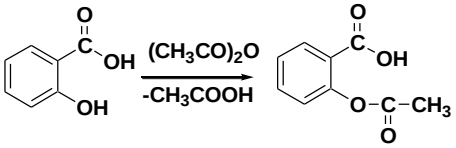
8. Aspirin (acetylsalicylic acid), is an antipyretic and anticoagulant:



Specify the reagent used for the synthesis of aspirin from salicylic acid:

A. C_2H_5OH
B. $H_3C–COOH$
C. $H_3C–COOC_2H_5$
D. $CH_3C(O)NH_2$
E. $(CH_3CO)_2O$

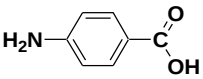
9. Aspirin is generally obtained by acetylating of the salicylic acid:



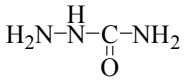
Specify the reagent which could confirm the presence of salicylic acid as an impurity:

A. Br_2
B. NaOH
C. $FeCl_3$
D. $Cu(OH)_2$
E. $Ag(NH_3)_2OH$

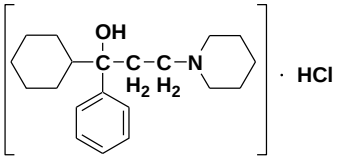
10. PABA (*p*-aminobenzoic acid), is a part of the folic acid and paracetamol:



Specify the reagent to get its hydrazide:

A. $H_2N–NH_2$
B. $H_2N–NH–C_6H_5$
C. $H_2N–C_6H_5$
D. $H_2N–OH$
E. 

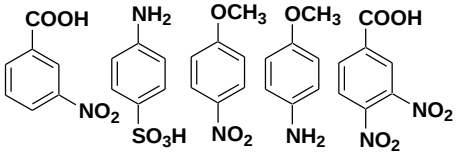
11. Cyclodol is an anticholinergic.



Specify the number of asymmetric carbon atoms in the molecule:

A. 0
B. 1
C. 2
D. 3
E. 4

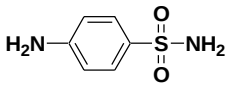
12. Which of following benzene heterofunctional derivatives is the most active in the S_E reaction:



1 2 3 4 5

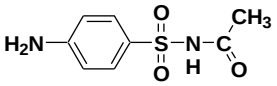
A. 1
B. 2
C. 3
D. 4
E. 5

13. Determine the class of organic compounds of Streptocide:



A. aromatic amine
B. carbocyclic amine
C. aromatic acid
D. aromatic sulfonic acid
E. amide of aromatic sulfonic acid

14. Specify the functional group which is absent in the molecule of Sulfacetamid (Albucid):

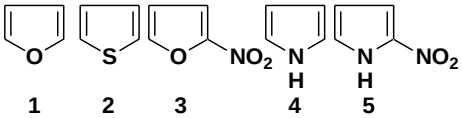


A. aliphatic amino group
B. aromatic amino group
C. aromatic ring
D. acetyl group
E. amide group

15. Indicate the type and sign of electronic effects of the oxygen atom in the molecule of furan:

A. -I
B. +I
C. -M
D. +M
E. -I; +M

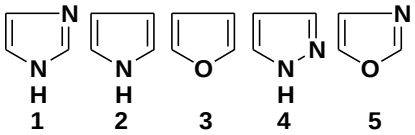
16. There are some five-membered heterocyclic compounds components of the many drugs:



Which of them has the strongest acidic properties.

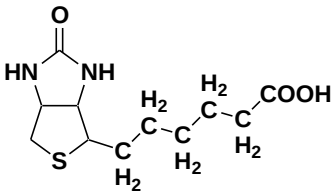
A. 3
B. 5
C. 1
D. 2
E. 4

17. Select the compound with the strongest basic properties among the next compounds:



A. 4
B. 2
C. 3
D. 1
E. 5

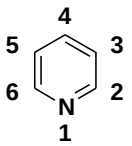
18. Biotin (vit H) has the following structure:



What heterocycles it consists of ?

A. pyrazole and thiophene
B. hydrogenated pyrazole and thiophene
C. hydrogenated pyrrole and thiazole
D. imidazole and hydrogenated thiophene
E. hydrogenated imidazole and thiophene

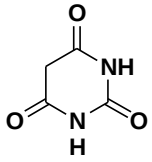
19. Pyridine is a part of many drugs:



Indicate how many monomethyl-substitued pyridines (picolines) could be formed.

A. 1
B. 3
C. 2
D. 4
E. 5

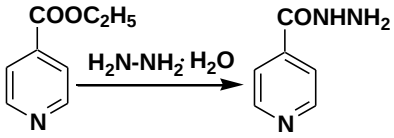
20. Barbituric acid is the basis of many sedatives and anticonvulsants:



Specify the tautomerism which is typical of barbituric acid.

A. lactim-lactam, azole
B. lactim-lactam, keto-enol
C. keto-enol, amine-imine
D. oxo-hydroxy, azole
E. lactamim-lactam, tion-thiol

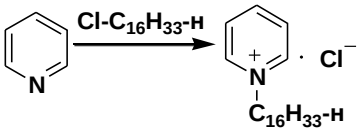
21. Isoniazid is an antituberculosis drug, is obtained according to the next reaction:



Indicate the mechanism of this reaction.

A. S_E
B. S_N1
C. S_R
D. S_N2
E. A_N

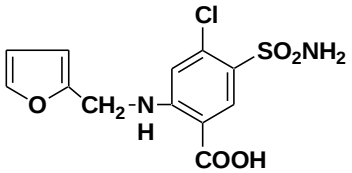
22. Cetylpyridinium chloride (Septolete®) is antibacterial drug is obtained by the next reaction:



What pyridine's property makes possible the above reaction.

A. aromaticity.
B. basicity.
C. electrophilicity.
D. nucleophilicity
E. polarity

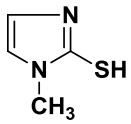
23. Furosemide is a strong diuretic:



Specify it's senior functional group.

A. SO_2NH_2
B. furan ring
C. secondary amino group
D. COOH
E. Cl

24. Merkazolil is an antithyroid drug:



Choose it's correct IUPAC name.

A. 1-methyl-2-thiopyrazol
B. 1-methyl-1*H*-imidazol-2-thiol
C. 1-methyl-2-thiopyrrol
D. 2-mercapto-3-methylimidazol
E. 1-methyl-2-thiopyrazol

.

CHALLENGE QUESTIONS

1. What compounds give positive Tollence test? ("Silver Mirror")? Is there any characteristic redox reactions for hydroquinone in human body?
2. Show the electronic structure of the oxo group, and explain why nucleophilic addition (A_N) at C=O bond is characteristic for aldehydes and ketones in comparison with the C=C bond. Explain the role of acid catalysis and compare the effect of substituents on the reactivity of the oxo-group of aldehydes and ketones. Write the reaction of the following aldehydes and ketones: formaldehyde, acetaldehyde, trichloroacetic aldehyde, and acetone with HCN, ethylamine, methyl and ethyl alcohols, water, and lithium aluminum hydride. Describe the mechanism of these reactions and indicate the nucleophiles. Justify the acid catalysis in the synthesis of acetals. Write the hydrolysis of acetals. What role plays reaction of aldehydes with alcohols and amines in the human body? What explains the stability of the hydrated forms of aldehydes? How hydrates of aldehydes are used in medicine?
3. Explain the CH-acidity of the α-carbon atom next to the oxo group. Write the acetal formation with acetic and propionic aldehyde. Could trimethylacetic aldehyde interact in aldol condensation? Write "iodoform test" for acetone and acetaldehyde. Why does this haloform reaction is used in medicine?
4. Write disproportionation (dismutation, Cannizzaro reaction) for formaldehyde and benzaldehyde. What structural features determine the possibility of this reaction for aldehydes?

Literature

1. Organic Chemistry / J. McMurry. – 8th ed. Brooks/Cole. 2012; 1262 p.
2. Principles of general, organic, and biological chemistry / J.G. Smith. – 1st ed. McGraw-Hill. 2012; 596 p.
3. Organic Chemistry / W.H. Brown, Ch.S. Foote, B.L. Iverson, E.V. Anslyn. – 5th ed. Brooks/Cole. 2011; 1146 p.
4. Organic Chemistry / I. Blei, G. Odian – 2nd ed. W. H. Freeman and Company. 2006; 787 p.
5. General, Organic, and Biological Chemistry: An Integrated Approach / K.W. Raymond. – 2nd ed. John Wiley & Sons, Inc. 2008; 541 p.
6. Lectures.

Lesson №12

Subject: α-AMINO ACIDS. PEPTIDES. STRUCTURE, NOMENCLATURE, CHEMICAL PROPERTIES.

Subject motivation: Life is a way of "protein bodies" being. Natural proteins composed of α-amino acids, is inherent in the implementation of a wide variety of functions characteristic for living organisms: the catalytic function – universal, uncharacteristic to other polymer molecules, nutritious (reserve), transportation, security, contractile, structural, hormonal and others. The amino acids alone are used as effective drugs (methionine, sarcolysin, aminalon, etc.). Knowledge of the structure and chemistry of α-amino acids and peptides is necessary for the successful assimilation of the proteins functions at the molecular level.

Learning goal: To build a knowledge about structure and properties of the most important α-amino acids and peptides, as well as their chemical transformations *in vivo* and *in vitro*.

THEORETICAL QUESTIONS

1. Classification of amino acids found in proteins.
2. Nonpolar (hydrophobic) side chains. Polar (uncharged) side chains.
3. Negatively charged (acidic) side chains. Positively charged (basic) side chains.
4. Stereochemistry of amino acids. Absorption of light by amino acids.
5. Acid-base behavior of amino acids.
6. Reactions of amino acids.
7. Specific reactions of the amino group.
8. Specific reactions of the carboxyl group.
9. Separation of amino acids. Electrophoresis of amino acid mixtures. Ion-exchange chromatography. High-performance liquid chromatography.
10. Stereochemistry of the peptide bond.
11. The amino acid sequence of polypeptide chains.

LABORATORY PRACTICE

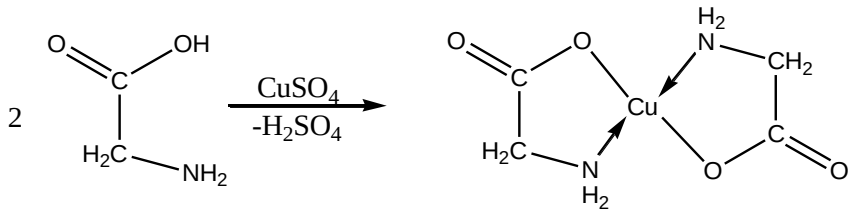
Protocol № 12 Date_____

Experiment 1.

The formation of glycine complex salt with copper(II).

Place 0.5 ml of 2% copper(II) sulfate solution and 0.5 ml of 1% glycine solution in the test tube. The stable blue chelate copper salt of glycine is formed.

The chemistry of the reaction:



Observations:

Conclusions:

Experiment 2.

Precipitation of proteins with concentrated mineral acids.

Put 1 ml of white egg and 1 ml of concentrated nitric acid in the test tube. White flocculent precipitate is formed.

Observations:

Conclusions:

Experiment 3.

Precipitation of proteins by heavy metals salts.

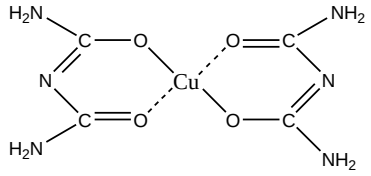
Add 1 ml of white egg, then dropwisely with stirring add 20% copper(II) sulfate solution till precipitate is formed in the first tube. And add the same amount of protein in the second test tube, then dropwisely add 20% aqueous solution of lead(II) acetate. The precipitation is observed in both test tubes.

Observations:

Conclusions:

CHALLENGE QUESTIONS

1. The biuret test requires formation of the next complex compound:



Explain the chemical reaction on the peptide bond.

2. Write a synthesis of the dipeptide alanine-valine (Ala-Val) using the operations "activation" and "protection". Specify the N-and C-ends of the amino acids.

3. What products are formed by oxidative and non- oxidative deamination of tryptophan?

4. What substance is formed by the treatment of nitrous acid with alanine?

Literature

1. Organic Chemistry / J. McMurry. – 8th ed. Brooks/Cole. 2012; 1262 p.

2. Principles of general, organic, and biological chemistry / J.G. Smith. – 1st ed. McGraw-Hill. 2012; 596 p.

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6. Lectures.

Lesson № 13

Subject: STRUCTURAL ORGANIZATION, PHYSICAL AND CHEMICAL PROPERTIES OF PROTEINS. SYNTHESIS AND ANALYSIS.

Subject motivation: Antibodies - are specialized proteins involved in defending the body from antigens (foreign invaders). They can travel through the

bloodstream and are utilized by the immune system to identify and defend against bacteria, viruses, and other foreign intruders. Contractile proteins - are responsible for movement. Examples include actin and myosin. These proteins are involved in muscle contraction and movement. Enzymes - are proteins that facilitate biochemical reactions. They are often referred to as catalysts because they speed up chemical reactions. Examples include the enzymes lactase and pepsin. Lactase breaks down the sugar lactose found in milk. Pepsin is a digestive enzyme that works in the stomach to break down proteins in food. Hormonal proteins - are messenger proteins which help to coordinate certain bodily activities. Examples include insulin, oxytocin, and somatotropin. Insulin regulates glucose metabolism by controlling the blood-sugar concentration. Oxytocin stimulates contractions in females during childbirth. Somatotropin is a growth hormone that stimulates protein production in muscle cells. Structural proteins - are fibrous and stringy and provide support. Examples include keratin, collagen, and elastin. Keratins strengthen protective coverings such as skin, hair, quills, feathers, horns, and beaks. Collagens and elastin provide support for connective tissues such as tendons and ligaments. Storage proteins - store amino acids. Examples include ovalbumin, casein, ferritin. Ovalbumin is found in egg whites and casein is a milk-based protein. Ferritin stores iron in hemoglobin. Transport proteins - are carrier proteins which move molecules from one place to another around the body. Examples include hemoglobin and cytochromes. Hemoglobin transports oxygen through the blood *via* red blood cells. Cytochromes operate in the electron transport chain as electron carrier proteins.

Learning goal: To form deep knowledge about structure and properties of proteins, their synthesis and identification.

THEORETICAL QUESTIONS

1. Stereochemistry of the peptide bond.
2. The amino acid sequence of polypeptide chains.
3. Principle of sequence analysis
4. Identification of amino- and carboxyl-terminal residues.
5. Cleaving the polypeptide chain.
6. The Edman degradation and Sanger method.
7. Steps of chemical synthesis of peptides.
8. Naturally occurring peptides.
9. Structure and function of proteins. Functional roles of proteins.
10. Physical and chemical properties of proteins.
11. Purification of proteins.

12. The three-dimensional structure of proteins.
13. The secondary structure of proteins. The tertiary structure. Protein quaternary structure.
14. Common structural patterns in the conformation of proteins.

LABORATORY PRACTICE

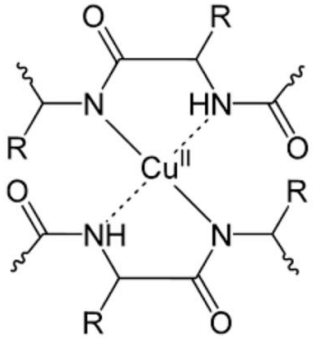
Protocol № 13 Date_____

Experiment № 1

Test: Take two test tubes. In the first add in each 1 ml of 5% sodium hydroxide solution, 1 ml of 1% copper sulphate solution. In the first add 1 ml of fresh albumin (white egg). Compare the colors.

When an amino group and a carboxyl group join to form a peptide bond, the amino group (-NH_2) becomes an amide group (-NH). Therefore, proteins will also complex with copper ions at a basic pH. Because this reaction was the first observed with biuret, it is called the biuret reaction, and when this reaction is used to measure protein concentrations, it is called the Biuret Protein Assay. The amount of blue color that forms is directly proportional to the quantity of protein in the samples.

The chemistry of the reaction:



Observations:

Conclusions:

ADDITIONAL PROBLEMS

1. Beta pleated sheets are examples of protein's

A. primary structure

B. secondary structure*

C. tertiary structure

D. quaternary structure

2. BRACl, an inherited form of breast cancer, regulates cell division by

A. binding to a DNA sequence

B. complexing with cyclins

C. binding to the cell outer membrane

D. binding to the protein RAD 51 which repairs DNA damage*

3. Metastasis involves

A. ability of cells to dissolve cellular matrix

B. metalloprotein levels

C. decreased levels of proteins that regulate metalloproteins

D. all of the above*

4. Signal sequences are part of a protein that

A. signal folding of the protein

B. signal the protein synthesis on the ribosomes is ended

C. transport proteins to other sites within the cell*

D. refold proteins in prion-associated diseases

5. Individuals with PKU disease are mentally retarded unless

A. phenylalanine in the diet is restricted*

B. tyrosine in the diet is restricted

C. homogentisic acid in the diet is restricted

D. none of the above

6. Marfan's syndrome is thought to be a mutation affecting

A. hemoglobin synthesis

B. collagen synthesis*

C. metabolism of homogentisic acid

D. insufficient thyroid production

7. Over 50% of common cancers are associated with damage to a protein, p53. This protein:

A. is a cyclin

B. is a tumor supressor*

C. is an oncogene

D. regulates apoptosis

8. Protein folding is

A. automatic, mediated by the protein itself

B. mediated by other proteins called chaperones*

C. mediated by the ribosomes

D. none of the above

9. Sickle cell disease is due to

A. a mutation in the beta chain of Hb*

B. a mutation in the alpha chain of Hb

C. infection with a parasite

D. none of the above

10. The four subunits of the hemoglobin (Hb) gene represent protein's

A. primary structure

B. secondary structure

C. tertiary structure

D. quaternary structure*

Questions:

1. What are proteins? How can diversity of proteins in living organisms be explained?
2. What is the importance of proteins for living organisms?
3. What units are proteins composed of?
4. What is an oligopeptide? How is it different from a polypeptide?
5. How many amino acids are known to form proteins in living organisms?
6. What is the primary structure of a protein? What is the importance of the primary structure?
7. What is the secondary structure of a protein?
8. What is the difference between alpha-helix and beta-sheet protein conformations? What is the tertiary structure of a protein? What are the main types of tertiary structures? What is the quaternary structure of a protein? Do all proteins have a quaternary structure?
9. What is a protein denaturation? Are there any changes in the primary structure when a protein is denatured?
10. In sickle cell anemia, a hereditary disease, one amino acid is substituted by another in one of the four polypeptide chains of hemoglobin. In this case are all of the structural levels of the protein modified?
11. What are some of the remarkable functions of myosin, CD4, albumin, keratin, immunoglobulin, reverse transcriptase, hemoglobin and insulin?

Literature

1. Organic Chemistry / J. McMurry. – 8th ed. Brooks/Cole. 2012; 1262 p.
2. Principles of general, organic, and biological chemistry / J.G. Smith. – 1st ed. McGraw-Hill. 2012; 596 p.
3. Organic Chemistry / W.H. Brown, Ch.S. Foote, B.L. Iverson, E.V. Anslyn. – 5th ed. Brooks/Cole. 2011; 1146 p.
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6. Lectures.

Lesson № 14

Subject: CARBOHYDRATES. THE STRUCTURE, CLASSIFICATION AND CHEMICAL PROPERTIES OF MONOSACCHARIDES.

Subject motivation: The carbohydrates occupy an important place among the natural compounds. They take part in the construction of vital structures, serve as material for the biosynthesis of various classes of compounds; they play an important role in bioenergetics of the cells. The carbohydrates are part of the physiologically active glycosides, nucleic acids, polysaccharides, glycolipids and glycoproteins. The immunochemical properties of tissues and specific reactions at external chemical stimuli depend on carbohydrates. Deep knowledge of the structure and chemistry of carbohydrates are necessary to master the biological chemistry, pharmacology and other medicinal disciplines.

Learning goal: To form deep knowledge about stereomerism, tautomeric equilibrium, and the chemical properties of monosaccharides; to be able to identify the most important monosaccharides.

THEORETICAL QUESTIONS

1. Nomenclature and classification of monosaccharides.
2. The stereoisomers of glucose (dextrose), fructose (laevulose), galactose, xylose and ribose.
3. Configurations of monosaccharides: D and L designations.
4. Cyclo-oxo-(ring-chain) tautomerism.
5. Determination of the configurations of monosaccharides. The cyclic structures of monosaccharides.
6. Mutarotation.
7. Chemical reactions of monosaccharides. Reduction. Oxidation.
8. Identification of aldoses and ketoses by oxidizing agents.
9. Formation of glycosides.
10. Ethers and esters, ozazones formation.
11. Chain shortening and lengthening. Ruff degradation. Kiliani-Fischer synthesis.
12. Epimerization.

LABORATORY PRACTICE

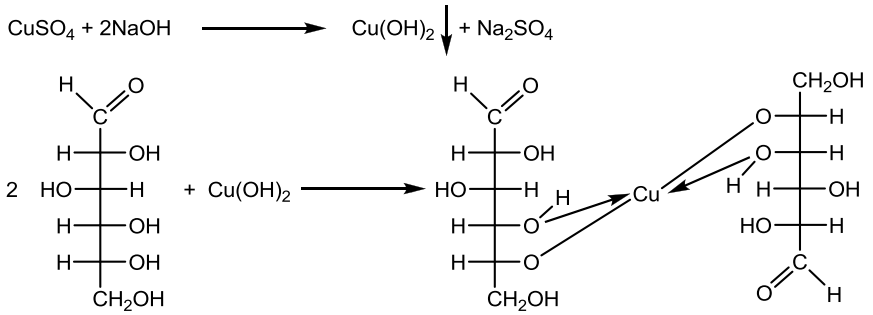
Protocol № 14 Date_____

Experiment № 1

Evidence of the hydroxyl groups in D-glucose.

Place a drop of 0.5% D-glucose solution and 6 drops of 10% sodium hydroxide solution in the test tube. Add 1 drop of 2% copper(II) sulphate solution ($CuSO_4$) to this mixture. The resulting precipitate of copper(II) hydroxide ($Cu(OH)_2$) rapidly dissolves and blue solution turns clear. Save the latter solution for the next experiment.

The chemistry of the reaction:



Observations:

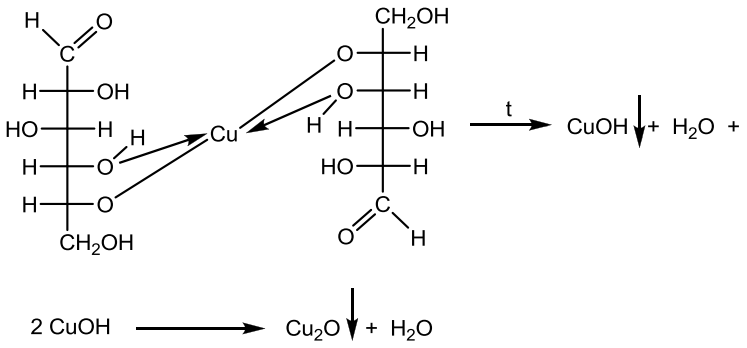
Conclusions:

Experiment № 2

Reduction of the copper(II) hydroxide by glucose in the alkaline medium (Trommer's test).

Put 2 ml of water to the saved solution from the previous experiment. Heat the upper part of the solution over a burner flame only to the boiling point. The color of the upper part of the solution changes from blue to yellow-red because of cuprous oxide formation. This reaction is called Trommer's test and used to identify the glucose in the urine.

The chemistry of the reaction:



Observations:

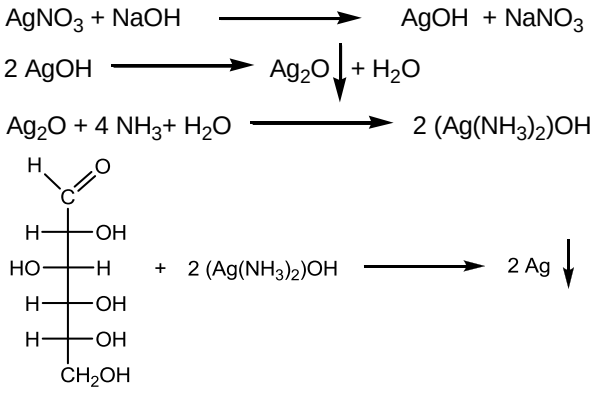
Conclusions:

Experiment № 3

Reduction of the ammonia hydroxide solution of silver by glucose.

Place 1 drop of 5% silver nitrate solution ($AgNO_3$), add 2 drops of 10% sodium hydroxide solution in the test tube. Add 3-4 drops of 10% aqueous ammonia solution to dissolve the resulting precipitate of silver hydroxide. The resulting clear solution of ammonium solution of silver hydroxide is a reagent, which oxidizes the glucose (Tollen's reagent). Add to the resulting mixture 1 drop of 0.5% glucose solution and gently heat the test tube over the burner flame till solution turns brown. Then, the reaction proceeds without heating and metallic silver falls either in the form of a black precipitate or precipitates on the walls of the tubes as a mirror film ("Silver Mirror" reaction).

The chemistry of the reaction:



Observations:

Conclusions:

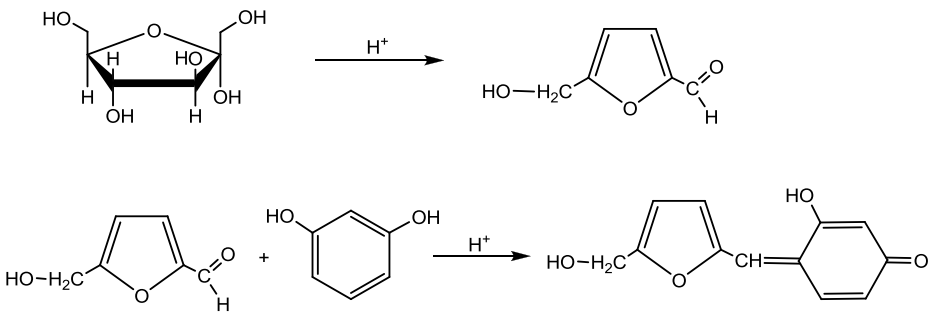
Experiment № 4

Selivanov's test for fructose.

Place few dry crystals of resorcinol and 2 drops of concentrated hydrochloric acid in the test tube. Add 2 drops of 0.5% fructose solution and heat it. Formation of burgundy-red color after heating indicates the fructose. The

reaction is caused by the formation of unstable compound – hydroxymethylfurfural (HMF). In the acidic media (concentrated hydrochloric acid) HMF condenses with resorcinol, giving a colored condensed product.

The chemistry of the reaction:



Observations:

Conclusions:

CHALLENGE QUESTIONS

1. Write the Fischer projection and Haworth perspective formula of *β*-D-galactopyranose. Specify the configuration of an atom that determines the D-series.
2. Write the reaction of galactaric (mucic) acid synthesis. Specify the conditions.
3. Write the reaction of *β*-D-galactopyranose (Haworth formula) with ethanol in the presence of HCl. Name the resulting compound and write its hydrolysis.

Literature

1. Organic Chemistry / J. McMurry. – 8th ed. Brooks/Cole. 2012; 1262 p.
2. Principles of general, organic, and biological chemistry / J.G. Smith. – 1st ed. McGraw-Hill. 2012; 596 p.
3. Organic Chemistry / W.H. Brown, Ch.S. Foote, B.L. Iverson, E.V. Anslyn. – 5th ed. Brooks/Cole. 2011; 1146 p.
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6. Lectures.

Lesson № 15

Subject: THE STRUCTURE AND FUNCTIONS OF DI- AND POLYSACCHARIDES.

Subject motivation: Life processes go along with complex chemical transformations of carbohydrates (carbohydrate metabolism). Carbohydrates occupy a special place in the body dealing with highly specialized functions (nucleotides – carriers of genetic code, specific polysaccharides – antigens of the immune system; glycoproteins – the specific components of blood etc.). Certain types of carbohydrates are units of plant cells and play a supporting role. Profound knowledge of the structure and chemistry of disaccharides and polysaccharides are necessary for the acquisition of skills in the study of the relevant sections of biological chemistry, pharmacology, therapy and other disciplines.

Learning goal: To form knowledge of the principles and basic structure of the chemical transformations of the most important di- and polysaccharides in relation to their biological functions.

THEORETICAL QUESTIONS

1. Configurations of monosaccharides: D and L designations.
2. Oligosaccharides. Disaccharides (bioses): cellobiose, maltose, lactosa, and sucrose.
3. Reducing and nonreducing disaccharides. Mutarotation.
4. Sweeteners in food.
5. Homopolysaccharides: starch, glycogen, chitin, cellulose, insulin.
6. Heteropolysaccharides: hyaluronic acid, chondroitin sulfates, pectin, lignin, glycoproteins, glycolipids, and mucopolysaccharides.
7. The structure of bacterial cell wall.

LABORATORY PRACTICE

Protocol № 15 Date _____

Experiment № 1

The absence of the reducing properties of the sucrose.

Place 1 drop of 1% sucrose solution and 6 drops of 10% sodium hydroxide solution in the test tube. Add 10 drops of the water (to height of the liquid layer 15-20mm). Add 1 drop of 2% copper(II) sulphate solution ($CuSO_4$). A clear blue

solution of the complex sucrose salt with copper(II) is formed. Warm up gently the test tube in the burner flame heating only the upper part of the solution, and remain the lower part unheated (control). Don't boil the solution. No change of color is observed.

Remember (***Protocol № 11, Experiment № 2***) that the reducing saccharide *D*-glucose changes color of the upper part of the solution to the yellow-red under the similar conditions.

Observations:

Conclusions:

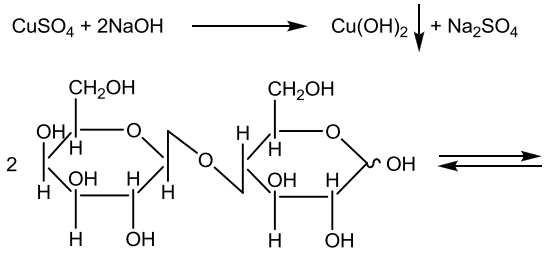
Experiment № 2

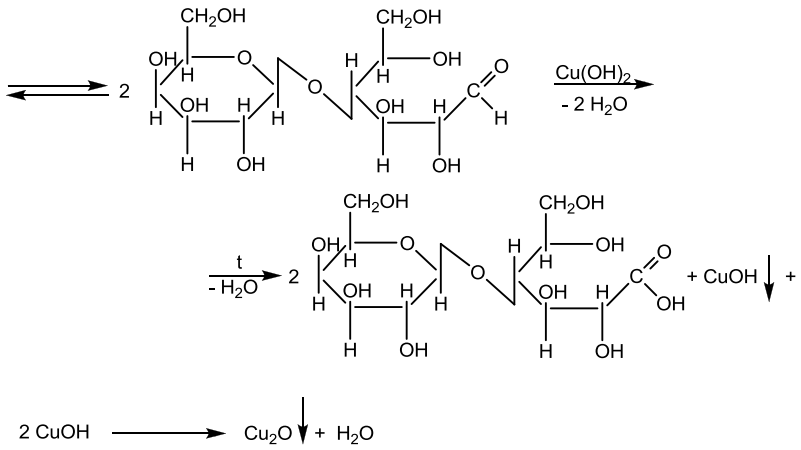
Reducing properties of lactose.

Place 1 drop of 1% lactose solution and 4 drops of 10% sodium hydroxide solution in the test tube. Add 1 drop of 2% copper(II) sulfate solution ($CuSO_4$). The resulting blue precipitate of the copper(II) hydroxide dissolves by shaking the tube, forming a blue solution of the complex lactose salt with copper(II). Add 10 drops of water in the test tube. Gently heat only the upper part of the test tube, remaining the bottom without heating (control). Heat to boiling point. The color of the upper part of the solution changes to yellow-red during the heating.

Remember (***Protocol № 11, Experiment № 2***) that the reducing saccharide *D*-glucose changes color of the upper part of the solution to the yellow-red under the similar conditions.

The chemistry of the reaction:





Observations:

Conclusions:

Experiment № 3

Starch identification reaction.

Place 5 drops of 0.5% starch and 1 drop of very dilute iodine solution in the test tube. The solution becomes blue (it is supposed that the starch forms with iodine compounds (clathrates), painted in blue color (f_{max} = 620-680 nm) for amylose and red (f_{max} = 520-555 nm) for amylopectin. Amylose coils into a helical secondary structure resembling a tube with a hollow core. The iodine can lodge inside the core. The complex of iodine stuck inside the amylose coil produces a characteristic blue-black color. The starch itself is not altered. Starch-iodine complex becomes unstable at temperatures above 35 °C. This complex in presence of an oxidizing agent the solution turns blue, in the presence of reducing agent, the blue color disappears because triiodide (I_3^-) ions break up into three iodide ions, disassembling the complex. So starch turns into glucose molecules. Therefore the blue black color disappears. However, when it cools down again, then the glucose macromolecules bonded up together again in a long chain, becoming starch. That is why it tested positive for starch and turns back into blue-black color.

Observations:

Conclusions:

Experiment № 4

Acid hydrolysis of starch.

Place a drop of 0.5% starch paste in the test tube. Add 2 drops of 10% sulfuric acid solution (H_2SO_4), and place the tube in a boiling water bath. Turbid solution of starch paste becomes clear after 20 minutes. Put 1 drop of the hydrolyzate on a glass slide with pipette and add 1 drop of iodine in potassium iodide dilute solution. If a sample does not give a positive reaction with iodine (blue color), add 8 drops of 10% sodium hydroxide (NaOH) into the tube to achieve an alkaline medium. Then add 1 drop of 2% of copper(II) sulphate solution ($CuSO_4$.). Will the Trommer's test be positive?

The chemistry of the hydrolysis of starch:

$$(C_6H_{10}O_5)n \xrightarrow{H_2O;\ H^+} (C_6H_{10}O_5)x \xrightarrow{H_2O;\ H^+} (C_{12}H_{22}O_{11})x \xrightarrow{H_2O;\ H^+} C_6H_{12}O_6$$

$x < n$

Observations:

Conclusions:

CHALLENGE QUESTIONS

1. Write the structural and conformational formulas of milk sugar (lactose). Give its full name. Write the hydrolysis of lactose.
2. Write the reaction of maltose with an excess of dimethyl sulfate. Name the product and show its hydrolysis. Will the obtained compound have the reducing properties?
3. Write the structural formula of the disaccharide consisting of *D*-glucuronic acid and *N*-acetylglucosamine, which are connected by *β*-1,3-glycosidic bond. What biopolymer this fragment is a part of?

Literature

1. Organic Chemistry / J. McMurry. – 8th ed. Brooks/Cole. 2012; 1262 p.
2. Principles of general, organic, and biological chemistry / J.G. Smith. – 1st ed. McGraw-Hill. 2012; 596 p.

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6. Lectures.

Lesson № 16

Subject: CLASSIFICATION, STRUCTURE, NOMENCLATURE, CHEMICAL PROPERTIES AND BIOLOGICAL VALUE OF HETEROCYCLIC COMPOUNDS.

Subject motivation: Knowledge of the nomenclature of organic compounds and their conformational features and configuration, the mutual influence of atoms in the molecules is critical in predicting of organic substances physico-chemical properties and reactivity. It contributes the understanding of the radical, electrophilic mechanisms of reactions *in vivo* and *in vitro*, as well as to form the conception about the pharmacological properties of drugs.
Learning goal: To develop knowledge about the chemical behavior of the major classes of organic compounds depending on their chemical structure.

THEORETICAL QUESTIONS

1. Biologically important derivatives of heterocyclic compounds containing nitrogén atom.
2. Five-membered heterocycles.
3. Six-membered heterocycles.
4. Structure and chemical properties of the 5-pyrazolone derivatives (amidopyrine, antipyrine, analgin). Lactim-lactam tautomerism.
5. Polycyclic compounds containing nitrogén heteroatom.
6. Alkaloids. Pyrrolidine alkaloids e.g., Hygrine; Piperidine alkaloids e.g., Lobeline; Pyrrolizidine alkaloids e.g., Senecionine; Tropane alkaloids e.g., Atropine; Quinoline alkaloids e.g., Quinine; Isoquinoline alkaloids e.g., Morphine; Aporphine alkaloids e.g., Boldine; Indole alkaloids e.g., Ergometrine; Imidazole alkaloids e.g., Pilocarpine; Diazocin alkaloids e.g., Lupanine; Purine alkaloids e.g., Caffeine;
7. Heterocyclic vitamins. Vitamin B1 (Thiamin), Vitamin B2 (Riboflavin), Vitamin B3 (Niacin), Vitamin B6 (Pyridoxine), Vitamin B7 (Biotin), Vitamin

B9 (Folic Acid), Vitamin B12 (Cobalamin).

8. Cofactors. Coenzymes.

LABORATORY PRACTICE

Protocol № 9 Date_____

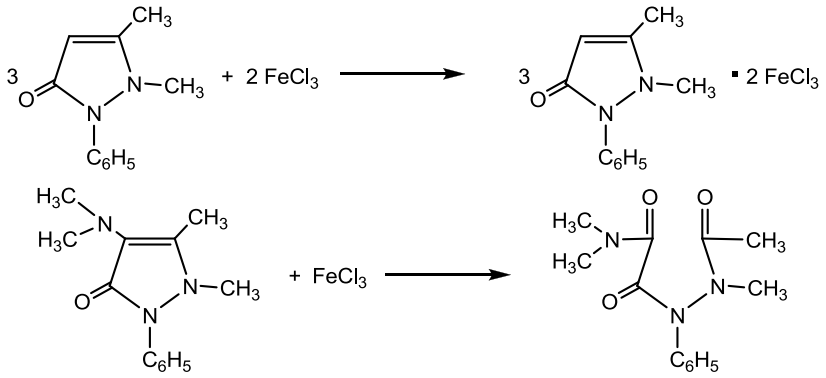
Experiment № 1

The reactions of antipyrine and amidopyrine with iron(III) chloride.

Put a few crystals of antipyrine, 2 drops of water and a drop of 1% solution of iron(III) chloride in the test tube. An intense orange-red colored complex compound ferropyrine appears and does not disappear on standing.

Put a few crystals of amidopyrine, 2 drops of water and 1 drop of 1% iron(III) chloride solution in another test tube. The violet color oxidation products appear, quickly disappearing. Add more 3 drops of iron(III) chloride. The violet color reappears for longer time, but gradually fades.

The chemistry of the reaction:



Observations:

Conclusions:

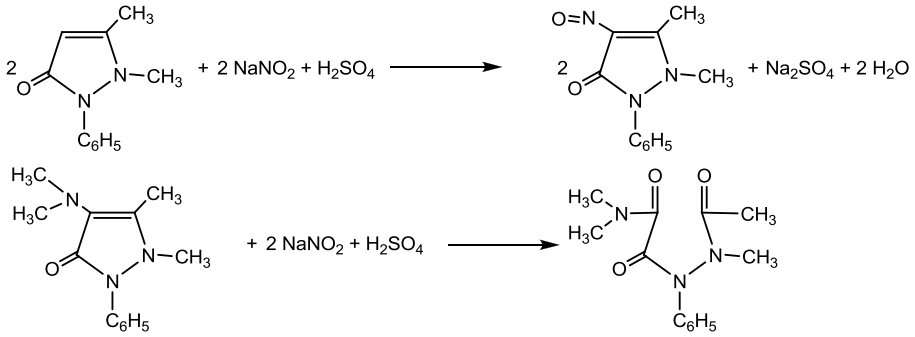
Experiment № 2

Reaction of antipyrine and amidopyrine with nitrous acid.

Place a few crystals of antipyrine, 2 drops of water, 1 drop of 5% sodium nitrite solution in the test tube. The emerald green color appears, gradually fading, especially with an excess of sodium nitrite.

In the second test tube, place a few crystals of amidopyrine. Add 2 drops of water, 1 drop of 10% sulfuric acid solution and 1 drop of 5% sodium nitrite solution. The unstable violet color products of amidopyrine oxidation are formed. If the color disappears too quickly, add a little more of amidopyrine. The reaction with nitrous acid is used in pharmaceutical practice to distinguish the antipyrine and amidopyrine.

The chemistry of the reaction:



Observations:

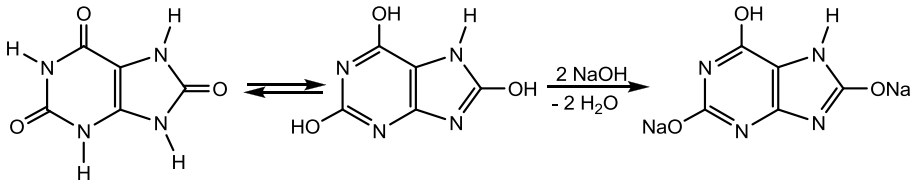
Conclusions:

Experiment № 3

The solubility of uric acid and its sodium salt in water.

Place a bit of uric acid in the test tube. Add water drop by drop, each time shaking the test tube. Pay attention to the poor solubility of uric acid in the water. In the cold water it almost insoluble: 1 part dissolves in 39,000 parts of water. Add only 1 drop of 10% sodium hydroxide solution - the solution becomes clear immediately because the soluble dibasic uric acid sodium salt is formed. Save the latter solution for the next experiment.

The chemistry of the reaction:



Observations:

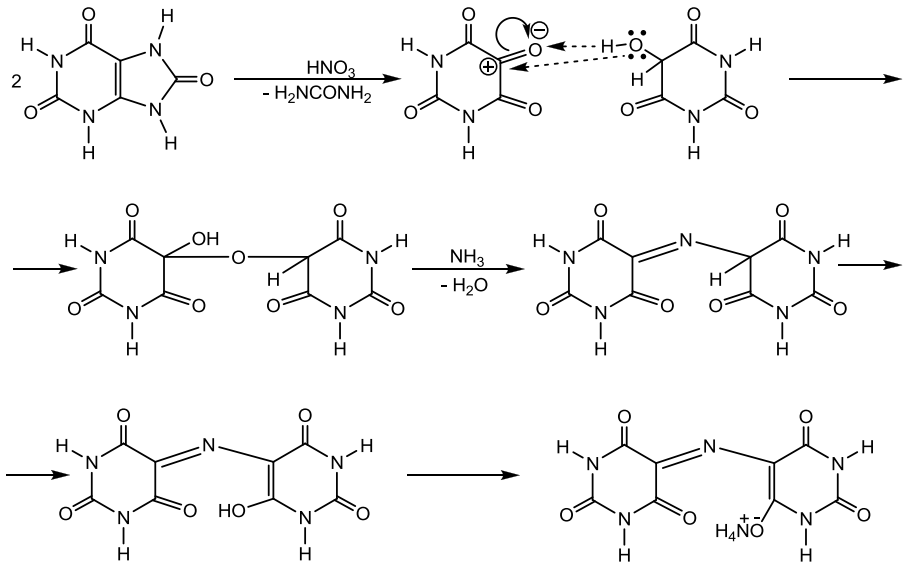
Conclusions:

Experiment № 4

The identification of the uric acid (The murexide test).

Place a drop of uric acid sodium salt solution saved from the previous experiment on a microscope slide. Add one drop of concentrated nitric acid and evaporate gently, holding the glass above the burner flame at some distance (approximately 10 cm). Once the solution is evaporated and the red spots will faint on the former site of the drop, stop heating. When the glass cools place 1 drop of 10% ammonia solution near the red spot. At the contact line the purple-violet stripes (murexide) appear. The murexide test is used in the analysis of urinary stones. This test applies also for identification of caffeine, theobromine and other purine bases.

The chemistry of the reaction:



Observations:

Conclusions:

CHALLENGE QUESTIONS

1. Write to the oxidative and non-oxidative deamination of histidine. Justify the value of this reaction for living organisms.
2. Explain the different solubility of uric acid salts. Which disorders in the body causes the formation of insoluble salts of uric acid.
3. Give the structure of pyridine, pyrimidine, purine. Explain the aromaticity of these compounds, justify their reactivity.

Literature

1. Organic Chemistry / J. McMurry. – 8th ed. Brooks/Cole. 2012; 1262 p.
2. Principles of general, organic, and biological chemistry / J.G. Smith. – 1st ed. McGraw-Hill. 2012; 596 p.
3. Organic Chemistry / W.H. Brown, Ch.S. Foote, B.L. Iverson, E.V. Anslyn. – 5th ed. Brooks/Cole. 2011; 1146 p.
4. Organic Chemistry / I. Blei, G. Odian – 2nd ed. W. H. Freeman and Company. 2006; 787 p.
5. General, Organic, and Biological Chemistry: An Integrated Approach / K.W. Raymond. – 2nd ed. John Wiley & Sons, Inc. 2008; 541 p.
6. Lectures.

Lesson № 17

Subject: THE STRUCTURE AND BIOCHEMICAL FUNCTIONS OF NUCLEOSIDES, NUCLEOTIDES AND NUCLEIC ACIDS.

Subject motivation: Knowledge of structural and stereochemical features of the nucleosides, nucleotides, and nucleic acids contributes the understanding the protein biosynthesis mechanism, genetic information transfer, coenzyme functioning, as well as the role of ATP as an energy "supplier" in the various biochemical processes.

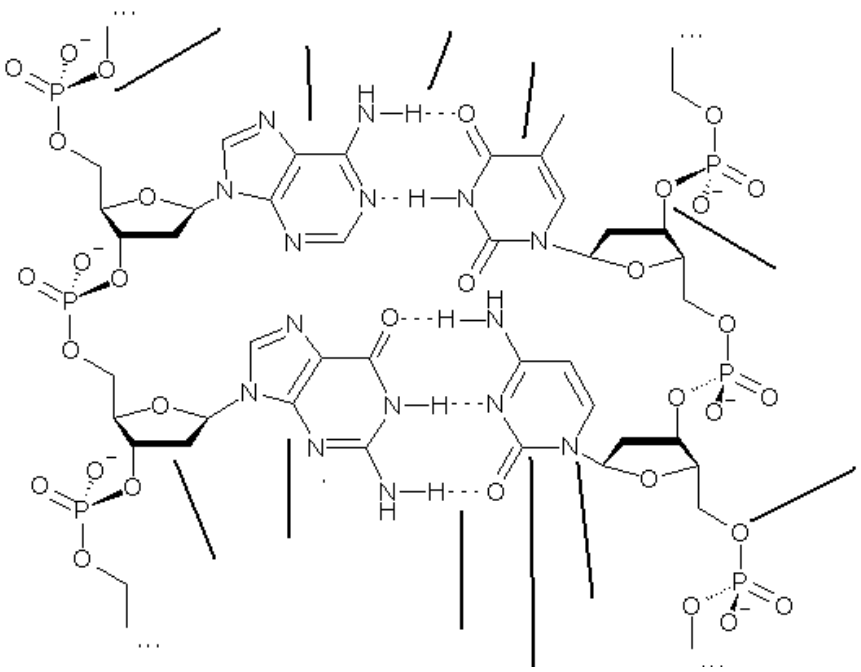
Learning goal: To form knowledge of the nucleic acids primary, secondary, tertiary, and quaternary structure, that is a necessary prerequisite to understanding of their biosynthesis and biological role. The central dogma of molecular biology deals with the detailed residue-by-residue transfer of sequential information. It states that such information cannot be transferred back from protein to either protein or nucleic acid. DNA makes RNA and RNA makes protein.

THEORETICAL QUESTIONS

1. Classification and nomenclature of nucleic bases.
2. Lactim-lactam tautomerism.
3. The complementarity of the bases.
4. The structure of the nucleoside.
5. The structure of the nucleotide.
6. Polynucleotídes.
7. Chemical structure of DNA. Double helix.
8. Denaturation of double-stranded DNA.
9. Principle of hybridization.
10. Types of DNA structure. Determination of DNA sequences.
11. Chemical structure of RNA. Secondary and tertiary structures of RNA.
12. Types of RNA
13. Importance of nucleic acids in the life of plant and animal organisms.

CHALLENGE QUESTIONS

1. Write a scheme of deoxycytidylic acid hydrolytic cleavage in the acidic medium.
2. Write a tautomeric forms of thymine. Which of the tautomers predominates in the equilibrium mixture?
3. Which of the two base pairs UA or TA is the part of the DNA? Write the structure of this pair.
4. Name all the bonds and structural fragments and decide is it DNA or RNA part.



Literature

1. Organic Chemistry / J. McMurry. – 8th ed. Brooks/Cole. 2012; 1262 p.
2. Principles of general, organic, and biological chemistry / J.G. Smith. – 1st ed. McGraw-Hill. 2012; 596 p.
3. Organic Chemistry / W.H. Brown, Ch.S. Foote, B.L. Iverson, E.V. Anslyn. – 5th ed. Brooks/Cole. 2011; 1146 p.
4. Organic Chemistry / I. Blei, G. Odian – 2nd ed. W. H. Freeman and Company. 2006; 787 p.
5. General, Organic, and Biological Chemistry: An Integrated Approach / K.W. Raymond. – 2nd ed. John Wiley & Sons, Inc. 2008; 541 p.
6. Lectures.

Lesson №18

FINAL SUBMODULE CONTROL III

«Biologically important classes of bioorganic compounds. Heterocyclic. Biopolymers and their structural components"

1. Carbohydrates: definition, classification. Sugars (aldose and ketoses; triose, tetroze, pentose, hexose, heptoze), the biomedical significance of the individual representatives.
2. Monosaccharides: pentoses (ribose, 2-deoxyribose, xylose), hexose (glucose, galactose, mannose, fructose) - structure, properties. Identification of the glucose.
3. Structure and properties of amine derivatives of monosaccharides: glucosamine, galactosamine. Uronic acid. L-ascorbic acid (vitamin C). Sorbitol, mannitol.
4. Oligosaccharides: structure, properties. Disaccharides (sucrose, lactose, maltose), and their biomedical significance.
5. Polysaccharides. Homopolisaccharides: starch, glycogen, cellulose, dextrans - structure, hydrolysis, biomedical significance. Identification of the starch.
6. Heteropolysaccharides: definition, structure. The structure and biomedical significance of glycosaminoglycans (mucopolysaccharides) - hyaluronic acid, chondroitin sulfates, heparin.
7. Lipids: definition, classification. Fatty acids: palmitic, stearic, oleic, linoleic, linolenic, arachidonic. Lipids. Triacylglycerols (neutral fats): structure, physiologic significance, the hydrolysis.
8. Complex lipids. Phospholipids: phosphatidic acid, phosphatidyl-ethanolamine, phosphatidylcholine, phosphatidylserine. Sphingolipids. Glycolipids. The role of complex lipids in the structure of biological membranes.

9. Steroids as derivatives of sterane. The structure of biologically important representatives of steroids: cholesterol, vitamin D, bile acids, corticosteroids, sex hormones.

10. Amino acids. Classification, nomenclature, chemical properties of L-α-amino acids. Ninhydrine reaction.

11. Proteins and peptides: definition, classification and biological functions. The types of bonds between amino acid residues in protein molecules. Peptide bond: formation, structure: the biuret reaction.

12. Primary, secondary, tertiary, and quaternary structure of proteins. Oligomeric proteins.

13. Methods for fractionation and analysis of proteins and peptides (sedimentation, chromatography, electrophoresis). Analysis of the primary structure of proteins and peptides: methods Sanger and Edman.

14. Nucleosides. Nucleotides as phosphorylation derivatives of nucleosides (nucleozidmono-, di-and triphosphates). Nomenclature of nucleosides and nucleotides as components of RNA and DNA.

15. Structure and properties of DNA nucleotide composition, complementarities of the nitrogenous bases. Primary, secondary and tertiary structure of DNA.

16. RNA: structure, types of RNA and their role in protein biosynthesis.

17. Vitamins.The concept of the coenzyme activity of vitamins. Structure and properties of vitamins B1, B2, B6, PP.

18. Hormones: the concept of hormones as bioregulators. General characteristics of hormones of protein-peptide group, amino acid derivatives, steroids and eicosanoids.

19. Alkaloids: definition. The value of the alkaloids as the active drugs (class of pyridine and piperidine, quinoline and isoquinoline, trephine, indole).

LESSON № 19

FINAL MODULE CONTROL

"BIOLOGICALLY IMPORTANT CLASSES OF BIOORGANIC COMPOUNDS. BIOPOLYMERS AND THEIR STRUCTURAL COMPONENTS"

1. Bioorganic chemistry as a science: definition, object and tasks, methods of research. Its value for the higher medical education.
2. Classification of organic compounds by the structure of the carbon radical and the nature of functional groups.
3. The structure of the major classes of bioorganic compounds according to the functional groups: alcohols, phenols, thiols, aldehydes, ketones, carboxylic acids, esters, amides, nitro compounds, amines.
4. Nomenclature of organic compounds: trivial, rational, international. Principles of IUPAC nomenclature: substitution, radical-functional.
5. The theory of organic compounds structure. The concept of structural isomers.
6. The nature of chemical bonds in organic compounds: hybridization of orbitals, the electronic structure of carbon compounds.
7. The delocalization of the electrons and conjugate systems. Conjugated systems with open-chain: electronic structure and chemical properties of 1,3-dienes.
8. Conjugate compounds with close chain: the electronic structure of benzene, aromaticity of arenes and heterocyclic compounds.
9. Polar covalent bonds. Inductive and resonance effects. Substituent's effect in aromatic rings.
10. The spatial structure of bioorganic compounds: stereochemical formula, configuration and conformation. Stereoisomers: geometric, optical, rotary (conformers).

11. Geometric isomerism in substituted alkenes, cycloalkanes, unsaturated fatty acids, dicarboxylic acids. Cis, trans and E/Z-nomenclatures.

12. Optical isomerism, chirality of organic molecules. D/L-, R/S-stereochemical nomenclature. Enantiomers and diastereomers of bioorganic compounds. Relationship of the spatial structure – physiological activity.

13. Conformational isomers; Newman projection formulas. The energy characteristics of the conformational isomers of the syn-, anti-, and gauche conformations.

14. Conformational isomers of cyclic hydrocarbons. Axial and equatorial bonds in the molecule of cyclohexane. The input of the conformational isomerism for the formation of the spatial structure of biomolecules.

15. Types of reactions: classification by the direction and the reaction mechanism.

16. Characteristics and examples of specific types of reactions in bioorganic chemistry: addition, substitution, elimination, oxidation and reduction.

17. Characteristics and examples of nonpolar (radical) and polar (ionic) reactions in bioorganic chemistry. Electrophilic and nucleophilic reagents.

18. The oxidation-reduction reaction. Free radical reactions of bioorganic compounds, their importance in the normal and pathological conditions.

19. Acidic and basic properties of organic compounds: a proton Bronsted theory, Lewis theory of acids and bases.

20. Structure, properties and biomedical significance of the individual representatives of the alcohols and thiols.

21. Phenols: structure, properties and biomedical significance. Characteristics of the monatomic (phenol, cresol) and diatomic (pyrocatechol, resorcinol, hydroquinone) phenols.

22. Thiols (mercaptans), sulfides and disulfides. Structure and chemical properties.

23. Carbonyl compounds. Chemical properties and biomedical significance of aldehydes and ketones.

24. Carboxylic acids. Structure and chemical properties of functional derivatives of carboxylic acids (anhydrides, amides, esters). The reactions of decarboxylation.

25. Structure and properties of dicarboxylic acids: oxalic, malonic, succinic, glutaric, fumaric acid.

26. Structure and properties of carboxylic acid and its derivatives. Urethane, ureido acids, urea.

27. Carboxylic acids esters: nomenclature, preparation, properties.

28. Amines: nomenclature, properties. Biomedical significance of biogenic amines (adrenaline, noradrenaline, dopamine, tryptamine, serotonin, histamine) and polyamines (spermidine, spermine, putrescine, cadaverine).

29. Aromatic amines: structure, properties. Aniline as a precursor in the synthesis of pharmaceuticals - sulfanilamide, phenacetin, anaesthesin, novocaine.

30. Aminoalcohols: structure, properties. Biomedical significance of ethanolamine (colamin), choline, acetylcholine.

31. Hydroxy acids. Structure and properties of monocarboxylic, dicarboxylic and tricarboxylic hydroxy acids.

32. Amino acids: structure, stereoisomerism, and chemical properties. Biomedical importance of L-α-amino acids. Reactions of biochemical transformations of amino acids: deamination, transamination, decarboxylation.

33. Structure and properties of the most common oxo acids: pyruvic, acetoacetic, oxaloacetic, α-ketoglutaric. The concept of ketone bodies.

34. Phenolic acids. Salicylic acid and its anti-inflammatory derivatives (acetylsalicylic acid, methyl salicylate, sodium salicylate) and antimicrobial (phenyl salicylate) compounds.

35. Five-membered heterocycles with one heteroatom (pyrrol, furan, thiophene). Biomedical significance of tetrapyrrole compounds: porphyrin, heme.

36. Indole and its derivatives: Tryptophan and reaction of tryptamine and serotonin. Indoxyl, scatole, scatoxyl value in the process of putrefaction of proteins in the intestine.

37. Five-membered heterocycles with two nitrogen atoms: pyrazole, pyrazolone. The pyrazolone-5 derivatives as drugs (antipyrine, amidopyrine, analgin). Imidazole and its derivatives: histidine and histamine.

38. Five-membered heterocycles with two different heteroatoms: thiazole, oxazole. Thiazole as a structural component of the molecule of thiamine (vitamin B).

39. Six-membered heterocycles with a nitrogen atom: pyridine. Nicotinamide (vitamin PP) as a part of redox pyridine coenzymes. Pyridoxine and molecular forms of the vitamin B6.

40. Six-membered heterocycles with two nitrogen atoms. Diazine: pyrimidine, pyrazine, pyridazine. Nitrogenous bases - derivatives of pyrimidine (uracil, cytosine, thymine).

41. Pyrimidine derivatives as drugs: 5-fluorouracil, potassium orotate. Barbituric acid. Barbiturates as sedatives and antiepileptic drugs (phenobarbital, barbital).

42. Six-membered heterocycles with different heteroatoms. Phenothiazines (chlorpromazine, etc.) as psychotropic (neuroleptic) drugs.

43. Seven-membered heterocycles with two heteroatoms. Diazepine: benzo-1,4-diazepine as the most common tranquilizer and anxiolytic.

44. Purine and its derivatives. Amino derivatives of purine (adenine, guanine), their tautomeric forms, the biochemical significance in the formation of nucleotides and coenzymes.

45. Hydroxy purine: hypoxanthine, xanthine, uric acid. Methylated xanthine derivatives (caffeine, theophylline, theobromine) as physiologically active compounds with action on the central nervous and cardiovascular systems.

46. Carbohydrates: definition, classification. Sugars (aldose and ketoses; triose, tetroze, pentose, hexose, heptoze), the biomedical significance of the individual representatives.

47. Monosaccharides: pentoses (ribose, 2-deoxyribose, xylose), hexose (glucose, galactose, mannose, fructose) - structure, properties. Identification of the glucose.

48. Structure and properties of amine derivatives of monosaccharides: glucosamine, galactosamine. Uronic acid. L-ascorbic acid (vitamin C). Sorbitol, mannitol.

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

50. Polysaccharides. Homopolisaccharides: starch, glycogen, cellulose, dextrans - structure, hydrolysis, biomedical significance. Identification of the starch.

51. Heteropolysaccharides: definition, structure. The structure and biomedical significance of glycosaminoglycans (mucopolysaccharides) - hyaluronic acid, chondroitin sulfates, heparin.

52. Lipids: definition, classification. Fatty acids: palmitic, stearic, oleic, linoleic, linolenic, arachidonic. Lipids. Triacylglycerols (neutral fats): structure, physiologic significance, the hydrolysis.

53. Complex lipids. Phospholipids: phosphatidic acid, phosphatidyl-ethanolamine, phosphatidylcholine, phosphatidylserine. Sphingolipids. Glycolipids. The role of complex lipids in the structure of biological membranes.

54. Steroids as derivatives of sterane. The structure of biologically important representatives of steroids: cholesterol, vitamin D, bile acids, corticosteroids, sex hormones.

55. Amino acids. Classification, nomenclature, chemical properties of L-α-amino acids. Ninhydrine reaction.

56. Proteins and peptides: definition, classification and biological functions. The types of bonds between amino acid residues in protein molecules. Peptide bond: formation, structure: the biuret reaction.

57. Primary, secondary, tertiary, and quaternary structure of proteins. Oligomeric proteins.

58. Physico-chemical properties of proteins and their molecular mass. Denaturation of proteins.

59. Methods for fractionation and analysis of proteins and peptides (sedimentation, chromatography, electrophoresis). Analysis of the primary structure of proteins and peptides: methods Sanger and Edman.

60. Enzymes as biological catalysts of protein nature. The principles of classification and nomenclature of enzymes.

61. Nitrogenous bases of purine and pyrimidine series, which are part of the natural nucleotides. Minor nitrogenous bases.

62. Nucleosides. Nucleotides as phosphorylation derivatives of nucleosides (nucleozidmono-, di-and triphosphates). Nomenclature of nucleosides and nucleotides as components of RNA and DNA.

63. Structure and biochemical functions of the free nucleotides: nucleotid coenzymes, cyclic nucleotides 3',5'-AMP, 3',5'-GMP.

64. Nucleic acids (deoxyribonucleic, ribonucleic) as polynucleotides. The polarity of the polynucleotide chains of DNA and RNA.

65. Structure and properties of DNA nucleotide composition, complementarities of the nitrogenous bases. Primary, secondary and tertiary structure of DNA.

66. RNA: structure, types of RNA and their role in protein biosynthesis.

67. Vitamins: a general overview. The concept of the coenzyme activity of vitamins. Structure and properties of vitamins B1, B2, B6, PP.

68. Hormones: the concept of hormones as bioregulators. General characteristics of hormones of protein-peptide group, amino acid derivatives, steroids and eicosanoids.

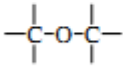
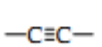
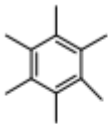
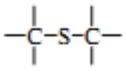
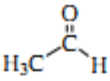
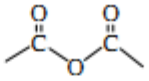
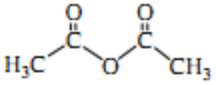
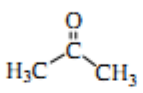
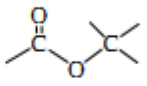
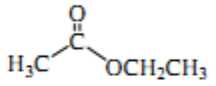
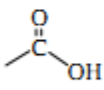
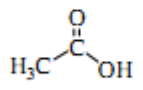
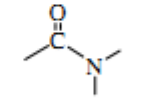
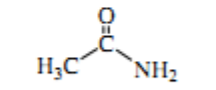
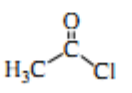
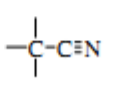
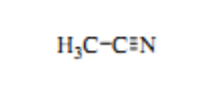
69. Alkaloids: definition. The value of the alkaloids as the active drugs (class of pyridine and piperidine, quinoline and isoquinoline, trephine, indole).

70. Antibiotics: a general concept, the characteristic classes of antibiotics: penicillins, cephalosporins, streptomycins.

71. Pesticides: definition, the most common phosphorus and organochlorine pesticides and their toxicological significance.

APPENDIX

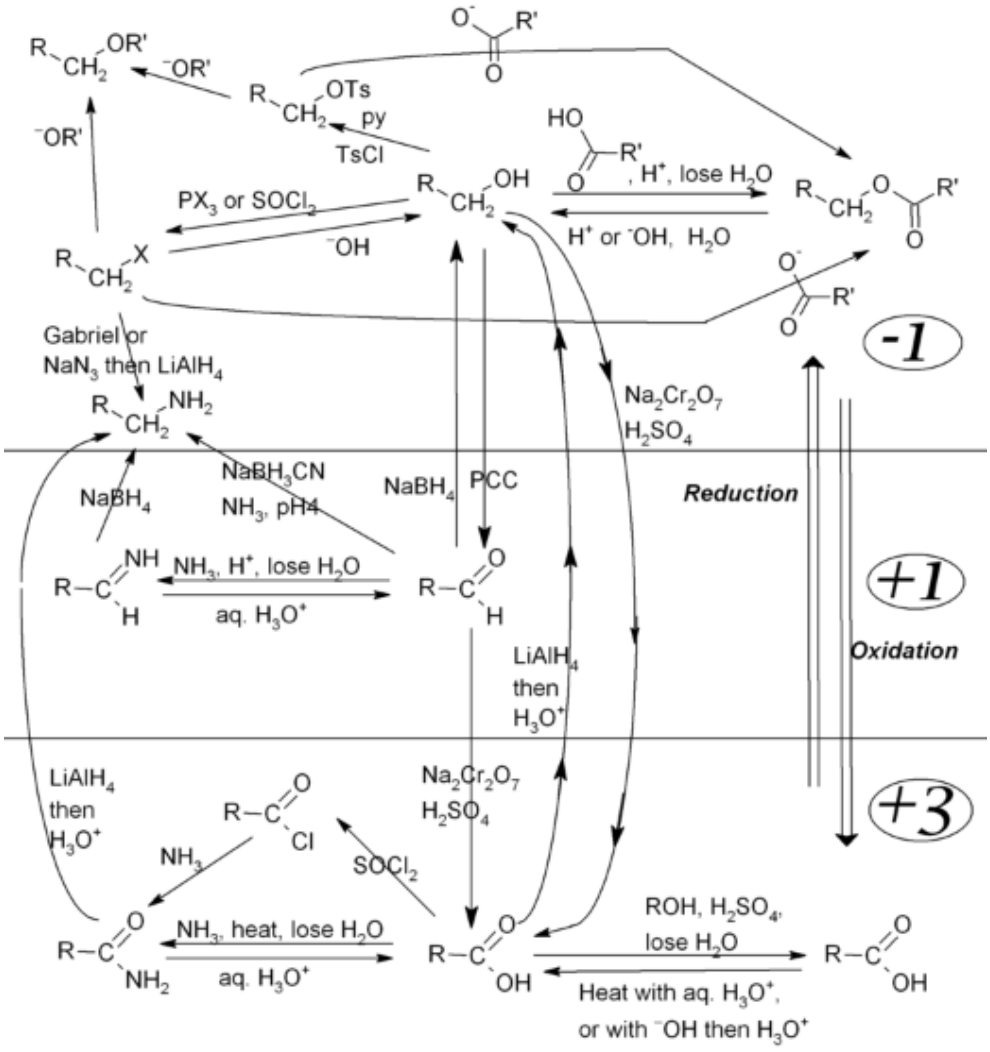
Organic compounds are generally classified based on the reactive parts of their structures, known as **FUNCTIONAL GROUPS**. The remainder of the molecule is usually based upon alkyl chains, which are relatively unreactive. Each functional group has its own characteristic reactions, and it tends to determine many of the chemical and physical properties of the overall compound.

Functional Group – General Structure	Example	Functional Group – General Structure	Example
	CH_3CH_3		CH_3CH_2OH
Alkane	**Ethane**	**Alcohol**	**Ethanol**
	$CH_2{=}CH_2$		$CH_3OCH_2CH_3$
Alkene	**Ethylene**	**Ether**	**Ethyl methyl ether**
			CH_3CH_2SH
Alkyne	**Acetylene**	**Thiol**	**Ethanethiol**
			CH_3SCH_3
Aromatic Ring (Arene)	**Benzene**	**Sulfide**	**Dimethyl sulfide**
 (X = F, Cl, Br, I)	CH_3CH_2Br		$CH_3CH_2NH_2$
Alkyl Halide	**Ethyl bromide**	**Amine**	**Ethylamine**
			
Aldehyde	**Acetaldehyde**	**Acid anhydride**	**Acetic anhydride**
			
Ketone	**Acetone**	**Ester**	**Ethyl acetate**
			
Carboxylic acid	**Acetic acid**	**Amide**	**Acetamide**
			
Acid chloride	**Acetyl chloride**	**Nitrile**	**Acetonitrile**

The IUPAC names of the first 10 alkanes

Number of Carbon Atoms	Prefix	Name	Molecular Formula
1	Meth	Methane	CH_4
2	Eth	Ethane	C_2H_6
3	Prop	Propane	C_3H_8
4	But	Butane	C_4H_{10}
5	Pent	Pentane	C_5H_{12}
6	Hex	Hexane	C_6H_{14}
7	Hept	Heptane	C_7H_{16}
8	Oct	Octane	C_8H_{18}
9	Non	Nonane	C_9H_{20}
10	Dec	Decane	$C_{10}H_{22}$

The **REACTION MAP** shown below shows most of the common functional groups, and how to convert between them. The large numbers on the right hand side indicate the oxidation state for the carbon attached to the functional group.[1]



James B. Hendrickson, *J. Chem. Educ.*, **1978**, *55* (4), 216. DOI: 10.1021/ed055p216.