

**MINISTRY OF HEALTH OF REPUBLIC OF BELARUS
VITEBSK STATE MEDICAL UNIVERSITY**

LABORATORY CLASSES IN BIOORGANIC CHEMISTRY

L.G. Hidranovich, O.A. Khodos

(2-е изд.)

For Foreign students of the 1-st year

Vitebsk 2013

УДК 54 (042.3/4)
ББК 24.239

L.G. Hidranovich, O.A. Khodos
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THEMATIC PLAN OF THE LECTURES IN BIOORGANIC CHEMISTRY

| № | The theme of the lectures |
|----|---|
| 1 | Introduction. Modern theory of organic compounds. Electronic structure of chemical bonds. Inductive and resonance effects. |
| 2 | Stereochemistry of organic compounds. Configuration and conformation of the organic compounds. |
| 3 | Acid-base properties of organic compounds. |
| 4 | Classification and the mechanisms of the reactions in organic chemistry. Saturated, unsaturated and aromatic hydrocarbons. S_R , S_E , A_E reactions. |
| 5 | Alcohols, phenols, thiols, amines. S_N and E reactions. |
| 6 | Carbonyl compounds. Aldehydes, ketones A_N reactions. |
| 7 | Carboxylic acids and derivatives. S_N reactions. |
| 8 | Heterofunctional compounds. |
| 9 | Carbohydrates. Classification. Cyclic forms of monosaccharides. Reactions of monosaccharides. |
| 10 | Carbohydrates. Oligosaccharides and polysaccharides. |
| 11 | Natural amino acids. Structure, properties, functions. |
| 12 | Peptides and proteins. Four levels of protein structural organization. Strategy of peptide synthesis. |
| 13 | Nucleosides. Nucleotides. Nucleic acids. |
| 14 | Saponified lipids. Simple and complex lipids. |
| 15 | Non-saponified lipids. Terpenes. Steroids. |
| 16 | Classification and IUPAC nomenclature of organic compounds. |
| 17 | Reaction centres of organic compounds. Reactivity of the main families of organic compounds. |

**THEMATIC PLAN
OF THE LABORATORY CLASSES IN BIOORGANIC CHEMISTRY**

| № | The theme of the laboratory classes | Duration (hours) |
|----|---|------------------|
| 1 | Classification and IUPAC nomenclature of organic compounds. | 2 |
| 2 | Electronic structure of chemical bonds. Inductive and resonance effects. | 2 |
| 3 | Stereochemistry of organic compounds. Configuration and conformation of the organic compounds. | 2 |
| 4 | Acid-base properties of organic compounds. | 2 |
| 5 | Classification and mechanisms of the reactions in organic chemistry. Saturated, unsaturated and aromatic hydrocarbons. S_R , S_E , A_E reactions. | 2 |
| 6 | Alcohols, phenols, thiols, amines. S_N and E reaction. | 2 |
| 7 | Carbonyl compounds. Aldehydes, ketones A_N reactions. | 2 |
| 8 | Carboxylic acids and derivatives. S_N reactions. | 2 |
| 9 | Heterofunctional compounds. | 2 |
| 10 | Test № 1. | 2 |
| 11 | Carbohydrates. Monosaccharides. | 2 |
| 12 | Carbohydrates. Oligosaccharides and polysaccharides. | 2 |
| 13 | Natural amino acids. Structure, properties, functions. | 2 |
| 14 | Peptides and proteins. Four levels of protein structural organization. Strategy of peptide synthesis. | 2 |
| 15 | Purine and pyrimidine bases. Nucleosides. Nucleotides. Nucleic acids. Test №2. | 2 |
| 16 | Saponified lipids. Peroxide oxidation of lipids. | 2 |
| 17 | Non-saponified lipids. Terpenes, steroids. | 2 |
| 18 | Credit Test. | 2 |

ACCIDENT PREVENTION.

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

THEME 1

Classification and IUPAC nomenclature of organic compounds.

1. Program questions:

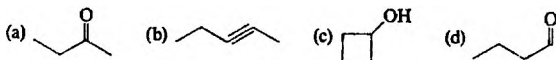
- 1.1. Representation of structural formulas.
- 1.2. Classification of the organic compounds according to the structure of carbon skeleton and according to the functional groups.
- 1.3. Classification of carbon atoms.
- 1.4. Alkyl groups.
- 1.5. IUPAC nomenclature of organic compounds. The parent structure, senior group, locants, prefixes and suffixes.

Literature:

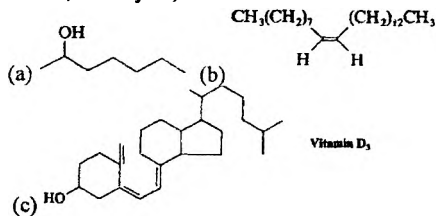
- [1] L.G. Hidranovich. Bioorganic chemistry lecture course. Vitebsk, 2004. p. 4 – 16.
- [2] T.W. Graham Solomons. Fundamentals of organic chemistry. John Wiley and sons, 1994. p. 116 – 127, 501 - 504, 643 - 644, 715 - 723, 770 - 772
- [3] George H. Schmid. Organic chemistry. Mosby, 1996. p. 57 – 70, 76 - 82, 451 - 454, 550 - 553, 591 - 594, 652 - 656, 699 - 702, 963 - 966
- [4] Richard F. Daley, Sally J. Dalley. Organic chemistry Wm. C. Brown Publishers, 1996. p. 73 - 111

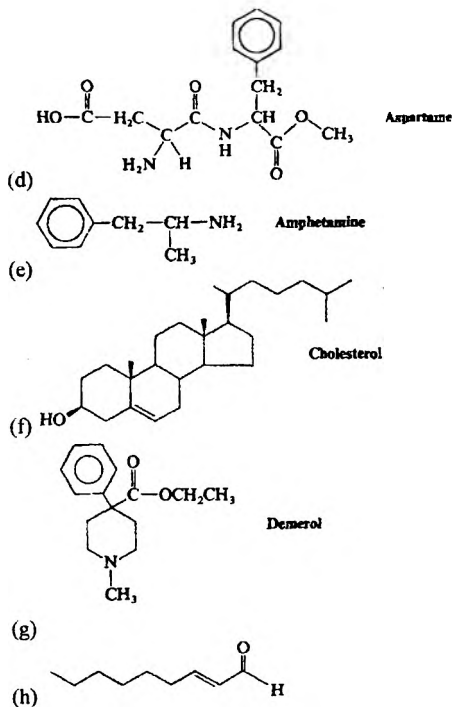
2. Problems.

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



2. Classify each of the following compounds as an alkane, alkene, alkyne, alcohol, aldehyde, amine and so forth.

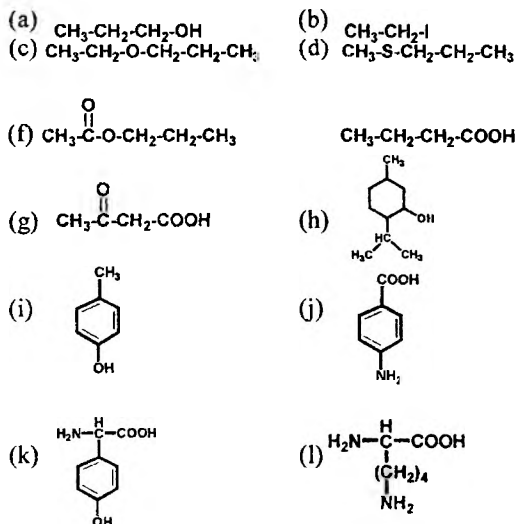




3. Write structural formulas for each of the following:

- Three ethers with the formula $C_4H_{10}O$.
- Three primary alcohols with the formula C_4H_8O .
- A secondary alcohol with the formula C_3H_6O .
- A tertiary alcohol with the formula C_4H_8O .
- Two esters with the formula $C_3H_6O_2$.
- Four primary alkyl halides with the formula $C_5H_{11}Br$.
- Three secondary alkyl halides with the formula $C_5H_{11}Br$.
- A tertiary alkyl halide with the formula $C_5H_{11}Br$.
- Three aldehydes with the formula $C_5H_{10}O$.
- Three ketones with the formula $C_5H_{10}O$.
- Two primary amines with the formula $C_3H_{11}N$.
- A secondary amine with the formula $C_3H_{11}N$.
- A tertiary amine with the formula $C_3H_{11}N$.
- Two amides with the formula C_2H_5NO .

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



5. Write a structural formula for each of the following compounds:

- 4-isopropylheptane
- 4-methylpentanol-2
- 5,6-dichlorocyclohexene
- 2-chlorohexyn-3-ol-1
- 2-phenylethanol
- 4-nitrobenzoic acid
- 2,4,6-trinitrophenol
- Benzoyl chloride
- 2-amino-1-(3,4-dihydroxyphenyl)-ethanol-1
- N,N-diethylhexanamide
- Methyl benzoate

THEME 2

Electronic structure of chemical bonds. Inductive and resonance effects.

1. Program questions:

- Hybridization of carbon atom.
- Chemical bonding in organic compounds.
 - Covalent bond formation.

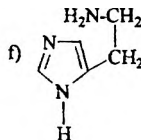
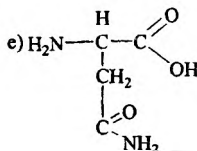
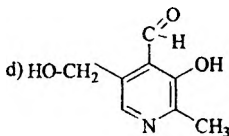
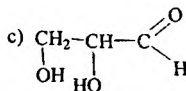
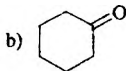
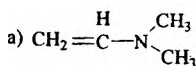
- 2.2. Non-polar covalent bonds (carbon-carbon single, double and triple bonds).
- 2.3. Polar covalent bonds.
- 2.4. Ionic bonds.
3. Intermolecular forces.
4. Inductive effects on bond polarity.
5. Conjugation. Electron structure of π , π and p , π conjugated systems.
6. Resonance (mesomeric) effect.

Literature:

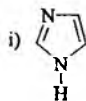
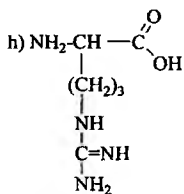
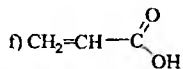
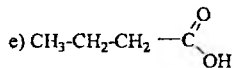
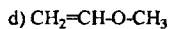
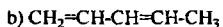
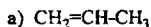
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p. 16 – 33
- [2] T.W. Graham Solomons. Fundamentals of organic chemistry. John Willey and sons, 1994. p. 27 - 52
- [3] George H. Schmid. Organic chemistry. Mosby, 1996. p. 17 – 44
- [4] Richard F. Daley, Sally J. Dalley. Organic chemistry Wm. C. Brown Publishers, 1996. p. 34 - 65

2. Problems.

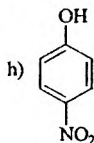
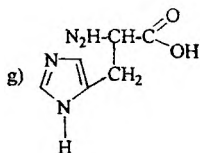
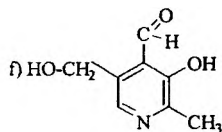
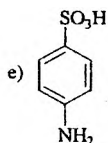
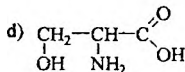
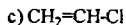
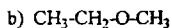
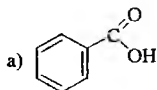
1. Define the hybridization type of carbon atoms and heteroatoms (pyridine and pyrrole type) in following compounds:



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



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



THEME 3

Stereochemistry of organic compounds.

Configuration and conformation of the organic compounds.

1. Program questions:

1. Conformation. Newman projection formulas. Conformation analysis. Conformations of ethane and butane.

2. Conformations of cyclohexane. Chair conformations. Conformational inversion of cyclohexane. Conformational analysis of substituted cyclohexanes.

3. Stereoisomerism, configuration. Stereocenter. Enantiomers and diastereomers.

4. Fischer projection formulas. Molecules with one and more than one stereocenters.

5. Naming of enantiomers: the (D-L-) and (R-S-) systems.

6. Mesocompounds.

Literature:

[1] L.G. Hidranovich. Bioorganic chemistry lecture course. Vitebsk, 2004.

p. 33 - 54

[2] T.W. Graham Solomons. Fundamentals of organic chemistry. John Wiley and sons, 1994. p. 164 - 198

[3] George H. Schmid. Organic chemistry. Mosby, 1996. p. 128 - 163, 226 - 271

[4] Richard F. Daley, Sally J. Dalley. Organic chemistry Wm. C. Brown Publishers, 1996. p. 128 - 153, 162 - 163, 510 - 537

2. Problems.

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

- 1,2-diiodoethane;
- 2-methylbutane (along C2-C3 bond);
- 2-aminoethanol
- butandioic acid (along C2-C3 bond)

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



a.



b.



c.



d.

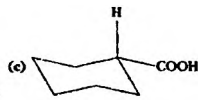
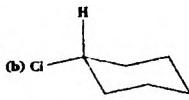
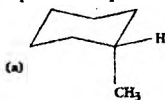


e.

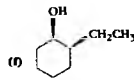
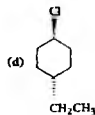
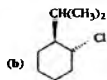
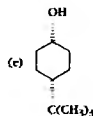
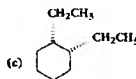
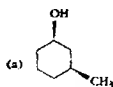


f.

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



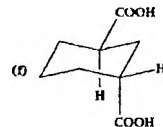
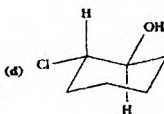
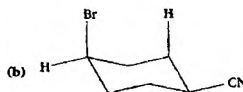
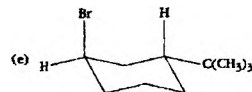
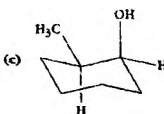
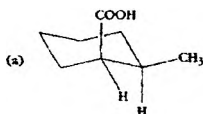
4. Convert each of the following structures into its two chair conformations. In each case indicate which one should be the more stable conformation.



5. Write the structure of the preferred conformation of:

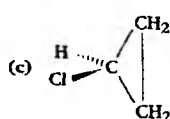
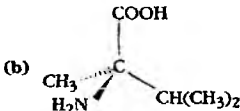
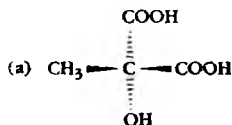
- 1-Isopropyl-2-methylcyclohexane
- cis-1-Bromo-2-isopropylcyclohexane
- trans-1-Methyl-3-isopropylcyclohexane
- cis-1-Chloro-4-isopropylcyclohexane

6. Identify each of the following compounds as either the *cis*- or the *trans*-isomer:



7. Write the two chair conformations of all trans-1,2,3,4,5,6-hexachlorocyclohexane.

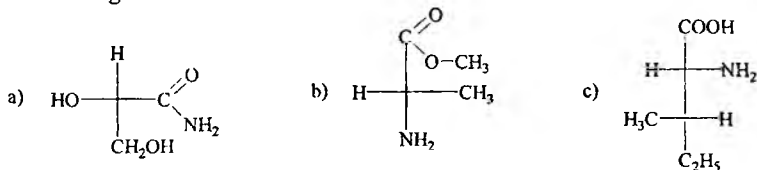
8. The following three-dimensional structures represent one particular stereoisomer. Which would you expect to be optically active?



9. Draw the standard Fischer projection formulas of stereoisomers that correspond to each of the following compounds. Indicate enantiomers and diastereoisomers.

- 2-hydroxypropanal;
- 2-aminopropanoic acid;
- 2-amino-3-hydroxybutanoic acid;
- 2,3-dihydroxybutandioic acid.

10. Assign the R or S and D or L configuration to the stereocenter in each of the following:



THEME 4

Acid-base properties of organic compounds.

1. Program questions:

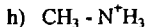
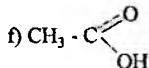
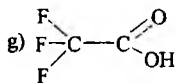
- The Brensted-Lowry definition of acids and bases.
- The Lewis definition of acids and bases.
- The strength of acids and bases: the acidity constant (K_a) and pK_a .
- Organic acids and bases. Relative acidity and basicity.
- The relationship between structure and acidity. The effect of hybridization. Inductive effects (influence of electron attracting and electron donating groups).
- The relationship between structure and basicity.

Literature:

- [1] L.G. Hidranovich. Bioorganic chemistry lecture course. Vitebsk, 2004.
p. 54 - 74
- [2] T.W. Graham Solomons. Fundamentals of organic chemistry. John Wiley and sons, 1994. p. 86 - 102, 130 - 150
- [3] George H. Schmid. Organic chemistry. Mosby, 1996. p. 88 - 103
- [4] Richard F. Daley, Sally J. Dalley. Organic chemistry Wm. C. Brown Publishers, 1996. p. 206 - 234

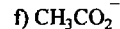
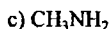
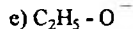
2. Problems.

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



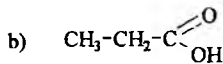
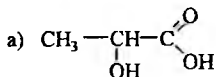
2. List the bases you gave as answers to Problem 1 in order of decreasing basicity.

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

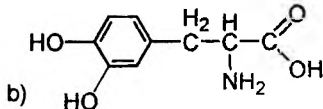
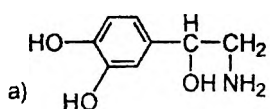


4. List the acids you gave as answers to Problem 3 in order of decreasing acidity.

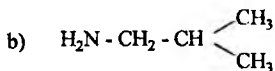
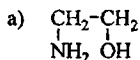
5. Compare the strength of acids:



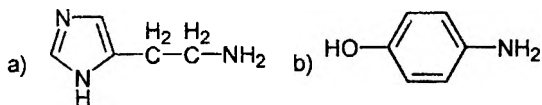
6. Compare the strength of acidic centers of each of the following acids.



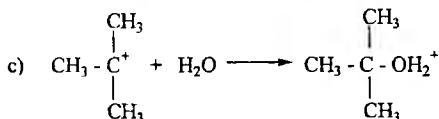
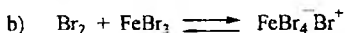
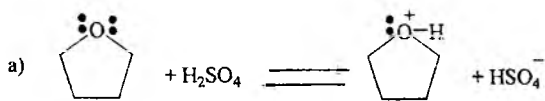
7. Compare the strength of bases:



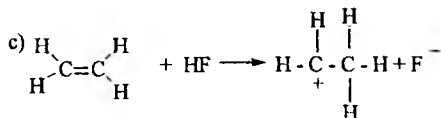
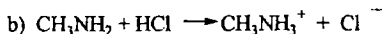
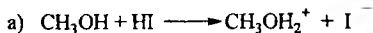
8. Compare the strength of basic centers of each of the following bases.



9. Designate the Lewis acid and Lewis base in each of the following reactions:



10. Rewrite each of the following reactions using curved arrows and show all nonbonding electron pairs.



THEME 5

Classification and mechanisms of the reactions in organic chemistry.

Saturated, unsaturated and aromatic hydrocarbons.

S_R , S_E , A_E reactions.

1. Program questions:

1. Homolysis and heterolysis of covalent bonds. Ionic and radical reactions.

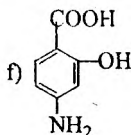
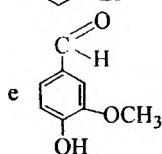
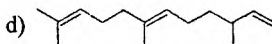
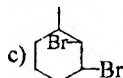
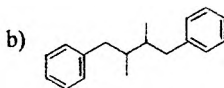
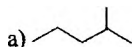
2. Reactive intermediates in organic chemistry.
3. Organic reaction terminology. Classification of reagents in organic reactions. Substitution, addition and elimination reactions.
4. Classification of the hydrocarbons.
5. Reactions of alkanes and cycloalkanes (common cycles). S_R reactions.
6. Reactions of alkenes and alkadienes. A_E reactions: hydrohalogenation, hydration. Markovnikov's rule. Addition reactions of conjugated alkadienes.
7. Reactions of aromatic hydrocarbons. S_E reactions. Halogenation, nitration, sulfonation, alkylation, acylation. Orientation rule in benzene ring.

Literature:

- [1] L.G. Hidranovich. Bioorganic chemistry lecture course. Vitebsk, 2004. p. 75 - 91
- [2] T.W. Graham Solomons. Fundamentals of organic chemistry. John Wiley and sons, 1994. p. 111-130, 152-153, 267-273, 297-314, 323-328, 340-354, 371-372, 500-519, 599-606, 614-627
- [3] George H. Schmid. Organic chemistry. Mosby, 1996. p. 51-76, 277-290, 292-312, 368-372, 373-379, 381-388, 799-807, 885-895, 922-924, 929-954
- [4] Richard F. Daley, Sally J. Dalley. Organic chemistry Wm. C. Brown Publishers, 1996. p. 77-78, 1068-1072, 708-710, 714-715, 725-729, 690-702, 884-925, 839-866

2. Problems.

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



2. Write a structural formula for each of the following compounds:

- a) 2-methyl-4,4-diethylheptane;
- b) 2-isopropyl-5-methylcyclohexanol;

- c) trans-2,2,5,5-tetramethylhexene-3;
- d) 2,4,6-trinitrophenol;
- e) 3,4,5-trihydroxybenzoic acid;
- f) pentadiene-1,3.

3. Write the products formed in the reactions of Br_2 with following compounds:

- a) ethane;
- b) 2-methylpropane;
- c) methylcyclohexane;
- d) 3-ethylpentane;

4. Draw all possible monochlorination products from the radical chlorination of 2,2,4-trimethylpentane. Estimate approximately the amounts of each isomer of product that forms.

5. Write the structures and names of the product or products expected from the addition of HCl and H_2O to each of the following compounds:

- a) methylpropene;
- b) 3-methyl-butene-1;
- c) $\text{H}_2\text{C} = \underset{\text{CH}_3}{\text{C}} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$



- e) $\text{H}_2\text{C} = \text{CHBr}$
- f) $\text{CH}_3 - \text{CH} = \text{CH} - \underset{\text{OH}}{\overset{\text{O}}{\text{C}}}$
- g) $\text{HOOC} - \text{CH} = \underset{\text{COOH}}{\text{C}} - \text{CH}_2 - \text{COOH}$

6. What reaction products, if any, result from the reaction of cyclohexene with the following reagents?

- a) H_2 (Pt);
- b) Br_2 ;
- c) KMnO_4 ;
- d) HBr .

7. Predict the major mononitration products from each of the following aromatic compounds:

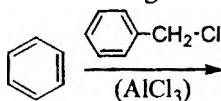
- a) Toluene;

- b) Benzoic acid;
- c) 1,3-dimethylbenzene;
- d) 4-methylphenol;
- e) 4-ethylbenzoic acid.

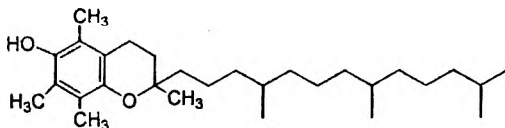
8. Predict the major products of the monosulphonation of the following substances:

- a) phenol;
- b) methoxybenzene;
- c) nitrobenzene;
- d) bromobenzene;
- e) 3-nitrobenzoic acid.

9. What product is formed in the following reaction?



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



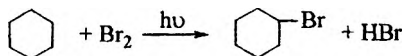
3. Laboratory work:

Experiment №1. Reaction of alkanes with bromine water.

Sequence of operations: Place 3 ml of cyclohexane in two test-tubes. Add 4 drops of the bromine in CCl_4 solution. Keep the test-tube № 1 on the light and the test-tube № 2 in the darkness during 1 or 2 days.

Check the result: the change of colour in test-tube № 1 .

Write:



cyclohexane

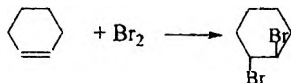
Explain the result and write conclusion.

Experiment №2. Reaction of alkenes with bromine water.

Sequence of operations: Place 3 drops of bromine water in two test-tubes. Add one by one several drops of cyclohexene in the test-tube № 1 and several drops of cyclohexane in the test-tube № 2.

Check the result: the change of colour in the test-tube № 1.

Write:



cyclohexene

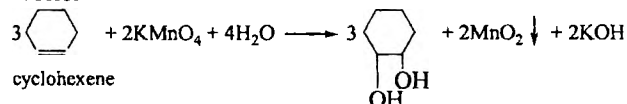
Explain the result and write conclusion.

Experiment №3. Oxidation of alkenes by KMnO_4 .

Sequence of operations: Place 2 drops of KMnO_4 solution in two test-tubes. Add one by one several drops of cyclohexene in the test-tube № 1 and several drops of cyclohexane in the test-tube № 2.

Check the result: the change of colour and brown precipitate in the test-tube № 1.

Write:



Explain the result and write conclusion.

Experiment №4. Reaction of benzene and toluene with bromine water and their oxidation by KMnO_4 .

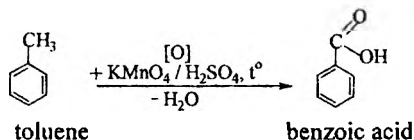
a) **Sequence of operations:** Place 2 drops of benzene in the test-tube № 1 and 2 drops of toluene in the test-tube № 2. Add 3 drops of bromine water in these test-tubes.

Check the result: there is no change of colour.

b) **Sequence of operations:** Place 2 drops of benzene in the test-tube № 1 and 2 drops of toluene in the test-tube № 2. Add 2 drops of KMnO_4 solution and 1 drop of H_2SO_4 in these test-tubes. Warm the test-tubes.

Check the result: the change of colour in the test-tube № 2.

Write:



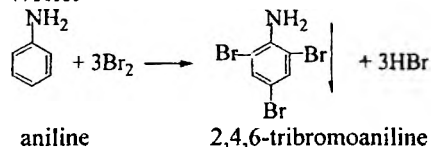
Explain the result and write conclusion.

Experiment №5. Reaction of aniline with bromine water.

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

Check the result: white precipitate.

Write:



Explain the result and write conclusion.

THEME 6**Alcohols, phenols, thiols, amines.****S_N and E reactions.****1. Program questions:**

1. Nomenclature of alcohols, ethers, thiols, phenols, amines.
2. Alcohols, thiols, phenols, amines as acids and bases.
3. Alkyl phosphates.
4. Reaction centres and reactions of alcohols. S_N1 and S_N2 reactions. Factors affecting the rates of S_N1 and S_N2 reactions. Conversion of alcohols in to alkyl halides. Alcohol dehydration. Synthesis of ethers.
5. Mechanism of alcohol dehydration: an E1 reaction (synthesis of alkenes).
6. Reactions of ethers.
7. Reactions of phenols. Formation of quinones by oxidation of phenols. Hydroquinone – quinone oxidation – reduction equilibria.
8. Reactions of thiols.
9. Classification and reaction centres of amines. Basic and nucleophilic properties of amines.

Literature:

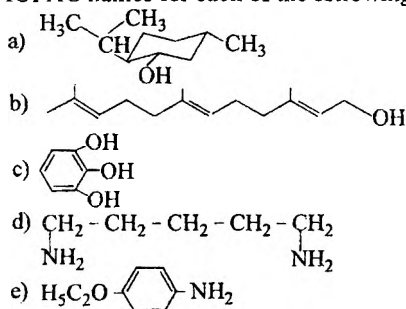
- [1] L.G. Hidranovich. Bioorganic chemistry lecture course. Vitebsk, 2004. p. 92 - 117
- [2] T.W. Graham Solomons. Fundamentals of organic chemistry. John Willey and sons, 1994. p. 216-218, 227-242, 384-391, 400-403, 406-417, 433-444, 770-784, 792-797, 857-870, 872-873

[3] George H. Schmid. Organic chemistry. Mosby, 1996. p. 451-455, 481-489, 505-540, 550-555, 557-560, 567-569, 963-969, 971-974, 986-990, 1015-1018, 1021-1031, 1033-1037

[4] Richard F. Daley, Sally J. Dalley. Organic chemistry Wm. C. Brown Publishers, 1996. p. 566-596, 631-643, 656-659, 305-310

2. Problems.

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



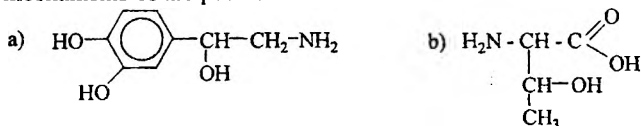
2. Write a structural formula for each of the following compounds:

- 2-ethoxypentane;
- 2,2-dimethylpropanol-1;
- 1,4-pentanediol;
- 5-chloro-4-methylpentanol-2;
- 1-cyclohexylbutanol-1;
- N-ethyl-N-methylaniline;
- 4-aminophenol;
- ethylthioethane;
- 2-amino-1-(3,4-dihydroxyphenyl)-ethanol-1.

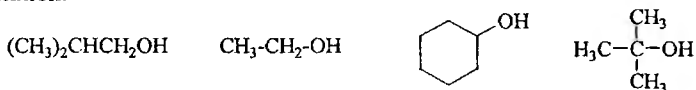
3. Arrange each of the following sets of compounds in decreasing order of their expected acid strength in solution:

- 2-chlorohexanol; 3-chlorohexanol; 4-chlorohexanol; 2,2-dichlorohexanol.
- 2,2-dimethylbutanol-1; 2,2-dimethylbutanamine; butanol-1.

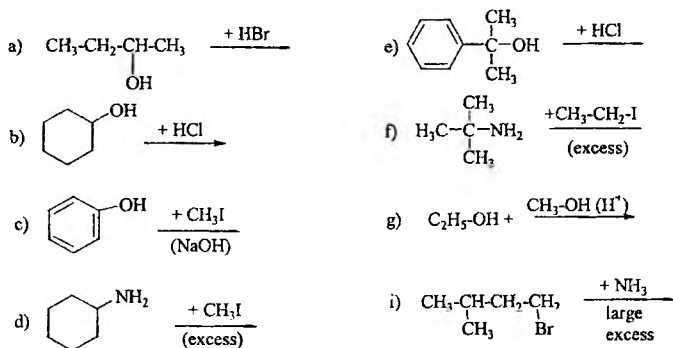
4. Find the reaction centres in following compounds. Write the schemes and outline mechanisms of the possible reactions for these reaction centres.



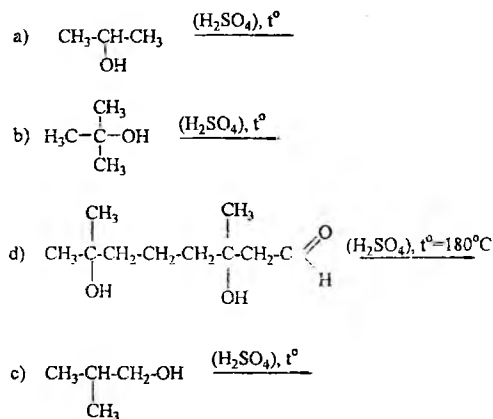
5. Rank the following compounds in order of increasing reactivity towards S_N1 substitution. Then rank them in order of increasing reactivity towards S_N2 substitution.



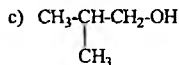
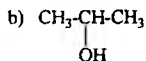
6. Predict the major products of each of the following reactions. Determine whether the reaction is primarily S_N1 or S_N2 .



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



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

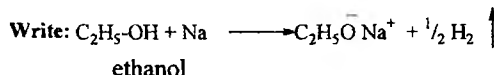


3. Laboratory work:

Experiment №1. Reaction of alcohol with metallic Na.

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

Check the result: bubbles of hydrogen gas and precipitate of C_2H_5ONa .



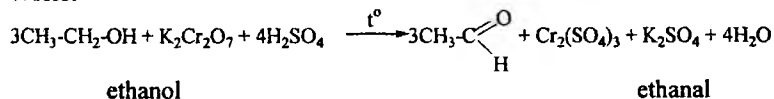
Explain the result and write conclusion.

Experiment №2. Oxidation reaction of alcohol.

Sequence of operations: Place 2 drops of $\text{C}_2\text{H}_5\text{OH}$ in the first test-tube. Add 2 drops of H_2SO_4 and 2 drops of $\text{K}_2\text{Cr}_2\text{O}_7$ solution. Warm the mixture.

Check the result: the change of colour.

Write:



Explain the result and write conclusion.

Experiment №3. Reaction of glycerol with $\text{Cu}(\text{OH})_2$.

Sequence of operations:

a) Place 3 drops of CuSO_4 solution and 3 drops of NaOH solution in the first and in the second test-tubes

Check the result: blue precipitate.

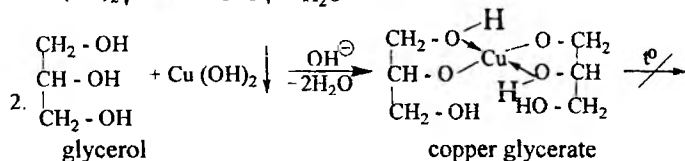
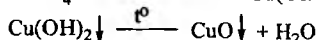
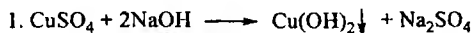
b) Add 2 drops of glycerol in the second test-tube.

Check the result: blue solution.

c) Warm the mixtures.

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

Write:



Explain the result and write conclusion.

Experiment №4. Formation of sodium phenoxide ($\text{C}_6\text{H}_5\text{ONa}$).

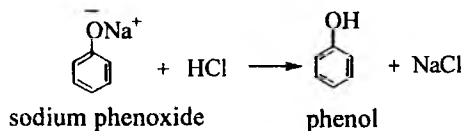
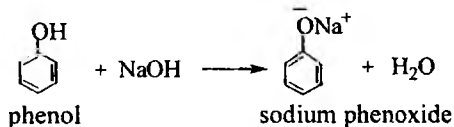
Sequence of operations: a) Place 3 drops of water and 2 drops of $\text{C}_6\text{H}_5\text{OH}$ in the test-tube. Add several drops of NaOH solution.

Check the result: the formation of solution.

b) Add several drops of HCl solution.

Check the result: emulsion.

Write:



Explain the result and write conclusion.

Experiment №5. Basicity of amines.

Sequence of operations:

a) Place 1 drop of methanamine ($\text{CH}_3\text{-NH}_2$) on the indicator paper.

Check the result: the change of colour.

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

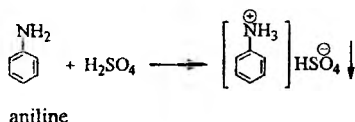
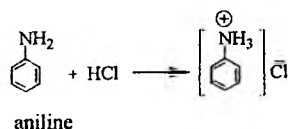
Place 1 drop of this solution on the indicator paper strip.

Check the result: there is no change of colour.

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

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

Write:



Explain the result and write conclusion.

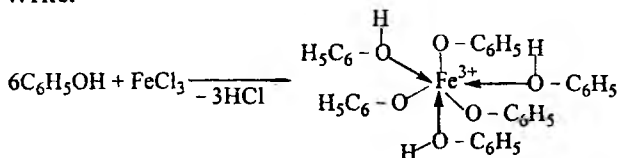
Experiment №6. Coloured reactions of phenols with FeCl_3 .

Sequence of operations: Place 1 drop of FeCl_3 in each of 5 test-tubes. Add 3 drops of one of the phenol in the test-tubes:

Check the result: the change of colour.

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

Write:



Explain the result and write conclusion.

THEME 7

Carbonyl compounds. Aldehydes, ketones. A_N reactions.

1. Program questions:

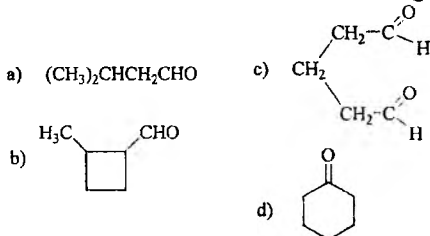
1. Nomenclature of aldehydes and ketones.
2. Reaction centres of aldehydes and ketones.
3. Nucleophilic addition (A_N) to the carbon-oxygen double bond. The addition of water and alcohols: hydrates, hemiacetals, hemiketals, acetals and ketals. Thioacetals and thioketals.
4. The addition of derivatives of ammonia: A_N-E mechanism. Reactions with hydroxylamine, hydrazine, 2,4-dinitrophenylhydrazine.
5. Reactions of the α -CH acidic centre. Keto and enol tautomers. The iodoform test. The aldol reaction: the addition of enolate ions to aldehydes and ketones.
6. Oxidation of aldehydes and ketones. Tollen's test (silver mirror test), reaction with Fehling's solution. Disproportionation reaction.

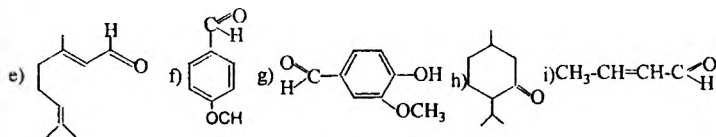
Literature:

- [1] L.G. Hidranovich. Bioorganic chemistry lecture course. Vitebsk, 2004. p. 117 - 135
- [2] T.W. Graham Solomons. Fundamentals of organic chemistry. John Willey and sons, 1994. p. 642-646, 653-667, 674-676, 686-703
- [3] George H. Schmid. Organic chemistry. Mosby, 1996. p. 589-598, 606-609, 611-624, 634-643
- [4] Richard F. Daley, Sally J. Dalley. Organic chemistry Wm. C. Brown Publishers, 1996. p. 285 - 293, 297 - 310

2. Problems.

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





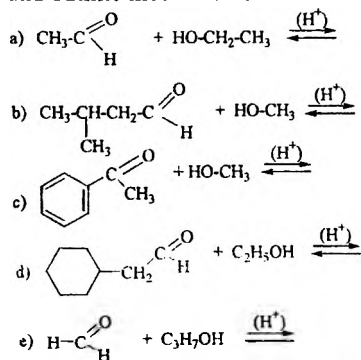
2. Write the structural formula for each of the following compounds:

- Trichloroethanal;
- 2,3,4,5,6-pentahydroxyhexanal;
- 2-methylcyclohexanone;
- Butandione-2,3;
- 1,2-diphenylethandione;
- 3-bromo-2-isopropylpentanedial;
- 3-methylcyclopentanone;
- 2,5-octanedione;
- 4-hydroxy-2-pentanone.

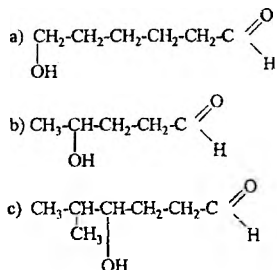
3. Write the structure of the hemiacetal and acetal formed by the acid-catalyzed reaction and outline mechanisms for the reactions of each of the following aldehydes or ketones with ethanol:

- propanal;
- ethyl methyl ketone;
- benzaldehyde.

4. Write the schemes and outline mechanisms of the following reactions:



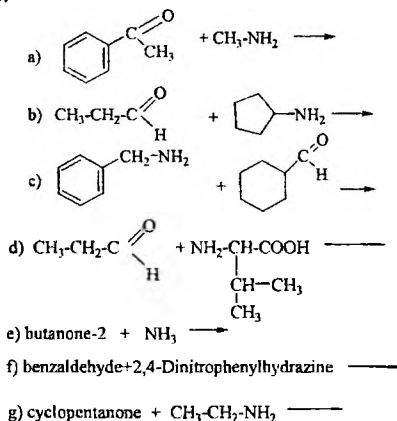
5. Write the schemes and mechanisms of the forming of cyclic hemiacetals from following compounds:



6. Write the mechanism of the acid-catalyzed hydrolysis of the following compounds:

- a) 1,1-diethoxypropane;
 b) 1,1-dimethoxyethane.

7. Write the structure of the product and outline the mechanism of each of the following reactions:



8. For all practical purposes, the compound 2,4-cyclohexadien-1-one exists totally in its enol form. Write the structure of 2,4-cyclohexadien-1-one and of its enol form. What the special factor accounts for the stability of the enol form?

9. Which of the following compounds would give a positive iodoform test?

- a) acetone; d) 3-pentanone;
 b) pentanal; e) 1-phenylethanol;
 c) 2-pentanone; f) 2-butanol.

10. Write the mechanism for an aldol condensation (aldol-type addition) of the following compounds in base:

- propanal;
- 3-methylbutanal;
- acetone.

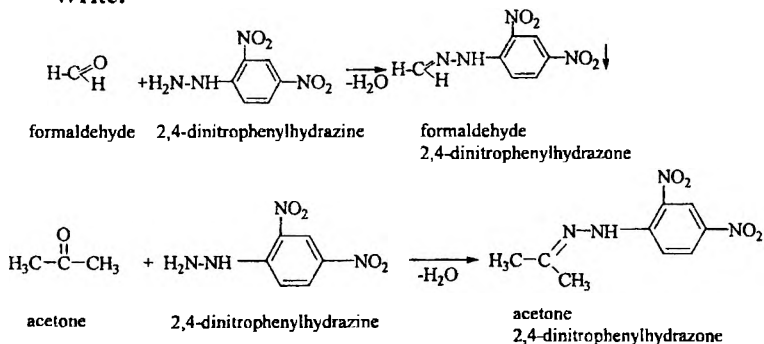
3. Laboratory work:

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

Sequence of operations: Place 1 drop of acetone in the test-tube № 1 and 2 drops of formalin in the test-tube № 2. Add 2 drops of 2,4-dinitrophenylhydrazine in two test-tubes.

Check the result: orange precipitate.

Write:



Explain the result and write conclusion.

Experiment №2. Reactions of difference aldehydes from ketones.

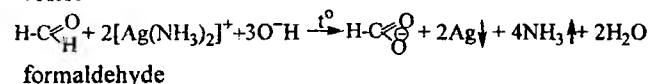
Sequence of operations:

a) Silver mirror reaction.

Take 2 test-tubes. Place 1 drop of AgNO_3 solution and 2 drops of NaOH solution in each test-tube. Add 4 drops of NH_4OH in these test-tubes. This solution is named Tollen's reagent. Add 2 drops of formalin in the test-tube № 1 and 2 drops of acetone in the test-tube № 2. Warm test-tubes.

Check the result: silver coating in the test-tube № 1.

Write:



b) Copper mirror reaction.

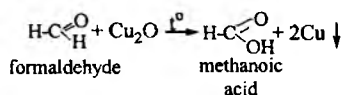
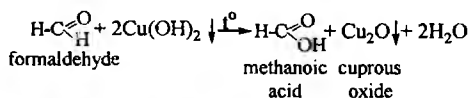
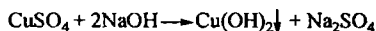
Sequence of operations: Place 6 drops of NaOH and 1 drop of CuSO_4 solutions in two test-tubes.

Check the result: blue precipitate.

Add 2 drops of formalin in the test-tube № 1 and 2 drops of acetone in the test-tube № 2. Warm test-tubes.

Check the result: brick-red precipitate and copper coating in the test-tube № 1 and black precipitate in the test-tube № 2.

Write:



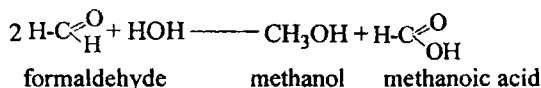
Explain the result and write conclusion.

Experiment №3. Formaldehyde disproportionation in water solutions.

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

Check the result: the change of colour.

Write:



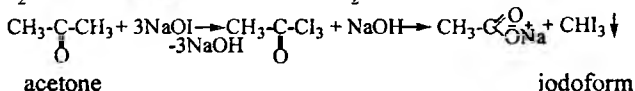
Explain the result and write conclusion.

Experiment №4. Iodoform test.

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

Check the result: white-yellow precipitate.

Write:



Explain the result and write conclusion.

Experiment №5. Reaction of acetone with sodium nitroprussiate.

Sequence of operations: Place 1 drop of sodium nitroprussiate solution ($\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$), 5 drops of water and 1 drop of acetone in the test-tube. Add 1 drop of NaOH solution.

Check the result: the change of colour.

Pour the part of the mixture in the other test-tube. Add 1 drop of CH_3COOH in one of the test-tubes.

Check the result: the change of colour.

Explain the result and write conclusion.

THEME 8**Carboxylic acids and derivatives.** **S_N reactions.****1. Program questions:**

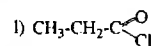
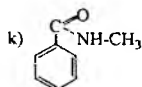
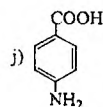
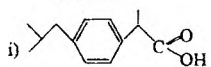
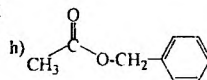
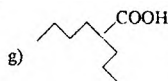
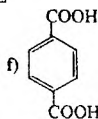
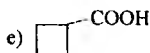
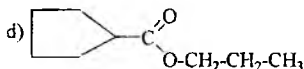
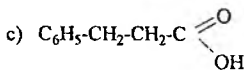
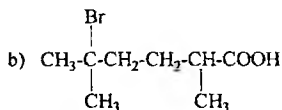
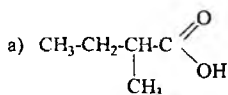
1. Nomenclature of carboxylic acids and derivatives (esters, anhydrides, acyl chlorides, amides, nitriles).
2. Reaction centres of carboxylic acids and derivatives.
3. Acidity of carboxylic acids.
4. Nucleophilic substitution (S_N) at the acyl carbon. Forming of esters (esterification), amides, acyl chlorides, anhydrides).
5. Relative reactivity of acyl compounds (acyl chlorides, acid anhydrides, esters, amides).
6. Decarboxylation of carboxylic acids.
7. Hydrolysis of amides and esters.
8. Acyl transfer reactions of anhydrides, thioesters and esters.
9. Acyl transfer reactions in living systems.

Literature:

- [1] L.G. Hidranovich. Bioorganic chemistry lecture course. Vitebsk, 2004. p. 136 - 153
- [2] T.W. Graham Solomons. Fundamentals of organic chemistry. John Wiley and sons, 1994. p. 714-748, 752-770
- [3] George H. Schmid. Organic chemistry. Mosby, 1996. p. 652-659, 665-673, 697-706, 709-713, 718-726
- [4] Richard F. Daley, Sally J. Dalley. Organic chemistry Wm. C. Brown Publishers, 1996. p. 346 – 363, 366 - 368

2. Problems.

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



2. Write the structural formula for each of the following compounds:

a) hexanedioic acid;

g) trans-butenedioic acid;

b) N,N-diethylhexanamide;

h) hexen-4-oic acid;

c) tert-butyl propanoate;

i) propanoyl chloride;

d) hexadiene-2,4-oic acid;

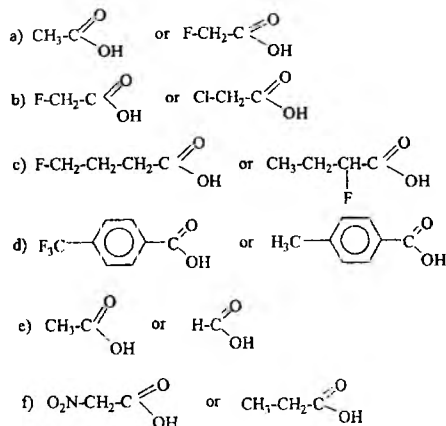
j) 2-bromopropanoyl bromide;

e) 2-hydroxybenzoic acid;

k) N,N-Dimethylformamide.

f) 3-hydroxy-3-carboxypentanedioic acid;

3. Which acid of each pair shown here would you expect to be stronger?



4. What major organic product would you expect to obtain when acetyl chloride reacts with each of the following compounds? Outline mechanisms of these reactions.

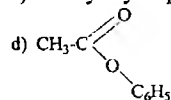
- a) H_2O ;
 b) CH_3NH_2 (excess);
 c) $(\text{CH}_3)_2\text{NH}$ (excess);
 d) $\text{C}_2\text{H}_5\text{OH}$;
 e) $\text{CH}_3\text{-C}(=\text{O})\text{ONa}$ +
 f) phenol

5. What major organic product would you expect to obtain when acetic anhydride reacts with each of the following compounds? Outline mechanisms of these reactions.

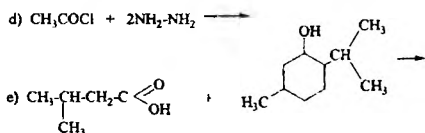
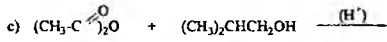
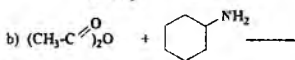
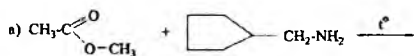
- a) NH_3 (excess); c) $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-OH}$;
 b) H_2O ; d) $\text{C}_6\text{H}_5\text{-NH}_2$ (excess).

6. Write the scheme and mechanism of the esterification reaction for the synthesis of the following esters:

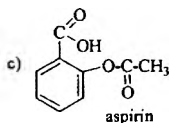
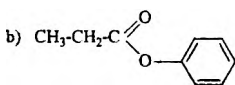
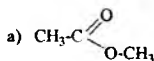
- a) ethyl benzoate;
 b) methyl methanoate;
 c) methyl cyclopentanecarboxylate;



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

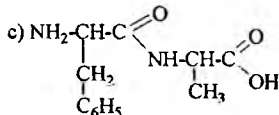
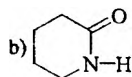


8. Write the mechanism for the acidic and basic hydrolysis of the following compounds:



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

a) N,N-Diethylbenzamide;



10. Acid catalyzed hydrolysis of an ester of molecular formula $\text{C}_8\text{H}_{16}\text{O}_2$ forms a carboxylic acid, compound A, and an alcohol, compound B. Reaction of compound B with acidic KMnO_4 forms compound A. Write a structure of the original ester.

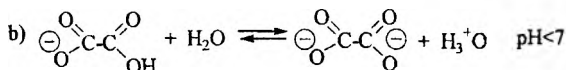
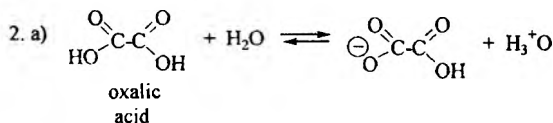
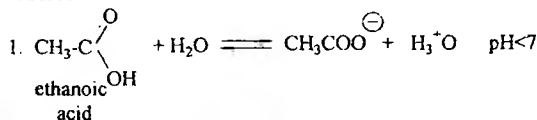
3. Laboratory work:

Experiment №1. Carboxylic acids dissociation reaction.

Sequence of operations: Place the small drops of CH_3COOH and HOOC-COOH solutions on the indicator paper.

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

Write:



Explain the result and write conclusion.

Experiment №2. Formation of sodium benzoate.

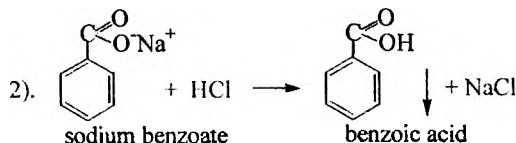
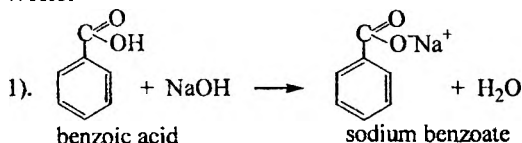
Sequence of operations: Place several crystals of benzoic acid and 2 drops of water in the test-tube. Add 3 drops of NaOH.

Check the result: the solution.

Add 3 drops of HCl.

Check the result: the precipitate.

Write:



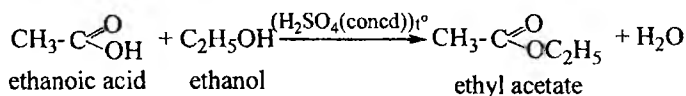
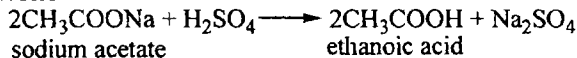
Explain the result and write conclusion.

Experiment №3. Formation of ethyl acetate.

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

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

Write:



Explain the result and write conclusion.

Experiment №4. Discover of oxalic acid.

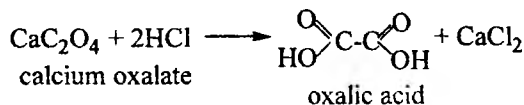
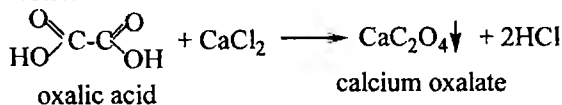
Sequence of operations: Place some oxalic acid and 3 drops of H_2O in the test-tube. Add 2 drops of $CaCl_2$ solution.

Check the result: white precipitate.

Pour the part of the mixture in to other test-tube. Add 3 drops of CH_3COOH in the test-tube № 1 and 3 drops of HCl in the test-tube № 2.

Check the result: the precipitate in the test-tube № 1 and solution in the test-tube № 2.

Write:



Explain the result and write conclusion.

Experiment №5. Decarboxylation of oxalic acid.

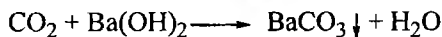
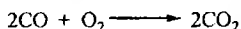
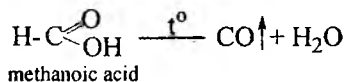
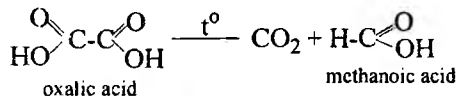
Sequence of operations: Place some oxalic acid in the first test-tube. Close the test-tube with the cork having the glass pipe. Lower the end of the glass pipe in the second test-tube with 3 drops of barium hydrate solution ($Ba(OH)_2$) in it. Warm the first test-tube.

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

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

Check the result: blue flame.

Write:



Explain the result and write conclusion.

THEME 9

Heterofunctional compounds.

1. Program questions:

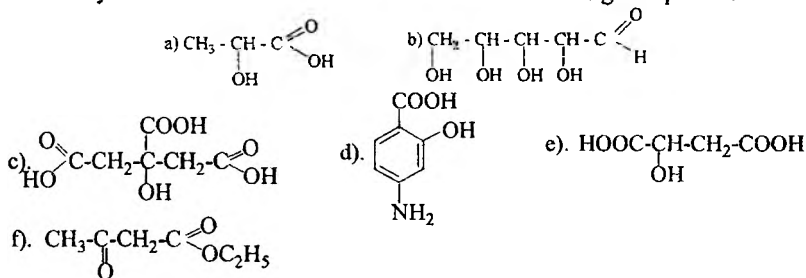
1. Polyfunctional compounds reactivity features.
2. Classification of heterofunctional compounds. Aminoalcohols: colamine, choline, adrenaline, noradrenaline. Their biological role.
3. Hydroxy and aminoacids. Monocarboxylic (lactic), dicarboxylic (2-hydroxybutanedioic acid, tartaric acid), tricarboxylic (citric) acids. Typical and specific chemical properties of α , β , γ hydroxy and aminoacids.
4. Oxo acids (aldehyde and keto acids). Glyoxyl, pyruvic, acetoacetic, 2-oxobutanoic, α -oxoglutaric acids. Keto-enol tautomerism. Decarboxylating reactions of β -oxo acids.
5. Heterofunctional benzene derivatives as pharmaceutical substances. Para-aminobenzoic acid and its derivatives. Anesthetics, novocaine).
6. Sulfanilic acid and its derivatives. Sulfanilamides. Streptocid.
7. Salicylic acid and its derivatives. Sodium salicylate, methyl salicylate, phenyl salicylate, acetylsalicylic acid (aspirin).

Literature:

- [1] L.G. Hidranovich. Bioorganic chemistry lecture course. Vitebsk, 2004. p. 154 - 170
[2] T.W. Graham Solomons. Fundamentals of organic chemistry. John Wiley and sons, 1994. p. 805 - 809, 827 - 837, 869 - 870
[3] George H. Schmid. Organic chemistry. Mosby, 1996. p. 922, 995 - 997, 1046 - 1063

2. Problems.

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



2. Write the structural formula for each of the following compounds:

- a) 2-amino-3-(4-hydroxyphenyl)-propanoic acid;
b) N-butyl propanamide;
c) N-4-ethoxyphenyl ethanamide;
d) trans-2-nitrocyclohexanecarboxylic acid;
e) 4-aminobenzenesulfonic acid;
f) pentanepentaol-1,2,3,4,5.

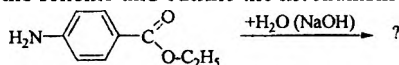
3. Show the reaction centres of 2-aminoethanol. Compare nucleophilic properties of amino and hydroxyl groups. Outline the synthesis of choline by the methylation reaction of 2-aminoethanol.

4. Show the reaction centres of lactic acid (2-hydroxypropanoic acid). Compare the strength of its OH acidic centres and electrophilic centres. Write the scheme of reaction of lactic acid with NaOH and outline mechanism for acid-catalyzed esterification reaction of lactic acid with $\text{C}_2\text{H}_5\text{OH}$.

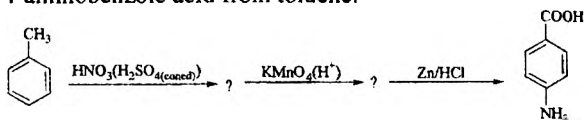
5. Show the reaction centres of 2-oxopropanoic acid. Write the scheme and outline mechanism of the acid-catalyzed esterification reaction of 2-oxopropanoic acid with $\text{C}_2\text{H}_5\text{OH}$.

6. Write the scheme and mechanism of acid-catalyzed hydrolysis of acetylcholine in living systems.

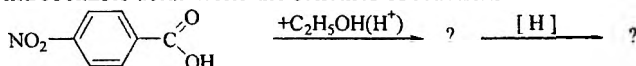
7. The base-catalyzed hydrolysis reaction is used for identification of anesthesine. Write the scheme and outline the mechanism of this reaction.



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



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



10. a) Write tautomeric forms of acetoacetic ester and outline schemes of reactions that prove existence of two tautomeric forms.

b) What tautomeric form do you expect to be a stronger acid? Write scheme of reaction that proves acidic properties of acetoacetic ester.

11. Write the scheme of the decarboxylation reaction of acetoacetic acid. Name the product of this reaction.

12. What products do you expect to get after the heating of 2-aminobutanedioic acid.

3. Laboratory work:

Experiment №1. Reactions of lactic acid.

A. Discovery of formic acid.

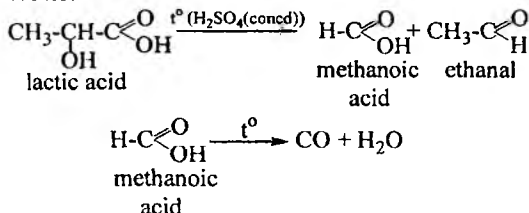
Sequence of operations: Place 1 drop of lactic acid and 1 drop of concentrated H_2SO_4 (Take care!) Warm the mixture.

Check the result: black foam.

To convince that CO is forming, set it on fire near the aperture of the test-tube.

Check the result: the blue flame.

Write:

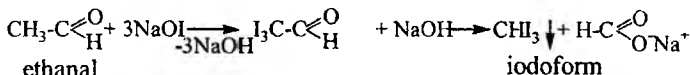
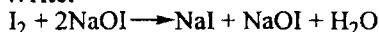


B. Discovery of ethanal.

Sequence of operations: Place 2 drops of H_2O , 1 drop of concentrated H_2SO_4 and 1 drop of lactic acid in the test-tube № 1. Close it with the cork with the glass pipe. Lower the end of the glass pipe in the test-tube № 2 with 1 drop of I_2 (in KI solution) and 2 drops of NaOH in it. Warm the test-tube № 1.

Check the result: white-yellow precipitate in the test-tube № 2.

Write:



Explain the result and write conclusion.

Experiment №2. Tartaric acid has 2 carboxy groups.

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

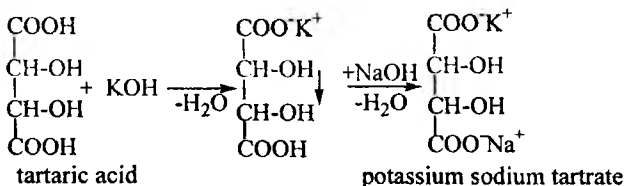
Check the result: white precipitate.

Add some more drops of KOH.

Check the result: the solution.

Attention: you need this solution for the next experiment.

Write:



Explain the result and write conclusion.

Experiment №3. Tartaric acid has 2 hydroxyl groups.

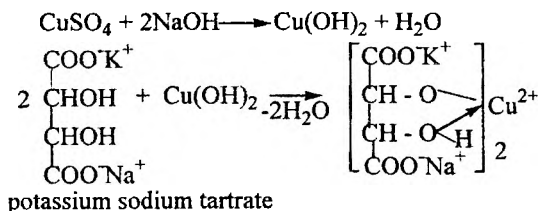
Sequence of operations: Place 2 drops of CuSO_4 in the test-tube. Add 2 drops of NaOH .

Check the result: blue precipitate.

Add the potassium sodium tartrate (you received it in the experiment № 2).

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

Write:



Explain the result and write conclusion.

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

Sequence of operations: Place 1 drop of acetoacetic ester and 1 drop of FeCl_3 solution.

Check the result: violet-red solution.

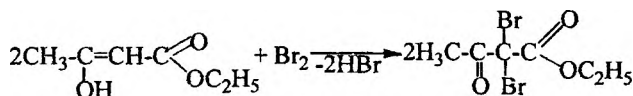
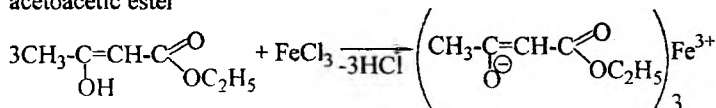
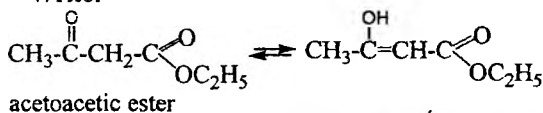
Add 1 drop of bromine water.

Check the result: violet colour disappears, but it appears again in several seconds.

Add one more drop of bromine water.

Check the result: the same change.

Write:



Explain the result and write conclusion.

Experiment №5. Hydrolysis of acetylsalicylic acid.

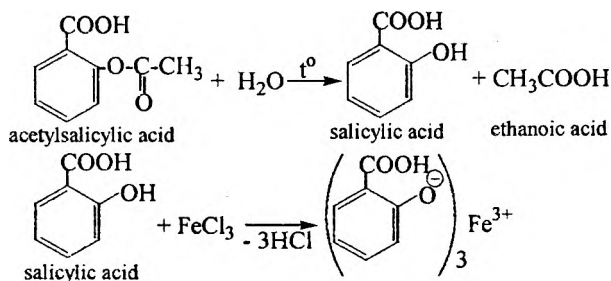
Sequence of operations: Place some acetylsalicylic acid and 6 drops of H_2O in the test-tube №1. Shake the test-tube. Pour the part of the mixture in the test-tube № 2. Add 1 drop of FeCl_3 solution in the test-tube № 2.

Check the result: violet colour is not appearing.

Warm the test-tube № 1 during 30 seconds. Add 1 drop of FeCl_3 solution.

Check the result: violet colour.

Write:



Explain the result and write conclusion.

THEME 10

Control-Test № 1.

I. Program questions:

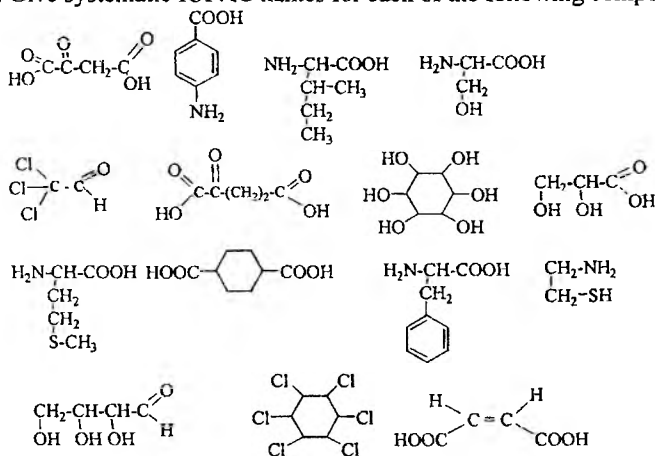
1. Remind yourself the program material from the theme № 1 to № 9.

Literature:

Study the literature from the themes № 1 - № 9.

2. Questions for the control-test № 1.

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

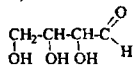


Write the structural formula for each of the following compounds:

N,N-diethylhexanamide; Trichloroethanal; 2,2-dimethylpropanol-1; 2-isopropyl-5-methylcyclohexanol; N-ethyl-N-methylaniline; 2-methylcyclohexanone; 3,4,5-trihydroxybenzoic acid; ethylthioethane; 2-amino-1-(3,4-dihydroxyphenyl)-ethanol-1.

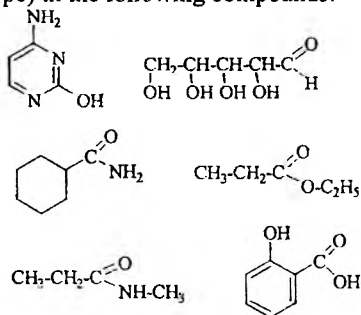
2. Write the Newman projection formulas of all staggered and eclipsed conformations and indicate the most stable for the following compounds: 2-aminobutanoic acid (along C₂-C₃ bond); 2-amino-3-hydroxypropanoic acid (along C₂-C₃ bond).

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

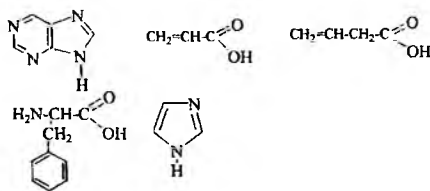


Write two chair conformations for cis-1,4-dimethylcyclohexane; trans-cyclohexanediol-1,3.

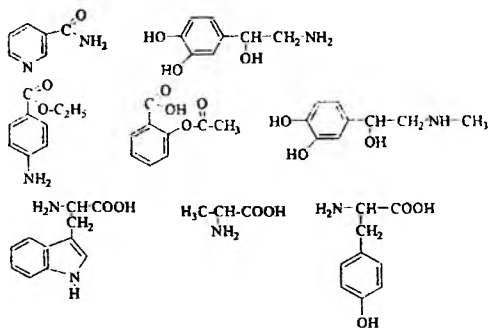
3. Define the hybridization type of carbon atoms and heteroatoms (pyridine and pyrrole type) in the following compounds:



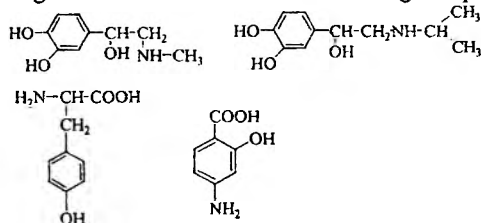
Write the definition of conjugation. Define the type of conjugation and show the electronic structure of the conjugated systems. Designate electron's movement with curved arrows:



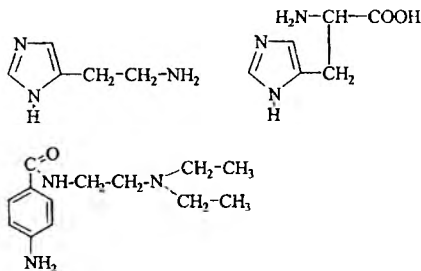
4. Write the definitions of inductive and resonance effects. Define the sign (negative or positive) of inductive and resonance effects of functional groups and heteroatoms. Show these effects with arrows:



5. Write the Brensted-Lowry definition of the acid and the base. Compare the strength of acidic centres of the following compounds:



Compare the strength of the basic centres of the following compounds:



Compare the strength of the following acids:

Ethanoic acid; 2-aminoethanoic acid; 2-hydroxyethanoic acid.

6. Write the schemes and outline mechanisms of monosulphonation reactions of benzoic acid and aniline, bromination reactions of aniline and benzoic acid, monomethylation reactions of phenol and nitrobenzene. Show the substituent effects of the functional groups. Write the schemes and outline mechanisms of the bromination reaction of 2-methylpropane and cyclohexane. Write the schemes and outline mechanisms of the hydrobromination reaction of 2-methylpropene and propenoic acid, the hydration reaction of propene.

7. Show the reaction centres of ethanol, propanol-2, butanol-2, 2-methylbutanol-2. Write the schemes and outline mechanisms of the reactions of propanol-2 and ethanol with HBr, butanol-2 with HCl. Write the scheme and outline mechanism of dehydration of butanol-2 to the ether. Write the schemes of reactions that prove nucleophilic properties of ethanol. Write the scheme and outline mechanism of the elimination reaction of 2-methylbutanol-2.

8. Show the reaction centres of ethanal, propanal, butanal, 4-hydroxybutanal, propanone.

Compare the reactivity of ethanal and propanone, propanone and propanal in A_N reactions. Write the schemes and outline mechanism of the reactions of ethanal with hydroxylamine, ethanal with methanol, propanal with methanamine. Write the schemes of reduction reactions for an aldehyde and ketone. Write the schemes and outline mechanisms for an aldol-type addition of propanal and butanal, for synthesizing of cyclic hemiacetal from 4-hydroxybutanal, for the acid-catalyzed hydrolysis of 1,1-dimethoxyethane.

9. Show the reaction centres of propanoic acid.

Compare the strength of electrophilic centres of ethanoic acid and ethanoyl chloride. Write the schemes and outline mechanisms of esterification reactions for the both compounds. Explain the role of acidic catalysis. Write the scheme and outline mechanism of the reaction of propanoic acid with ethanol. Propose the reaction and mechanism to form ethyl ethanoate from the anhydride of corresponding acid. Write the schemes of acid-catalyzed hydrolysis of propanoyl chloride and ethyl ethanoate and of base-catalyzed hydrolysis of ethyl propanoate and propanamide, outline mechanism of the base-catalyzed hydrolysis of methyl benzoate. Indicate the mechanisms of reactions. Write the schemes of the decarboxylation reactions for ethanoic acid and for ethanedioic acid.

10. Write the structural formulas of lactic, citric, acetoacetic acids and acetoacetic ester.

Write the schemes of specific reactions that proceed in heating for α -, β - and γ -aminoacids (lactic acid, 3-hydroxybutanoic, 4-hydroxybutanoic, 2-hydroxypropanoic and 2-aminopropanoic acids). Write the schemes of specific reactions that proceed in heating and H_2SO_4 and in heating but absence of H_2SO_4 for lactic acid. Compare the strength of OH acidic centres of the lactic acid. Write the schemes of reactions of lactic acid with Na and NaOH.

Compare the strength of the electrophilic centres of acetoacetic ester. Write the scheme of reaction of acetoacetic ester with NaOH solution. Show the tautomeric forms of acetoacetic acid. What is the type of tautomeric change take place here. Write the schemes of corresponding reactions of tautomeric forms (with HCN, NaOH, CH_3COCl).

THEME 11

Carbohydrates. Monosaccharides.

1. Program questions:

1. Classification of carbohydrates. Monosaccharides. Structural formulas of the main pentoses (D-ribose, D-xylose, D-ribulose, D-xylulose) and hexoses (D-glucose, D-mannose, D-galactose, D-fructose).

2. Stereochemistry of monosaccharides. D and L designation of monosaccharides. Fischer projection formulas. Diastereomers, enantiomers, epimers.

3. Open-chain forms and cyclic forms of monosaccharides. Haworth formulas: (pyranose and furanose rings). Anomers.

4. Conformations of monosaccharides. Most stable conformations of hexoses.

5. Reactions of monosaccharides: glycoside formation (O- and N-glycosides). Hydrolysis of glycosides.

6. Formation of ethers. Conversion to esters.

7. Reactions of oxo-group. Oxidation reactions of monosaccharides. Benedict's and Tollen's reagents. Reducing sugars.

8. The synthesis of aldonic acids (oxidation by bromine water). The synthesis of aldaric acids (nitric acid oxidation). Uronic acids. Reduction of monosaccharides: alditols.

9. Deoxy sugars. Amino sugars.

Literature:

[1] L.G. Hidranovich. Bioorganic chemistry lecture course. Vitebsk, 2004. p. 170 - 186

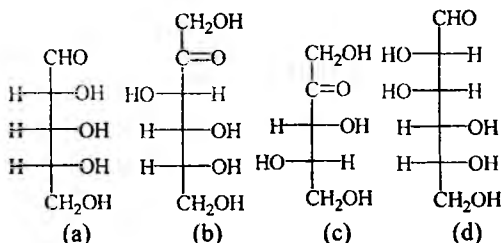
[2] T.W. Graham Solomons. Fundamentals of organic chemistry. John Wiley and sons, 1994. p. 891 - 920

[3] George H. Schmid. Organic chemistry. Mosby, 1996. p. 1092 - 1098, 1101 - 1118

[4] Richard F. Daley, Sally J. Dalley. Organic chemistry Wm. C. Brown Publishers, 1996. p. 1227 - 1237, 1240 - 1245

2. Problems.

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



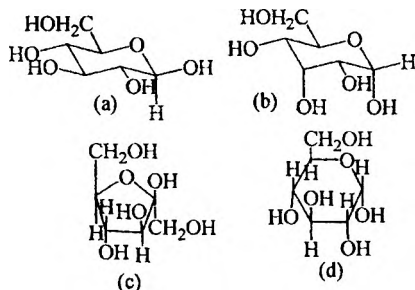
2. Label the stereocenters in each of the monosaccharides in Exercise 1 by an asterisk and determine the maximum number of stereoisomers of each.

Assign each of the monosaccharides in Exercise 1 to either the D- or L-family.

3. Write the cyclic forms for each of the monosaccharides in Exercise 1. Indicate which is the α -anomer and which is the β -anomer. Draw conformational formulas for each of the pyranose forms.

4. Write a chair representation of the pyranose form of each of the following monosaccharides in Exercise 1.

5. Write the Fischer projection formula for each of the following cyclic monosaccharides

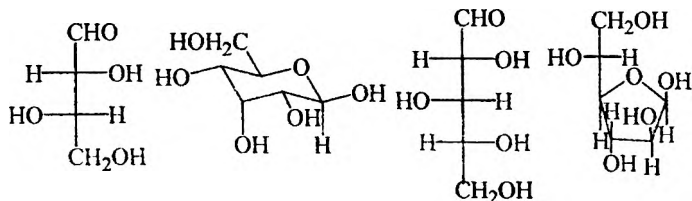


6. Write the structure of the products, if any, of the reaction of α -D-galactopyranose with each of the following reagents.

- (a) $\text{CH}_3\text{OH}/\text{HCl}$; (b) $(\text{CH}_3\text{O})_2\text{SO}_2/\text{NaOH}$; (c) $(\text{RCO})_2\text{O}/\text{CH}_3\text{COONa}$
 (d) Fehling's solution; (e) $\text{Br}_2/\text{H}_2\text{O}$; (f) HNO_3

7. Write the structure of the aldonic acids and aldonic acids obtained by oxidation of each of the following monosaccharides. Write the structure of alditols obtained by reduction of each of the following monosaccharides:

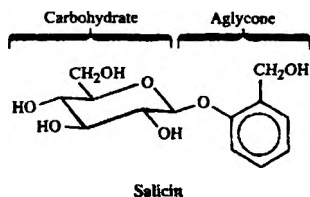
8.



Which of the products are optically active?

9. Write the reaction of the acid-catalyzed hydrolysis of methyl α -D-glucopyranoside and pentamethyl derivative.

10. Write the reaction of the acid-catalyzed and base-catalyzed hydrolysis of esters of β -D-mannopyranose.
11. Salicin is naturally occurring compound, find in the bark of willow trees.



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

3. Laboratory work.

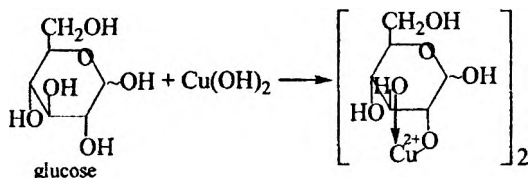
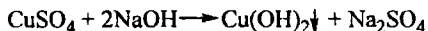
Experiment № 1. Glucose has hydroxyl groups.

Sequence of operations: Place 1 drop of glucose solution in the test-tube. Add 6 drops of NaOH and 1 drop of CuSO_4 .

Check the result: blue solution.

Attention: you need this solution for the next experiment.

Write:



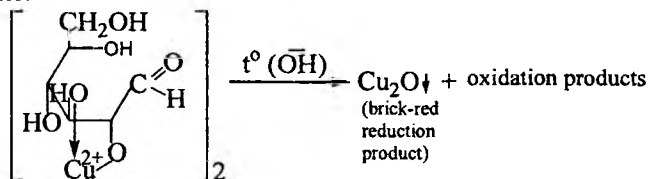
Explain the result and write conclusion.

Experiment № 2. Oxidation of glucose by Cu(OH)_2 .

Sequence of operations: Take the solution you received in the experiment № 1. Add 8 drops of H_2O . Warm the test-tube.

Check the result: brick-red precipitate.

Write:



Explain the result and write conclusion.

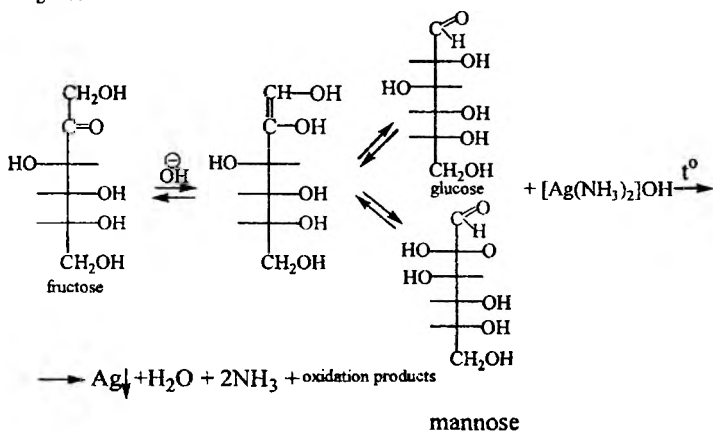
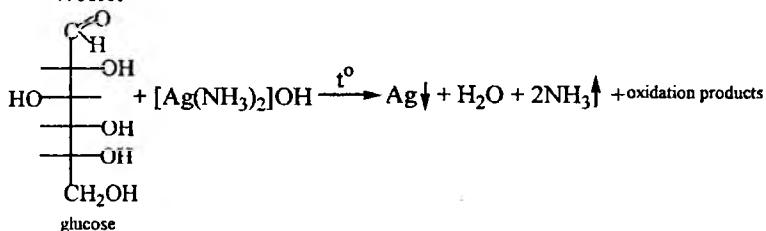
Experiment № 3. Oxidation of glucose and fructose by Tollen's reagent $[\text{Ag}(\text{NH}_3)_2]\text{OH}$.

Sequence of operations: Take 2 test-tubes. Place 1 drop of AgNO_3 solution and 2 drops of NaOH solution in each test-tube. Add 4 drops of NH_4OH in these test-tubes. This solution is named Tollen's reagent.

Add 1 drop of glucose solution in the test-tube № 1 and 1 drop of fructose solution in the test-tube № 2. Warm the test-tubes.

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

Write:



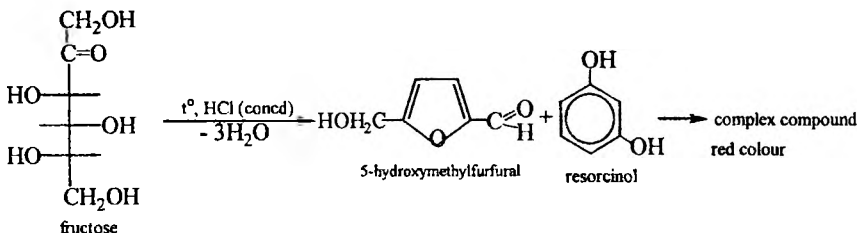
Explain the result and write conclusion.

Experiment № 4. Reaction of fructose with resorcinol.

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

Check the result: the change of colour.

Write:



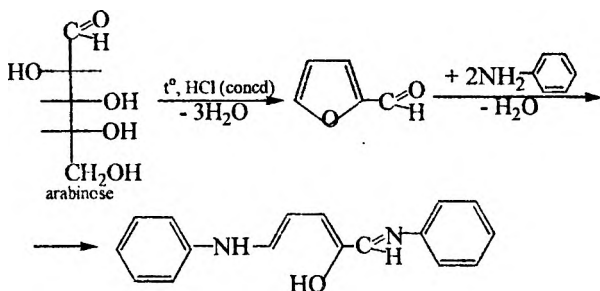
Explain the result and write conclusion.

Experiment № 5. Qualitative test for pentoses.

Sequence of operations: Place some arabinose in the test-tube № 1. Make the mixture of 3 drops of concentrated HCl (Take care!) and 3 drops of H_2O in the test-tube № 2. Add this mixture in the test-tube № 1. Place 1 drop of aniline and 1 drop of CH_3COOH on the filter paper. Place this filter paper on the inner border of the test-tube № 1. Warm the test-tube.

Check the result: the filter paper becomes red coloured.

Write:



Explain the result and write conclusion.

THEME 12

Carbohydrates. Oligosaccharides and polysaccharides.

1. Program questions:

1. Classification of polysaccharides.
2. Oligosaccharides. Disaccharides: maltose, cellobiose, lactose, sucrose. Structure, tautomerism. Reducing properties. Hydrolysis. Conformations of maltose and cellobiose.
3. Typical and special reactions of reducing and nonreducing disaccharides.
4. Homopolysaccharides. Starch (amylose and amylopectin), glycogen, cellulose. Primary structure, hydrolysis, secondary structure (amylose, cellulose).
5. Heteropolysaccharides. Hyaluronic acid, chondroitin sulfates, heparin. Primary structure. Biological role.
6. Glycolipids and glycoproteins.

Literature:

- [1] L.G. Hidranovich. Bioorganic chemistry lecture course. Vitebsk, 2004. p. 187 - 204
- [2] T.W. Graham Solomons. Fundamentals of organic chemistry. John Wiley and sons, 1994. p. 920 - 934
- [3] George H. Schmid. Organic chemistry. Mosby, 1996. p. 1118 - 1130
- [4] Richard F. Daley, Sally J. Dalley. Organic chemistry Wm. C. Brown Publishers, 1996. p. 1268 - 1271

2. Problems.

1. Write the structure of the product of the reaction of β -maltose with each of the following reagents:

- | | |
|-----------------------------|---|
| a) HOH/H^+ | c) Tollen's reagent |
| b) Br_2/HOH | d) $(\text{CH}_3\text{O})_2\text{SO}_2/\text{NaOH}$ |

2. Write the structure of the product of the reaction of α -cellobiose with each of the following reagents:

- | | | |
|-------------------------------------|--|-----------------------|
| a) HOH/H^+ | c) $(\text{CH}_3\text{CO})_2\text{O}/\text{CH}_3\text{COO}^-\text{Na}^+$ | |
| b) $\text{Br}_2/\text{H}_2\text{O}$ | d) NaBH_4 | e) Fehling's solution |

3. Direct oxidation of an aldose affects the aldehyde group first, converting in to a carboxylic acid, and most oxidizing agents that will attack 2° alcohol groups. Clearly, then, a laboratory synthesis of a uronic acid from an aldose

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

4. Show how the following experimental evidence can be used to deduce the structure of lactose.

- Acid hydrolysis of lactose ($C_{12}H_{22}O_{11}$) gives equimolar quantities of D-glucose and D-galactose. Lactose undergoes a similar hydrolysis in the presence of a β -galactosidase,
- Lactose is a reducing sugar.
- Oxidation of lactose with bromine water followed by hydrolysis with dilute acid gives D-galactose and D-gluconic acid.
- Bromine water oxidation of lactose followed by methylation and hydrolysis gives 2,3,6-tri-O-methylgluconolactone and 2,3,4,6-tetra-O-methyl-D-galactose.
- Methylation and hydrolysis of lactose gives 2,3,6-tri-O-methyl-D-glucose and 2,3,4,6-tetra-O-methyl-D-galactose.

5. Deduce the structure of the disaccharide melibiose from the following data:

- Melibiose is a reducing sugar.
- Hydrolysis of melibiose with acid or with an α -galactosidase gives D-galactose and D-glucose.
- Bromine water oxidation of melibiose gives *melibionc acid*. Hydrolysis of melibionc acid gives D-galactose and D-gluconic acid. Methylation of melibionc acid followed by hydrolysis gives 2,3,4,6-tetra-O-methyl-D-galactose and 2,3,4,5-tetra-O-methyl-D-gluconic acid.
- Methylation and hydrolysis of melibiose gives 2,3,4,6-tetra-O-methyl-D-galactose and 2,3,4-tri-O-methyl-D-glucose.

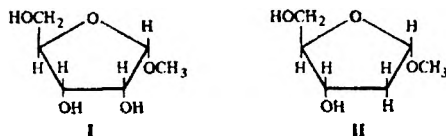
6. Trehalose is a disaccharide that can be obtained from yeasts, fungi, sea urchins, algae, and insects. Deduce the structure of trehalose from the following information:

- Acid hydrolysis of trehalose yields only α -D-glucose.
- Trehalose is hydrolyzed by D-glucosidases but not by β -glucosidases.
- Trehalose is a nonreducing sugar;
- Methylation of trehalose followed by hydrolysis yields two molar equivalents of 2,3,4,6-tetra-O-methyl-D-glucose.

7. Outline chemical tests that will distinguish between each of the following:

- D-Glucose and D-glucitol
- D-Glucitol and D-glucaric acid

- (c) α -Glucose and D-fructose
- (d) D-Glucose and D-galactose
- (e) Sucrose and maltose
- (f) Maltose and malonic acid
- (g) Methyl β -D-glucopyranoside and 2,3,4,6-tetra-O-methyl- β -D-glucopyranose
- (h) Methyl α -D-ribofuranoside (I) and methyl 2-deoxy- α -D-ribofuranoside (II)



8. A group of oligosaccharides called *Schardinger dextrans* can be isolated from *Bacillus macerans* when the bacillus is grown on a medium rich in amylose. These oligosaccharides are all *nonreducing*. A typical *Schardinger dextrin* undergoes hydrolysis when treated with an acid or an α -glucosidase to yield six, seven, or eight molecules of D-glucose. Complete methylation of a *Schardinger dextrin* followed by acid hydrolysis yields only 2,3,6-tri-O-methyl-D-glucose. Propose a general structure for a *Schardinger dextrin*.

9. Isomaltose is a disaccharide that can be obtained by enzymatic hydrolysis of amylopectin. Deduce the structure of isomaltose from the following data:

- a). Hydrolysis of 1 mol of isomaltose by acid or by an α -glucosidase gives 2 mol of D-glucose.
- b) Isomaltose is a reducing sugar.
- c) Isomaltose is oxidized by bromine water to isomaltonic acid. Methylation of isomaltonic acid and subsequent hydrolysis yields 2,3,4,6-tetra-O-methyl-D-glucose and 2,3,4,5-tetra-O-methyl-D-gluconic acid.
- d). Methylation of isomaltose itself followed by hydrolysis gives 2,3,4,6-tetra-O-methyl-D-glucose and 2,3,4-tri-O-methyl-D-glucose.

10. *Stachyose* occurs in the roots of several species of plants. Deduce the structure of stachyose from the following data:

- a) Acidic hydrolysis of 1 mol of stachyose yields 2 mol of D-galactose, 1 mol of D-glucose, and 1 mol of D-fructose.
- b) Stachyose is a nonreducing sugar.
- c) Treating stachyose with an α -galactosidase produces a mixture containing D-galactose, sucrose, and a nonreducing trisaccharide called raffinose.
- d) Acidic hydrolysis of raffinose gives D-glucose, D-fructose, and D-galactose. Treating raffinose with an α -galactosidase yields D-galactose and

sucrose. Treating raffinose with invertase (an enzyme that hydrolyzes sucrose) yields fructose and *melibiose*.

e) Methylation of stachyose followed by hydrolysis yields 2,3,4,6-tetra-O-methyl- α -galactose, 2,3,4-tri-O-methyl-D-galactose, 2,3,4-tri-O-methyl-D-glucose, and 1,3,4,6-tetra-O-methyl-D-fructose.

3. Laboratory work.

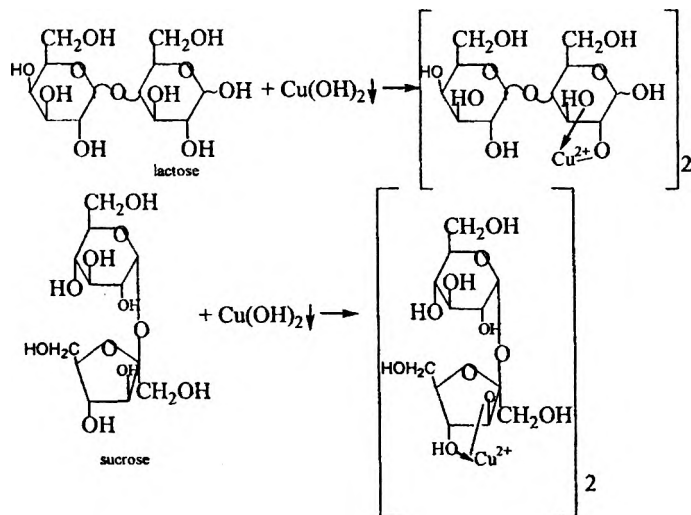
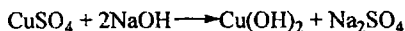
Experiment № 1. Lactose and sucrose have hydroxyl groups.

Sequence of operations: Place 1 drop of lactose solution in the test-tube № 1 and 1 drop of sucrose solution in the test-tube № 2. Add 6 drops of NaOH and 1 drop of CuSO_4 solutions in two test-tubes.

Check the result: blue solution.

Attention: you need these solutions for the next experiment.

Write:



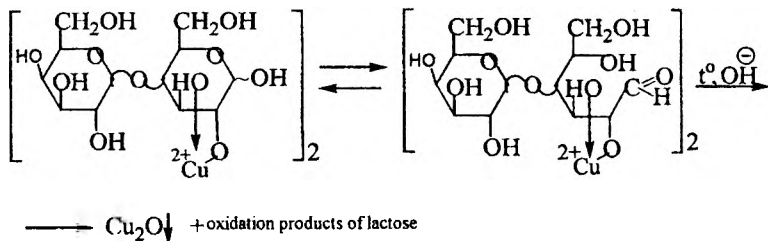
Explain the result and write conclusion.

Experiment № 2. Reducing power of lactose and sucrose.

Sequence of operations: Warm the test-tubes with solutions you received in the experiment № 1.

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

Write:



Explain the result and write conclusion.

Experiment № 3. Proof of sucrose hydrolysis.

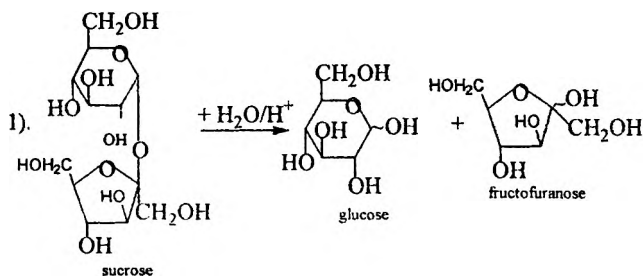
Sequence of operations: Take 2 test-tubes. Place 1 drop of sucrose solution in the test-tube № 1. Add 1 drop of HCl and 6 drops of H₂O. Warm the test-tube № 1 during 0,5-1 minute. Pour half of the solution, received in the test-tube № 1 in the test-tube № 2. Add 6 drops of NaOH, 4 drops of H₂O and 1 drop of CuSO₄ in the test-tube № 2. Warm the test-tube № 2.

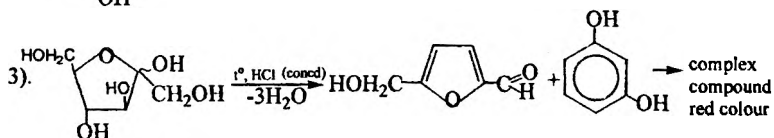
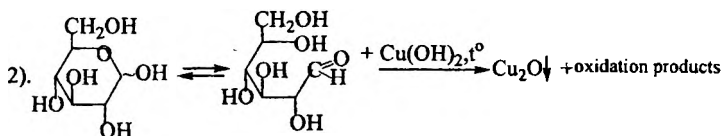
Check the result: brick-red precipitate.

Add 1 crystal of resorcinol and 2 drops of concentrated HCl (Take care!) in the test-tube № 1.

Check the result: the change of colour.

Write:





Explain the result and write conclusion.

Experiment № 4. Discovery of the starch.

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

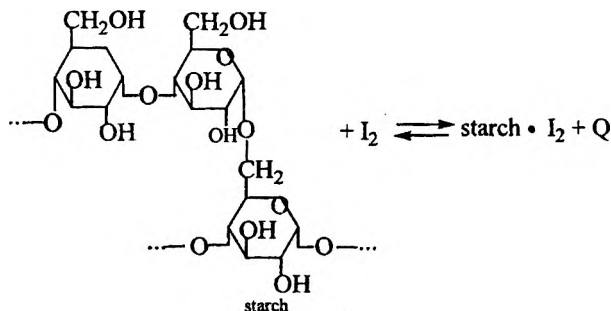
Check the result: blue solution.

Warm the test-tube.

Check the result: colourless solution.

In getting cold the solution become blue again.

Write:



Explain the result and write conclusion.

Experiment № 5. Starch has no reducing power.

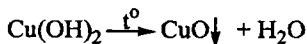
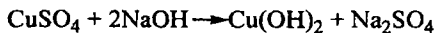
Sequence of operations: Place 10 drops of the starch paste in the test-tube. Add 3 drops of NaOH and 1 drop of $CuSO_4$ solution. Shake the test-tube.

Check the result: blue precipitate of $Cu(OH)_2$

Warm the test-tube.

Check the result: black precipitate of CuO .

Write:



Explain the result and write conclusion.

Experiment № 6. Acidic hydrolysis of the starch.

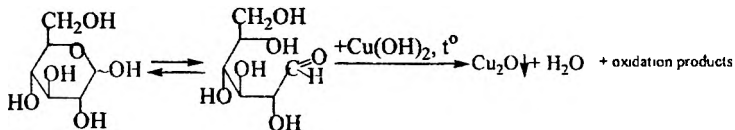
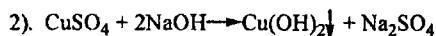
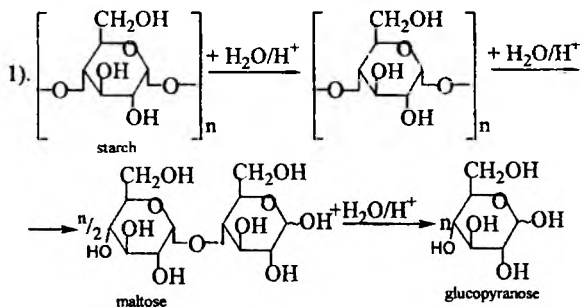
Sequence of operations: Place 1 drop of the starch paste solution in the test-tube. Add 2 drops of H_2SO_4 . Warm the test-tube on the water bath during 20 minutes. Place 1 drop of this solution on the glass. Add 1 drop of very diluted I_2 (with KI) solution.

Check the result: solution has no blue colour.

Add 8 drops of NaOH and 1 drop of CuSO_4 solutions in the test-tube. Warm the test-tube.

Check the result: brick-red precipitate.

Write:



Check the result and write conclusion.

THEME 13

Natural amino acids. Structure, properties, functions.

1. Program questions:

1. Classification, structure and stereochemistry of α -amino acids.
2. Reactions of amino acids as heterofunctional compounds. Acid-base properties. Dipolar ions.
3. Reactions of carboxyl group of amino acids. Esterification.
4. Reactions of amino group of amino acids. Reactions with aldehydes and ketones, carboxylic acids and their derivatives, nitrous acid (nitrosation).
5. Deamination and enzyme-catalyzed transamination reactions. Pyridoxal phosphate catalysis.

Literature:

- [1] L.G. Hidranovich. Bioorganic chemistry lecture course. Vitebsk, 2004. p. 205 - 217
- [2] T.W. Graham Solomons. Fundamentals of organic chemistry. John Wiley and sons, 1994. p. 972 - 979
- [3] George H. Schmid. Organic chemistry. Mosby, 1996. p. 1144 - 1151
- [4] Richard F. Daley, Sally J. Dalley. Organic chemistry Wm. C. Brown Publishers, 1996. p. 1166 - 1173

2. Problems.

1. Write Fischer projection formulas for each of the following amino acids:
(a) L-Valine, (b) D-Cysteine (c) L-Glutamine (d) L-Phenylalanine
2. Write the structure of each of the following amino acids in solution at pH=3, pH=8, pH=11
(a) Leu, (b) Met, (c) Asp, (d) Lys
3. Write the structure of the predominant form of each of the following amino acids at the pH of blood 7,4
(a) Ser (b) Glu (c) His (d) Gly
4. Write the structure of the predominant form of threonine in each solution of the following pH:
(a) pH=0,2 (b) pH=9,8 (c) pH=13 (d) pH=5,0

5. Explain why there is a difference of 2,4 units between the pK_a of carboxyl group of alanine (2,3) and the pK_a of acetic acid (4,7).

6. Which of the side chains of the 20 amino acids are charged at $pH=7$.

7. Write the structure of the product of the reaction of isoleucine with each of the following reagents:

- CH_3OH/HCl
- Basic aqueous solution of benzoyl chloride
- acetic anhydride

8. Write the structure of the product formed in each of the following reactions:

(a) Asn + NaOH/HOH (Heat) \rightarrow

(b) Lys + HCl \rightarrow

(c) Asp + NaOH \rightarrow

(d) Trp + $NaNO_2/HCl \rightarrow$

(e) Phe + $H_2C=O \rightarrow$

9. Write the structure of the product of each of the following reactions:

(a) 2-oxopropanoic acid + Glutamic acid $\xrightarrow{\text{aminotransferase}}$

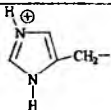
(b) 2-oxobutanedioic acid + alanine $\xrightarrow{\text{aminotransferase}}$

(c) Histidine $\xrightarrow{\text{decarboxylase}}$

(d) Write the scheme of the deamination reaction of Glu.

10. Arginine is the most basic of the 20 common α -amino acids. A molecule of Arg has a total of four nitrogen atoms. Which of the four is the most basic? Explain your choice and find most basic centre in the side chain of Arg:

pK_a 's of Side-Chains of Acidic and Basic Amino Acids

| Acidic Amino Acids | | | Basic Amino Acids | | |
|--------------------|---|----------|-------------------|--|-----------|
| Amino Acid | Side-Chain | pK_a | Amino Acid | Side-Chain | pK_a |
| Asp | $-\text{CH}_2\text{CO}_2\text{H}$ | 4.4 | Lys | $-(\text{CH}_2)_4\text{NH}_3^+$ | 10.2-10.5 |
| Glu | $-\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$ | 4.5 | Arg | $-(\text{CH}_2)_3\text{NH}-\text{C}(=\text{NH}_2)-\text{NH}_2$ | 12.5-13 |
| Cys | $-\text{CH}_2\text{SH}$ | 7.5-9.2 | | | |
| His |  | 6.8-7 | | | |
| Tyr | $-\text{CH}_2-\text{C}_6\text{H}_4-\text{OH}$ | 9.9-10.3 | | | |

3. Laboratory work.

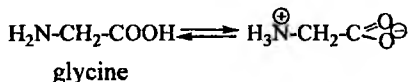
Experiment 1. Glycine solution has neutral pH value.

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

Check the result: change of colour.

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

Write:



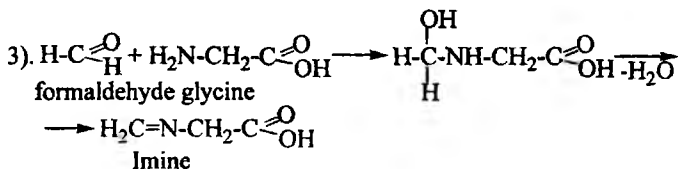
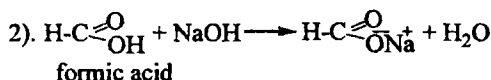
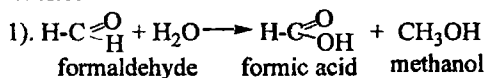
Explain the result and write conclusion.

Experiment 2. Glycine reacts with formaldehyde.

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

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

Write:



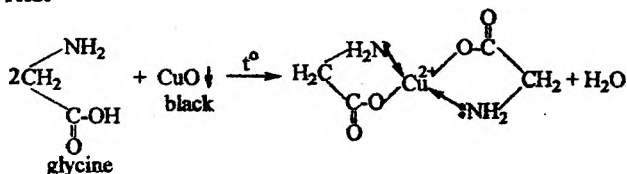
Explain the result (why the solution became acidic?) and write conclusion.

Experiment 3. Formation of copper and glycine complex compound.

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

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

Write:



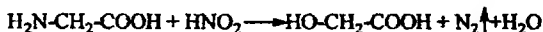
Explain the result and write conclusion.

Experiment 4. Glycine reacts with nitrous acid.

Sequence of operations: Place 5 drops of 0,2 M glycine solution in the test-tube. Add 5 drops of 5% sodium nitrite (NaNO_2) solution and 2 drops of concentrated acetic acid. Shake mixture carefully.

Check the result: bubbles of gas.

Write:



glycine

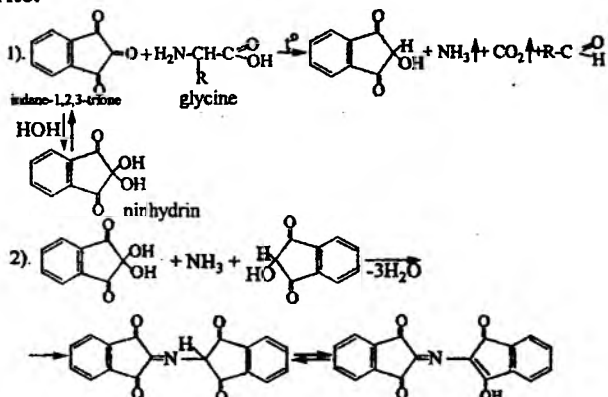
Explain the result and write conclusion.

Experiment 5. Glycine reacts with ninhydrin.

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

Check the result: blue-red colour.

Write:



Explain the result and write conclusion.

THEME 14

Peptides and proteins. Four levels of proteins structural organization. Strategy of peptide synthesis.

1. Program questions:

1. Biological functions of peptides and proteins.
2. Structure of peptides and proteins. Peptide bond, N -and C-terminal residues.
3. Properties of peptides. Isoelectric point (pI) of peptides. Acidic and basic hydrolysis of peptides.
4. Primary structure of peptides and proteins. Amino acid sequence. Terminal residue analysis. (Sanger method, Edman degradation). Partial hydrolysis.
5. Polypeptide and protein synthesis. Protecting groups. Activation of the carboxyl groups.
6. Secondary structure of proteins. α -Helix and β -sheet (β -configuration).
Tertiary and quaternary structures of proteins.

Literature:

- [1] L.G. Hidranovich. Bioorganic chemistry lecture course. Vitebsk, 2004. p. 217 - 237
- [2] T.W. Graham Solomons. Fundamentals of organic chemistry. John Willey and sons, 1994. p. 986 - 1005
- [3] George H. Schmid. Organic chemistry. Mosby, 1996. p. 1151-1175
- [4] Richard F. Daley, Sally J. Dalley. Organic chemistry Wm. C. Brown Publishers, 1996. p. 1176 - 1179, 1181 - 1194, 1197 - 1203

2. Problems.

1. Write the structure of tripeptide Ala-Met-Glu in solution at:
(a) pH= 1; (b) pH=3; (c) pH=11
2. Aspartame, a widely used nonnutritive sweetener, is the methyl ester of the dipeptide Asp-Phe. Draw the full structure of aspartame. The isoelectric point of aspartame is 5.9. Draw the structure present in aqueous solution at this Ph.
3. Write a reaction showing how 2,4-dinitrofluorobenzene could be used to identify the N-terminal amino acid of Val-Ala-Gly.

4. What products would you expect (after hydrolysis) when Val-Lys-Gly is treated with 2,4-dinitrofluorobenzene?

5. Write the reaction involved in a sequential Edman degradation of Met-Ile-Arg.

6. Indicate where $N\equiv CBr$, trypsin and chymotrypsin will cleave the following polypeptide chain:

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

7. The following peptide was subjected to:

- 1) Edman degradation;
- 2) trypsin hydrolysis;
- 3) chymotrypsin hydrolysis.

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

H_2N -Glu-Lys-Phe-Cys-Val-Tyr-Met-Ala-Phe-COOH.

8. Give the amino acid sequence of the following polypeptides using only the data given by partial acidic hydrolysis

(a) Ser, His, Pro, Thr \rightarrow Ser-Thr + Thr-His + Pro-Ser

(b) Ala, Arg, Cys, Val, Leu \rightarrow Ala-Cys + Cys-Arg + Arg-Val + Leu-

Ala

9. Show all steps in the synthesis of Gly-Met-Ser using the benzyloxycarbonyl group as a protecting group.

10. The synthesis of polypeptide containing lysine requires the protection of both amino groups. Show how you might do this in synthesis of Lys-Ile using the benzyloxycarbonyl group as a protecting group.

11. Bradykinin is a nonapeptide released by blood plasma globulins in response to a wasp sting. It is a very potent pain-causing agent. Its molecular formula is Arg_2 , Gly, Phe_2 , Pro_3 , Ser. The use of 2,4-dinitrofluorobenzene and carboxypeptidase show that both terminal residues are arginine. Partial acid hydrolysis of bradykinin gives the following di- and tripeptides:

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

What is the amino acid sequence of bradykinin?

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

Ala_2 , Glu, Leu, Lys, Phe, Val

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

a. Treatment of A with 2,4-dinitrofluorobenzene followed by hydrolysis gave DNP-labeled leucine and lysine labeled only at the ϵ -amino group.

b. Complete hydrolysis of B gave phenylalanine, glutamic acid, and alanine. When B was allowed to react with carboxypeptidase, the solution showed an initial high concentration of glutamic acid. Treatment of B with 2,4-dinitrofluorobenzene followed by hydrolysis gave labeled phenylalanine.

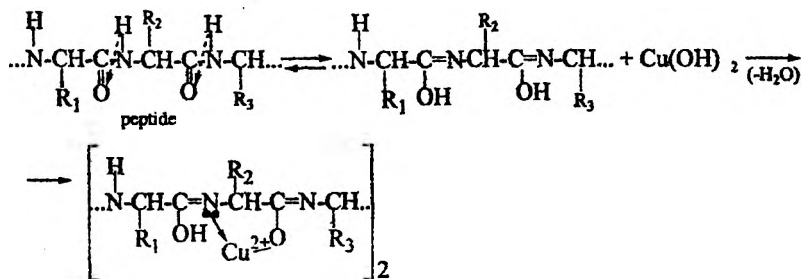
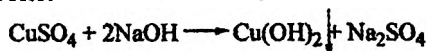
3. Laboratory work.

Experiment 1. Biuret test on peptide linkage.

Sequence of operations: Place 5-6 drops of white egg solution (the white protein) in the test-tube. Add 5-6 drops of 2 M NaOH solution and add 1-2 drops of copper (II)-sulphate (CuSO_4) solution alongside the test-tube.

Check the result: red-violet colour.

Write:



Explain the result and write conclusion.

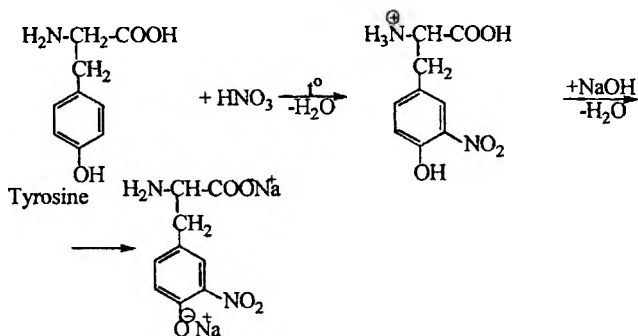
Experiment 2. Xanthoproteinic test.

Sequence of operations: Place 5 drops of white egg (the white protein) solution in a test-tube. Add 2 drops of concentrated nitric acid. Warm the test-

tube carefully, shaking it all the time. Solution and precipitate take in yellow colour. Cool the test-tube. Carefully add 1-3 drops of 2 M NaOH solution.

Check the result: brightly – orange colour.

Write:



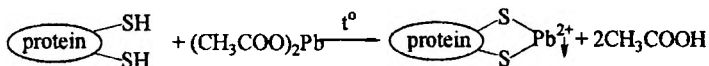
Explain the result and write conclusion.

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

Sequence of operations: Place 5 drops of white egg (the white protein) solution in test-tube. Add 10 drops of 2 M NaOH solution. Mix contents of the test-tube, warm it until boiling (1-2 minutes). Add 5 drops of 10% lead-(II)-acetate ($\text{Pb}(\text{CH}_3\text{COO})_2$) solution and boil it once again.

Check the result: grey-black precipitate.

Write:



Explain the result and write conclusion.

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

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

Check the result: precipitate of protein.

Explain the result and write conclusion.

Experiment 5. Dehydrating agents concret protein.

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

Check the result: precipitate of protein.

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

THEME 15

Purine and pyrimidine bases.

Nucleosides. Nucleotides. Nucleic acids.

Control-Test № 2.

1. Program questions:

1. Composition of nucleic acids. Heterocyclic bases. The structure of DNA and RNA nucleosides and nucleotides.
2. Coenzyme NAD^+ , ATP.
3. Medical applications (6-mercaptopurine, allopurinol, acyclovir).
4. DNA: primary and secondary structure. Complementary base pairing. Replication of DNA.
5. RNA: the structure. RNA and protein synthesis. Messenger RNA (mRNA), ribosomal RNA (rRNA) and transfer RNA (tRNA). Messenger RNA synthesis – transcription. The genetic code.

6. Remind yourself the program material from the theme № 11 to № 14.

Literature:

- [1] L.G. Hidranovich. Bioorganic chemistry lecture course. Vitebsk, 2004. p. 237 - 256
- [2] T.W. Graham Solomons. Fundamentals of organic chemistry. John Willey and sons, 1994. p. 1017 - 1039
- [3] George H. Schmid. Organic chemistry. Mosby, 1996. p. 1188 - 1205
- [4] Richard F. Daley, Sally J. Dalley. Organic chemistry Wm. C. Brown Publishers, 1996. p. 1283 – 1287, 1294 – 1298, 1302 – 1309

2. Problems.

1. Write the structure of the two tautomeric forms of guanine, cytosine, uracil, and thymine.

2. Write structural formulas showing the hydrogen bonds in complementary base pairs of DNA and RNA.
3. The most stable tautomeric form of guanine is the lactam form. This form is normally present in DNA and it pairs specifically with cytosine. Guanine can tautomerize to the abnormal lactim form and make the pair with thymine. Write structural formulas showing the hydrogen bonds in these base pairs.
4. Nitrous acid (HNO_2) is a potent chemical mutagen. Propose the reaction of adenine's amino group with HNO_2 and show the tautomerization of the product.
5. Write the structure and give the name of the nucleoside formed by combining each of the following pairs of heterocyclic bases and pentoses.

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

b. 5'-end T-G-C 3'-end

12. The portion of one chain of DNA molecule has the following nucleotides sequence:

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

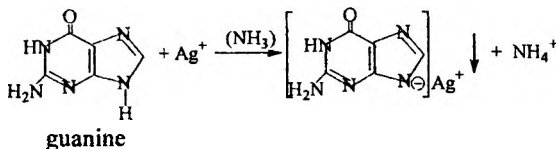
3. Laboratory work.

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

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

Check the result: bright-brown precipitate.

Write:



Explain the result and write conclusion.

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

a) Quantitative reaction for aldopentoses (Molish test).

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

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

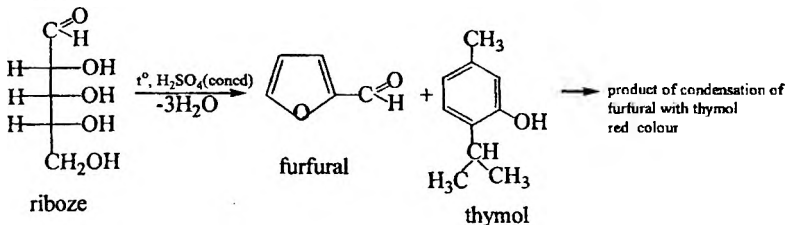
b) Discovering of ribose and deoxyribose.

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

Check the result: blue-green colour.

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

Write:



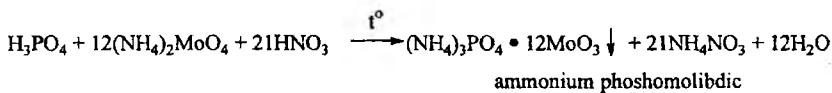
Explain the result and write conclusion.

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

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

Check the result: lemon-yellow precipitate.

Write:



Explain the result and write conclusion.

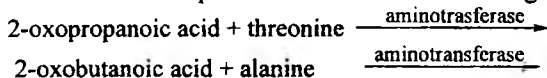
QUESTIONS FOR THE CONTROL-TEST №2

1. Draw the structures of tautomeric forms of D-mannose and D-ribose and name them. Write the schemes of the reactions of α -D-galactopyranose with $(\text{CH}_3\text{CO})_2\text{O}$ (excess) / NaOH, β -D-mannopyranose with CH_3OH / HCl, α -D-ribofuranose with CH_3COCl (excess) / NaOH, β -D-glucopyranose with CH_3I (excess) / KOH. Name the received compounds. Write the hydrolysis reactions of the products. Indicate mechanisms of these reactions. Write the schemes of oxidation reactions of D-glucose in aldonic and aldaric acids. Name the products. Write the scheme of oxidation reaction of D-ribose by Fehling's solution and scheme of reduction reaction for this monosaccharide.

2. Write the scheme of sucrose hydrolysis and methanolysis reaction of lactose. Write the scheme of the reaction of cellobiose with CH_3I and maltose with CH_3COCl . Indicate the mechanisms of these reactions. Give sys-

tematic names for sucrose, lactose, maltose, cellobiose. Explain why sucrose is a nonreducing sugar and lactose, maltose and cellobiose are reducing sugars. Draw the structure of starch, cellulose, hyaluronic acid, chondroitin-4-sulfate. Indicate the types of glycosidic linkages between structural units of these polysaccharides. Explain their biological role.

3. Write the structure of products formed in the following reactions:



Name the products of this reactions.

Write the schemes of the reactions of Cys with $\text{C}_2\text{H}_5\text{OH} / \text{HCl}$ and Asn with CH_3I . Indicate the mechanisms of these reactions. Write the scheme of the decarboxylation reaction of Trp and deamination reaction of Asp. Name the products. Write the scheme of the reaction of Met with NaOH and amino acid Trp with HCl .

Write the structure and name the predominant ionic form of glutamic acid (Glu) at the pH of blood 7,4. Write the structures and name the predominant ionic forms of amino acids Met, Leu and Phe at the pH of stomach 1,0; amino acids Lys and Cys at the pH of saliva 7,0; amino acids His and Arg at the pH of intestines 6,5.

4. Show the protection of amino group of Leu using benzyl chloroformate. Show the activation of carboxyl group of Ser by converting it to an acyl chloride. Show the protection of amino group of Thr using di-tert.-butylcarbonate. Write the reaction of Edman degradation of Glu-Arg. Write the structure of tripeptide His-Lys-Trp. Show the C- and N-terminal residues. Show the structure of the predominant ionic form of tripeptide at the pH of blood 7,4. Write the reaction showing how 2,4-dinitrofluorobenzene could be used to identify the N-terminal amino acid of Ala-Val. Write the reactions of Edman degradation of dipeptide Thr-Leu. Write the structure of tripeptide Asp-Leu-Gly. Show the C- and N-terminal residues. Show the structure of the predominant ionic form of tripeptide at the pH of intestines 7,0.

5. Write the schemes of base-catalyzed hydrolysis of adenosine 5'-monophosphate, guanosine 5'-monophosphate and acid-catalyzed hydrolysis of cytidine 5'-monophosphate and thymidine 5'-monophosphate. Indicate the mechanisms of these reactions.

Write the structures of mRNA portions with following nucleotides sequences:



5'end G-A-U 3'end.

Write the structures of one chain of DNA molecule portions with following nucleotides sequences:

5'end A-T-C 3'end.

5'end G-A-T 3'end.

THEME 16

Saponified lipids.

Peroxide oxidation of lipids.

1. Program questions:

1. Classification of lipids.
2. Fatty acids. The structure. Reactions of the carboxyl group, reactions of the alkyl chain of saturated and unsaturated fatty acids.
3. Triacylglycerols: biological functions, hydrogenation, acidic and basic hydrolysis (saponification). Soaps.
4. Phospholipids and cell membranes. Phosphatides (lecithins, cephalins, phosphatidyl serines, phosphatidyl derivatives – plasmalogens).
5. Sphingosine. Derivatives of sphingosine (sphingolipids): sphingomyelin and cerebroside.

Literature:

- [1] L.G. Hidranovich. Bioorganic chemistry lecture course. Vitebsk, 2004. p. 256 - 268
- [2] T.W. Graham Solomons. Fundamentals of organic chemistry. John Willey and sons, 1994. p. 938-947, 963-967
- [3] George H. Schmid. Organic chemistry. Mosby, 1996. p. 675-683
- [4] Richard F. Daley, Sally J. Dalley. Organic chemistry Wm. C. Brown Publishers, 1996. p. 192-195, 382-383

2. Problems.

1. How would you convert stearic acid into each of the following?
 - (a) Ethyl stearate
 - (b) Sodium stearate
 - (c) Stearyl chloride
 - (d) Stearamide
 - (e) N,N-Dimethylstearamide
2. Using oleic acid as an example illustrate the following reactions of the double bond.
 - (a) Addition of bromine

- (b) Addition of hydrogen
- (c) Hydroxylation
- (f) Addition of HCl

3. When oleic acid is heated to 180-200°C (in the presence of a small amount of selenium), an equilibrium is established between oleic acid (33%) and an isomeric compound called elaidic acid (67%). Suggest a possible structure for elaidic acid.

4. The formation of glycerides raises the question of stereochemistry. Glycerol is achiral. Its molecule has a plane of symmetry but many glyceride lipids are chiral due to the loss of molecular symmetry on acylation. Draw the general structures of all possible monoacylglycerols, diacylglycerols and triacylglycerols formed from glycerol and an achiral fatty acid, and specify whether each will be chiral or achiral.

5. Write the structure and name triacylglycerols formed by combining of the following fatty acids with glycerol:

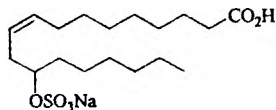
- (a) Palmitic acid, oleic acid, stearic acid
- (b) Linoleic acid, stearic acid, linolenic acid
- (c) Oleic acid, linoleic acid, stearic acid.

6. Both triacylglycerols and phospholipids have fatty acid ester components, but only one group can be considered amphipathic. Indicate which is amphipathic and explain why. Using 1-0-stearoyl-2-0-oleoyl-3-0-palmitoyl-glycerol and lecithin illustrate your answer.

7. Write the structure of phosphatidyl serine and show its hydrophilic and hydrophobic portions.

8. Under suitable conditions all of the ester linkages of phosphatide can be hydrolyzed. What organic compounds would you expect to obtain from the complete hydrolysis of (a) lecithin, (b) cephalin, (c) choline – containing plasmalogen.

9. Castor oil reacts with sulfuric acid to give a sulfated castor oil known as “Turkey-red oil” due to its use as a surfactant or wetting agent in “Turkey-red” dyeing using madder root (the active dye is alizarin). Turkey-red oil soaps, obtained by hydrolysis of the oil, are not particularly good detergents (i.e. they form micelles not so well). The structure of a typical Turkey-red oil soap is given below. Suggest why these amphipathic compound might not form micelles very well.



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

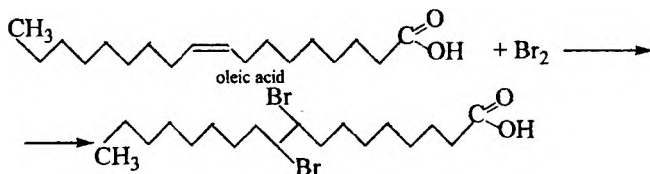
3. Laboratory work.

Experiment 1. Oleic acid reacts with bromine water.

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

Check the result: bleaching of solution.

Write:



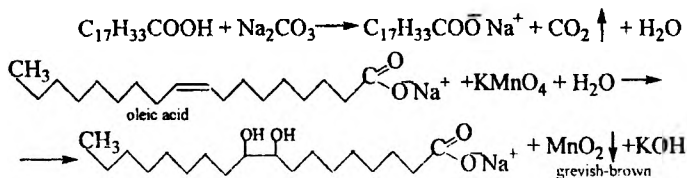
Explain the result and write conclusion.

Experiment 2. Oleic acid reacts with KMnO_4 solution.

Sequence of operations: Place 2 drops of oleic acid in a test-tube. Add 2 drops of 5% Na_2CO_3 solution and 2 drops KMnO_4 solution. Shake the test-tube.

Check the result: bleaching of solution.

Write:



Explain the result and write conclusion.

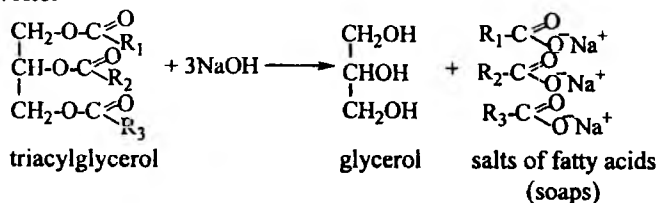
Experiment 3. Saponification of fats.

Sequence of operations: Place 0,5 ml of castor oil in a test-tube. Add 0,5 ml of alcohol and 0,5 ml of 35% NaOH solution. Mix and warm contents of the test-tube on water bath during 5-7 minutes. Place some drops of solution in a new test-tube, add 2-3 ml of distilled water and warm it. Complete dissolv-

ing of the substens in water shows its complete saponification. Add 3-4 ml of saturated hot NaCl solution. (Salting-out soap).

Check the result: layer of soap lift up.

Write:

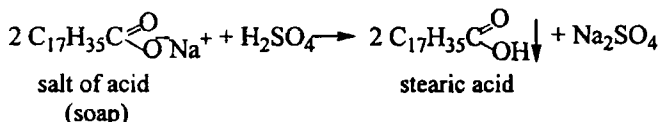


Explain the result and write conclusion.

Experiment 4. Extraction of free fat acids from soap.

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

Check the result: white flaky oily precipitate.



Explain the result and write conclusion.

THEME 17

Non-saponified lipids. Terpenes, steroids.

1. Program questions:

1. Classification of terpenes and terpenoids.
2. Isoprene, isoprene units.
3. Acyclic monoterpenes, monoterpenoids and sesquiterpens (myrcene, geraniol).
4. Cyclic terpenes and terpenoids (limonene, α -pinene, menthol, camphor).
5. Triterpenes. Squalene. α -, β -, γ -Carotenes. Vitamin A.
6. Natural rubber.
7. Steroids. Structure and systematic nomenclature of steroids. A, B; B, C and C, D ring junction. Basic ring system. 5α and 5β series of steroids.
8. Sex hormones: estrogens and androgens.

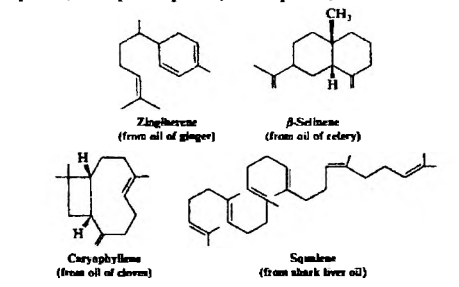
9. Progesterone.
10. Adrenocortical hormones: cortisone and cortisol.
11. Sterols: cholesterol, ergosterol. D-vitamins.
12. Cholic acid.

Literature:

- [1] L.G. Hidranovich. Bioorganic chemistry lecture course. Vitebsk, 2004. p. 269 - 281
- [2] T.W. Graham Solomons. Fundamentals of organic chemistry. John Wiley and sons, 1994. p. 947-961
- [3] George H. Schmid. Organic chemistry. Mosby, 1996. p. 579, 869-875
- [4] Richard F. Daley, Sally J. Dalley. Organic chemistry Wm. C. Brown Publishers, 1996. p. 1045

2. Problems.

1. (a) Show the isoprene units in each of the following terpenes. (b) Classify each as a monoterpene, sesquiterpene, diterpene, and so on.



2. Give structural formulas for the products that you would expect from the following reactions?

- a) β -pinene + hot $\text{KMnO}_4 \rightarrow$
- b) Zingiberene + $\text{H}_2 \xrightarrow{\text{Pt}}$
- c) Caryophyllene + $\text{HCl} \rightarrow$

3. What simple chemical test could you use to distinguish between geraniol and mentol?

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

5. Designate with the star the eight stereocenters of cholesterol.

6. The adrenocortical steroids are apparently involved in the regulation of a large number of biological activities including carbohydrate, protein, and lipid metabolism, water and electrolyte balance, and reactions to allergic and inflammatory phenomena. Cortisone and cortisol, two adrenocortical steroids, have the systematic name 17α , 21-dihydroxy-4-pregnene-3,11,20-dione and 17β , 21α , 21-trihydroxy-4-pregnene-3,20-dione. Draw a three-dimensional formula for cortisone and cortisol.

7. Androsterone, a secondary male sex hormone, has the systematic name 3α -hydroxy- 5α -androstan-17-one. Give a three-dimensional formula for androsterone.

8. Norethynodrel, a synthetic steroid that has been widely used in oral contraceptives, has the systematic name 17α -ethynyl- 17β -hydroxy-5(10)-estren-3-one. Give a three dimensional formula for norethynodrel.

9. Show how you might convert cholesterol into each of the following compounds:

- (a) $5\alpha, 6\beta$ -Dibromocholestan- 3β -ol
- (b) Cholestane - $3\beta, 5\alpha, 6\beta$ -triol
- (d) 5α -Cholestan-3-one

10. The estrogens (estrone and estradiol) are easily separated from the androgens (androsterone and testosterone) on the basis of one of their chemical properties. What is the property and how could such separation be accomplished?

11. Write the photochemical reaction of conversion of ergosterol to vitamin D.

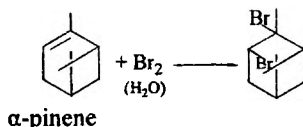
3. Laboratory work.

Experiment 1. Evidence of double bond presence in terpenes.

Sequence of operations: Place 2 drops of bromine water in a test-tube. Add 1 drop of turpentine.

Check the result: bleaching of solution.

Write:



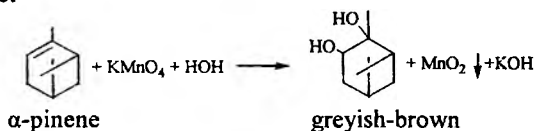
Explain the result and write conclusion.

Experiment 2. Easy oxydizability of terpens.

Sequense of operations: Place 1 drop of 0,1 M KMnO_4 solution in a test-tube. Add 5 drops of water and 1 drop of turpentine. Shake the test-tube.

Check the result: bleaching of solution and brown precipitate.

Write:



Explain the result and write conclusion.

THEME 18

Credit-Test.

1. Program questions:

1. Remind yourself the program material from the theme № 11 to № 17.

Literature:

- [1] L.G. Hidranovich. Bioorganic chemistry lecture course. Vitebsk, 2004. p. 170 - 281
- [2] T.W. Graham Solomons. Fundamentals of organic chemistry. John Willey and sons, 1994. p.
- [3] George H. Schmid. Organic chemistry. Mosby, 1996. p.
- [4] Richard F. Daley, Sally J. Dalley. Organic chemistry Wm. C. Brown Publishers, 1996. p.

EXAMINATION QUESTIONS.

1. CLASSIFICATION OF ORGANIC COMPOUNDS. FUNCTIONAL GROUPS, ALKYL GROUPS.
IUPAC NOMENCLATURE PRINCIPLES.
2. CHEMICAL BONDING IN ORGANIC COMPOUNDS. HYBRIDIZATION OF CARBON ATOM. COVALENT BOND FORMATION. COVALENT CARBON-CARBON BONDS (SINGLE, DOUBLE BONDS AND TRIPLE BONDS). σ AND π -BONDS.
3. STEREOISOMERISM. CONFORMATIONS OF THE MOLECULE, NEWMAN PROJECTION FORMULAS, STAGGERED AND ECLIPSED CONFORMATIONS OF ETHANE AND BUTANE. THEIR THE LEAST STABLE AND THE MOST STABLE CONFORMATIONS. TORSIONAL BARRIER.
4. CONFORMATIONS OF CYCLOHEXANE. CHAIR CONFORMATION. AXIAL AND EQUATORIAL BONDS.
5. STEREOISOMERS: ENANTIOMERS AND DIASTEREOMERS. THE CHIRAL MOLECULE, THE STEREOCENTER. CIS- AND TRANSISOMERS.
6. MOLECULES WITH ONE STEREOCENTER. FISCHER PROJECTION FORMULAS OF STEREOISOMERS. NOMENCLATURE OF ENANTIOMERS: THE (R-S) SYSTEM AND THE (D-L) SYSTEM.
7. MOLECULES WITH MORE THAN ONE STEREOCENTER (ISOLEUCINE). ENANTIOMERS AND DIASTEREOMERS. STEREOISOMERS OF TARTARIC ACID. MESO COMPOUNDS.
8. THE BROHNSTED-LOWRY AND THE LEWIS DEFINITIONS OF ACIDS AND BASES. THE STRENGTH OF ACIDS AND BASES; THE ACIDITY CONSTANT, K_a . ACIDITY AND pK_a .
THE USE OF CURVED ARROWS IN ILLUSTRATING REACTIONS.
9. PREDICTING THE STRENGTH OF ACIDS AND BASES.
THE RELATIONSHIP BETWEEN STRUCTURE AND ACIDITY. THE EFFECT OF HYBRIDIZATION. INFLUENCE OF INDUCTIVE EFFECTS.
10. ELECTRONIC STRUCTURE OF CHEMICAL BONDS. INDUCTIVE AND RESONANCE EFFECTS.
11. HOMOLYSIS AND HETEROLYSIS OF COVALENT BONDS. REACTIVE INTERMEDIATES IN ORGANIC CHEMISTRY. IONIC REACTIONS AND RADICAL REACTIONS. (EXAMPLES).
12. ORGANIC REACTION TERMINOLOGY. CLASSIFICATION OF REAGENTS IN ORGANIC REACTIONS. SUBSTITUTION, ADDITION AND ELIMINATION REACTIONS (EXAMPLES).
13. CLASSIFICATION OF THE HYDROCARBONS. REACTIONS OF ALKANES AND CYCLOALKANES (COMMON CYCLES). S_R REACTIONS.
14. REACTIONS OF ALKENES AND ALKADIENES. A_E REACTIONS ADDITION OF HYDROGEN HALIDES TO ALKENES. MARKOVNIKOV'S RULE. ADDITION OF WATER TO ALKENES: ACID-CATALYZED HYDRATION. ADDITION REACTIONS OF CONJUGATED ALKADIENES.
15. REACTIONS OF AROMATIC HYDROCARBONS. S_E REACTIONS. ORIENTATION RULE IN BENZENE RING.

16. REACTIONS OF ALCOHOLS. FACTORS AFFECTING THE RATES OF S_N1 AND S_N2 REACTIONS. CONVERSION OF ALCOHOLS INTO ALKYL HALIDES.
17. REACTIONS OF ALCOHOLS. ALCOHOLS AS ACIDS. ALKYL PHOSPHATES. OXIDATION OF ALCOHOLS.
18. ALCOHOL DEHYDRATION. SYNTHESIS OF ETHERS: S_N2 REACTIONS. REACTIONS OF ETHERS. NUCLEOPHILICITY OF ALCOHOLS.
19. MECHANISM OF ALCOHOL DEHYDRATION: E_1 REACTION. SYNTHESIS OF ALKENES.
20. PHENOLS. ACIDITY OF PHENOLS. FORMATION OF QUINONES BY OXIDATION OF PHENOLS. HYDROQUINONE – QUINONE OXIDATION-REDUCTION EQUILIBRIA. THIOLS.
21. AMINES. NAMING, BASICITY AND REACTIONS OF AMINES.
22. ALDEHYDES AND KETONES: NOMENCLATURE AND REACTION CENTRES. BASICITY OF ALDEHYDES AND KETONES.
23. NUCLEOPHILIC ADDITION TO THE CARBON-OXYGEN DOUBLE BOND OF ALDEHYDES AND KETONES. THE ADDITION OF WATER AND ALCOHOLS: HYDRATES ACETALS AND HEMIACETALS, KETALS AND HEMIKETALS. CYCLIC KETALS. THIOACETALS AND THIOKETALS.
24. ALDEHYDES AND KETONES: THE ADDITION OF DERIVATIVES OF AMMONIA. IMINES, 2,4-DINITROPHENYLHYDRAZONES, SEMICARBAZONES, OXIMES.
25. KETO AND ENOL TAUTOMERS. OF ALDEHYDES AND KETONES OXIDATION OF ALDEHYDES AND KETONES. THE IODOFORM TEST.
26. CARBOXYLIC ACIDS: NOMENCLATURE AND REACTIONS CENTRES. ACIDITY OF CARBOXYLIC ACIDS. CARBOXYLIC SALTS. DICARBOXYLIC ACIDS.
27. DERIVATIVES OF CARBOXYLIC ACIDS: ESTERS, CARBOXYLIC ANHYDRIDES, ACYL CHLORIDES, AMIDES, NITRILES. HYDROLYSIS OF AMIDES.
28. ACYL TRANSFER REACTIONS OF ANHYDRIDES, THIOESTERS AND ESTERS.
29. ACYL TRANSFER REACTIONS IN LIVING SYSTEMS.
30. CARBOXYLIC ACIDS. NUCLEOPHILIC SUBSTITUTIONS AT THE ACYL CARBON. RELATIVE REACTIVITY OF ACYL COMPOUNDS.
31. ESTERS. SYNTHESIS OF ESTERS: ESTERIFICATION. ACID-CATALYZED AND BASE-PROMOTED HYDROLYSIS OF ESTERS. REACTIONS AND MECHANISMS.
32. DICARBOXYLIC ACIDS. DECARBOXYLATION OF CARBOXYLIC ACIDS.
33. POLYFUNCTIONAL COMPOUNDS' REACTIVITY FEATURES (ACCUMULATION OF HYDROXY AND BASIC GROUPS).
34. CLASSIFICATION OF HETEROFUNCTIONAL COMPOUNDS: AMINO-ALCOHOLS AND AMINO-PHENOLS.
35. HETEROFUNCTIONAL COMPOUNDS: HYDROXY AND AMINOACIDS.
36. HETEROFUNCTIONAL COMPOUNDS: OXO ACIDS. KETO-ENOL TAUTOMERISM OF ACETOACETIC ESTER.
37. HETEROFUNCTIONAL BENZENE DERIVATIVES AS PHARMACEUTICAL SUBSTANCES. PARA-AMINO BENZOIC, SULFANILIC AND SALICYLIC ACIDS AND THEIR DERIVATES.

38. CLASSIFICATION OF CARBOHYDRATES. MONOSACCHARIDES. ALDOSES. KETOSES. FISCHER PROJECTION FORMULAS. STEREOISOMERISM OF MONOSACCHARIDES. D AND L DESIGNATIONS OF MONOSACCHARIDES.
39. STEREOISOMERISM OF MONOSACCHARIDES. D AND L DESIGNATIONS OF MONOSACCHARIDES. STRUCTURAL FORMULAS NATURALLY OCCURRING MONOSACCHARIDES.
40. THE CYCLIC FORMS OF MONOSACCHARIDES. THE HAWORTH FORMULAS FOR THE CYCLIC HEMIACETAL FORMS. PYRANOSE AND FURANOSE FORMS. EXAMPLES.
41. REACTIONS OF MONOSACCHARIDES. GLYCOSIDE FORMATION AND HYDROLYSIS.
42. REACTIONS OF MONOSACCHARIDES. FORMATION OF ETHERS AND ESTERS. ACYLATION REACTIONS.
43. REACTIONS OF MONOSACCHARIDES. KETO—ENOL TAUTOMERIZATIONS. OXIDATION REACTIONS OF MONOSACCHARIDES. BENEDICT'S OR TOLLENS' REAGENTS: REDUCING SUGARS.
44. OXIDATION REACTIONS OF MONOSACCHARIDES. BROMINE WATER: THE SYNTHESIS OF ALDONIC ACIDS. NITRIC ACID OXIDATION: ALDARIC ACIDS REDUCTION OF MONOSACCHARIDES: ALDITOLS.
45. MONOSACCHARIDE DERIVATIVES: URONIC ACIDS, DEOXY SUGARS, GLYCOSYLAMINE, AMINO SUGARS.
46. THE NONREDUCING DISACCHARIDE. THE STRUCTURE OF SUCROSE. CONFIGURATION OF THE GLYCOSIDE LINKAGE. HYDROLYSIS AND METHYLATION OF SUCROSE.
47. THE REDUCING DISACCHARIDE. THE STRUCTURE OF MALTOSE. CONFIGURATION OF THE GLYCOSIDE LINKAGE. THE MALTOSE ANOMERS. GLYCOSIDE FORMATION. HYDROLYSIS AND METHYLATION OF MALTOSE.
48. THE REDUCING DISACCHARIDE. THE STRUCTURE OF CELLOBIOSE. CONFIGURATION OF THE GLYCOSIDE LINKAGE. THE CELLOBIOSE ANOMERS. GLYCOSIDE FORMATION. HYDROLYSIS AND METHYLATION OF CELLOBIOSE.
49. THE REDUCING DISACCHARIDE. THE STRUCTURE OF LACTOSE. CONFIGURATION OF THE GLYCOSIDE LINKAGE. THE LACTOSE ANOMERS. GLYCOSIDE FORMATION. HYDROLYSIS AND METHYLATION OF LACTOSE.
50. HOMOPOLYSACCHARIDES. STARCH. AMYLOSE AND AMYLOPECTIN. GLYCOGEN. CONFIGURATION OF THE GLYCOSIDE LINKAGE. BIOLOGICAL ROLE OF STARCH AND GLYCOGEN.
51. HOMOPOLYSACCHARIDES. CELLULOSE. CONFIGURATION OF THE GLYCOSIDE LINKAGE. BIOLOGICAL ROLE OF CELLULOSE.
52. HETEROPOLYSACCHARIDES. HEPARIN. HYALURONIC ACID. CHONDROITIN SULFATES AND THEIR BIOLOGICAL ROLE. ALTERNATING UNITS OF HEPARIN, HYALURONIC ACID. CHONDROITIN SULFATE

53. AMINO ACIDS. STRUCTURE AND NAMING. NON POLAR, POLAR, NEGATIVE AND POSITIVE CHARGED AMINO ACIDS. ESSENTIAL AMINO ACIDS.
54. AMINO ACIDS AS DIPOLAR IONS. ISOELECTRIC POINT (pI) OF AN AMINO ACID.
55. REACTIONS OF CARBOXYL AND AMINO GROUP OF AMINO ACIDS. DEAMINATION AND TRANSAMINATION REACTIONS. AMINOTRANSFERASES AND PYRIDOXAL PHOSPHATE. STAGES OF AMINOTRANSFERASE-CATALYZED TRANSAMINATION REACTIONS OF AMINO ACIDS.
56. STRUCTURE OF PEPTIDES AND PROTEINS. PEPTIDE BOND. ANALYSIS OF AMINO ACID MIXTURES. CATION-EXCHANGE RESINS. REACTION WITH NINHYDRIN.
57. AMINO ACID SEQUENCE AND COVALENT STRUCTURE (OR PRIMARY STRUCTURE) OF THE POLYPEPTIDE. PARTIAL HYDROLYSIS. METHODS FOR DETERMINING THE N-TERMINAL AMINO ACID RESIDUE OF PEPTIDES AND PROTEINS: SANGER METHOD AND EDMAN DEGRADATION.
58. POLYPEPTIDE AND PROTEIN SYNTHESIS. PROTECTING GROUPS. ACTIVATION OF THE CARBOXYL GROUP.
59. SECONDARY STRUCTURES OF PROTEINS: β -PLEATED SHEET AND AN α -HELIX. TERTIARY STRUCTURES OF PROTEINS.
60. THE NUCLEIC ACIDS, DEOXYRIBONUCLEIC ACID (DNA) AND RIBONUCLEIC ACID (RNA).
61. NUCLEOSIDES AND NUCLEOTIDES THAT CAN BE OBTAINED FROM DNA.
62. NUCLEOSIDES AND NUCLEOTIDES THAT CAN BE OBTAINED FROM RNA. 3',5'-CYCLIC ADENYLIC ACID
63. DEOXYRIBONUCLEIC ACID: DNA. PRIMARY AND SECONDARY STRUCTURES.
64. THE NUCLEIC ACIDS AND PROTEIN SYNTHESIS. MESSENGER RNA. THE GENETIC CODE. RIBOSOMES RNA. TRANSFER RNA.
65. LIPIDS. FATTY ACIDS AND TRIACYLGLYCEROLS. BIOLOGICAL FUNCTIONS OF TRIACYLGLYCEROLS.
66. HYDROGENATION AND SAPONIFICATION OF TRIACYLGLYCEROLS. SYNTHETIC DETERGENTS.
67. REACTIONS OF THE CARBOXYL GROUP OF FATTY ACIDS.
68. REACTIONS OF THE ALKYL CHAIN OF SATURATED FATTY ACIDS AND ALKENYL CHAIN OF UNSATURATED FATTY ACIDS.
69. PHOSPHOLIPIDS AND CELL MEMBRANES. PHOSPHATIDES. DERIVATIVES OF SPHINGOSINE.
70. TERPENES AND TERPENOIDS.
71. STEROIDS. STRUCTURE AND SYSTEMATIC NOMENCLATURE OF STEROIDS. NAMES OF STEROID HYDROCARBONS.
72. STEROIDS. CHOLESTEROL. ERGOSTEROL. D VITAMINS.
73. STEROIDS. SEX HORMONES. ADRENOCORTICAL HORMONES.
74. STEROIDS. BILE ACIDS. CHOLIC ACID. CONJUGATED BILE ACIDS.

TESTS.

Classification and nomenclature of organic compounds. Electronic structure of organic compounds.

1. According to the classification for functional groups 4-hydroxy-3-ethoxybenzaldehyde is:

- + 1. phenol;
- + 2. ether;
- 3. ester;
- + 4. aldehyde;
- 5. alcohol.

2. Covalent sigma bond:

- 1. is formed by side-by-side overlap of p-orbitals;
- 2. has less energy;
- + 3. is formed by end-on overlap of two sp^3 hybrid orbitals;
- + 4. is not destroyed in the result of the rotation of the molecule part around the bond axis;
- 5. can be easily polarized.

3. There are only sp^3 hybrid oxygen atoms in the following compounds:

- + 1. ethoxyethane;
- 2. methoxybenzene;
- + 3. methanol;
- 4. 4-hydroxybenzyl alcohol;
- 5. oxaloacetic acid.

4. There are only pyridinic heteroatoms in the following compounds:

- 1. 4-ethoxyaniline;
- + 2. ethanal;
- + 3. cyclohexanone;
- 4. 4-nitrophenol;
- 5. 3-aminopropanoic acid.

5. There are pyrrolic heteroatoms in functional groups of the following families of organic compounds:

- + 1. arylamines;
- 2. saturated aliphatic amines;

- + 3. amides;
 - 4. alcohols;
 - + 5. carboxylic acids.
6. There is pi-pi conjugation in the structure of the following compounds:
- + 1. benzene;
 - + 2. pentadiene-1,3;
 - 3. pentadiene-1,4;
 - 4. propanal;
 - 5. propanoic acid.

7. There is p-pi conjugation in the structure of the following compounds:
- + 1. ethanoic acid;
 - + 2. 2-hydroxypropanoic acid;
 - 3. glycerol;
 - 4. pyridine;
 - 5. propene-2-al.

8. Aromatic compounds are:

- 1. cyclohexane;
- 2. cyclooctatetraene;
- + 3. naphthalene;
- + 4. pyrrole;
- + 5. benzene.

9. The functional group has only negative inductive effect in the following compounds:

- 1. phenol;
- + 2. ethylene glycol;
- + 3. propanamine-2;
- 4. ethanedioic acid;
- 5. methyl phenyl ketone.

10. The following compounds have only electron attracting functional groups:

- + 1. 2-aminoethanol-1;
- 2. 2-hydroxybenzoic acid;
- 3. 4-aminobenzenesulfonic acid;
- 4. 4-hydroxy-3-methylbenzaldehyde;
- + 5. 2,3-dihydroxypropanal.

11. Which of the following compounds have all functional groups as electron donating:

- 1. 2-isopropyl-5-methylcyclohexanol;
- + 2. 2-isopropyl-5-methylphenol;
- 3. n-aminobenzaldehyde;
- 4. succinic acid (butanedioic-1,4 acid);
- + 5. 4-ethoxyaniline.

Stereochemistry of organic compounds.

12. The Newman projection formulas are used to show the peculiarity of:

- 1. chemical structure of the compound;
- + 2. the conformation of the molecule;
- 3. the constitutional isomers;
- 4. the configuration;
- 5. the structure of E and Z pi-diastereomers.

13. The molecule of 1,2-dimethylcyclohexane has the maximum energy in chair conformation when:

- 1. both methyl groups are placed on the equatorial bonds;
- + 2. both methyl groups are placed on the axial bonds;
- 3. one of the methyl groups is placed on the axial bond;
- 4. one of the methyl groups is placed on the equatorial bond;
- 5. one of the methyl groups is placed on the axial bond and other on the equatorial bond.

14. The chiral molecules are:

- 1. glycine (2-aminoethanoic acid);
- + 2. proline;
- + 3. D-ribose;
- 4. butanol-1;
- + 5. butanol-2.

15. The chiral molecules are:

- + 1. D-glucose;
- + 2. alanine;
- 3. 2-aminoethanol-1;
- + 4. menthol;
- 5. furool (2-furancarbaldehyde).

Acid-base properties of organic compounds.

16. The functional groups of the following families of organic compounds have the acidic reaction centre:

- 1. esters;
- 2. ketones;

- + 3. sulfonic acids;
- + 4. amines;
- 5. ethers.

17. The weakest acid is:

- + 1. ethanamine;
- 2. ethanol;
- 3. phenol;
- 4. ethanoic acid;
- 5. ethanethiol.

18. The strongest base is:

- 1. 2-aminoethanol;
- 2. ethanamine;
- 3. methylamine;
- + 4. dimethylamine;
- 5. pyridine.

83. Which of the following compounds have acidic properties and form salts in reaction with strong base:

- + 1. pyrrole;
- 2. thiophene;
- 3. pyridine;
- + 4. barbituric acid (2,4,6-trihydroxypyrimidine);
- 5. oxazole (1-aza-3-oxocyclopenta-2,4-diene);

Classification and the mechanisms of the reactions in organic chemistry.

Hydrocarbons. S_R, S_E, A_E reactions.

19. According to the product the organic reactions types are:

- + 1. addition;
- + 2. substitution;
- 3. monomolecular;
- + 4. elimination;
- 5. synchronic.

20. Which of the following particles are formed by homolysis:

- 1. carbocation;
- 2. carbanion;
- + 3. free radical;
- 4. nucleophyl;
- 5. electrophyl.

21. Chemical reactions are divided into the following types (by kinds of reactive intermediates that form in reaction):

- + 1. radical;
- 2. unimolecular;
- + 3. ionic;
- 4. bimolecular;
- 5. elimination.

22. The general formula of alkanes is:

- + 1. C_nH_{2n+2} ;
- 2. C_nH_{2n} ;
- 3. C_nH_{2n-2} ;
- 4. C_nH_{2n-6} ;
- 5. C_nH_{2n-4} .

23. The alkanes react according to the following mechanisms:

- 1. $AN-E$;
- 2. A_R ;
- 3. S_E ;
- + 4. S_R ;
- 5. A_E .

24. The product of the reaction of 2-methylpentane and bromine is:

- 1. 1-bromo-4-methylpentane;
- 2. 2-bromo-4-methylpentane;
- 3. 3-bromo-4-methylpentane;
- + 4. 2-bromo-2-methylpentane;
- 5. 1-bromo-2-methylpentane.

25. The alkenes typical chemical bonds are:

- 1. ionic;
- + 2. covalent (single and double);
- 3. only sigma;
- + 4. sigma and pi;
- 5. only pi bonds.

26. Alkenes and alkadienes participate in the following reactions:

- + 1. addition;
- + 2. polymerization;
- + 3. oxidation;
- 4. elimination;
- 5. forming of the salts.

27. As the result of the hydration of α , β -unsaturated acids the following compounds are formed:

- 1. α -hydroxycarboxylic acids;
- + 2. β -hydroxycarboxylic acids;
- 3. γ -hydroxycarboxylic acids;
- 4. α , β -dihydroxycarboxylic acids;
- 5. α , γ -dihydroxycarboxylic acids.

28. The product of oxidation of 2-methyl-2-butene with KMnO_4 solution (without heating) is:

- 1. 2-methylbutanol-2;
- 2. acetone and ethanoic acid;
- 3. 2-methylbutane;
- 4. 2-methyl-2,3-epoxybutane;
- + 5. 2-methylbutanediol-2,3.

29. Qualitative test on unsaturated hydrocarbons can be realized with following compounds:

- 1. H_2SO_4 ;
- 2. $\text{O}_3/\text{H}_2\text{O}$;
- + 3. Br_2 , H_2O ;
- 4. HBr ;
- + 5. KMnO_4 , H_2O .

30. The aromatic ring is characterized by following:

- + 1. the cyclic structure;
- + 2. sp^2 hybridization type of all carbon atoms;
- + 3. plane structure;
- + 4. cyclic conjugate system;
- + 5. the number π -electrons according to the Hückel's rule.

31. Aromatic hydrocarbons are characterized by the following reactions:

- 1. S_N ;
- + 2. S_E ;
- 3. S_R ;
- 4. oxidation;
- 5. A_E .

32. The general sign of benzene homologues oxidation by $\text{KMnO}_4/\text{H}_2\text{SO}_4$ is:

- + 1. the brown precipitate forming;
- + 2. bleaching of the solution;

- 3. bubbles of the gas;
- 4. no changes;
- 5. change of pH meaning.

**Alcohols, phenols, thiols, amines.
S_N and E reactions.**

33. Ethanol is:

- 1. secondary alcohol;
- + 2. monohydric alcohol;
- 3. polyhydric alcohol;
- + 4. saturated alcohol;
- 5. unsaturated alcohol.

34. According to the IUPAC nomenclature the name of hydroquinone is:

- 1. phenylmethanol;
- 2. cyclohexanol;
- 3. 2-isopropyl-5-methylcyclohexanol-1;
- 4. 1,2-dihydroxybenzene;
- + 5. 1,4-dihydroxybenzene.

35. Which of the following can readily undergo dehydration:

- 1. CH₃OH;
- + 2. (CH₃)₃COH;
- 3. C₆H₅OH;
- 4. C₆H₅CH₂OH;
- 5. CH₃COOH.

36. Alcohols are:

- + 1. weaker acids than water;
- 2. stronger acids than water;
- 3. stronger acids than phenols;
- 4. stronger acids than carboxylic acids;
- 5. stronger acids than carbonic acid.

37. Which of the following compounds will react with sodium hydroxide:

- 1. CH₃CH₂OH;
- 2. C₆H₅CH₂OH;
- + 3. C₆H₅OH;
- 4. (CH₃)₂CHOH;
- 5. CH₃CH₂CH₂OH.

38. Secondary alcohols are:

- + 1. pentanol-3;
- + 2. isopropyl alcohol;
- 3. 2-methylbutanol-2;
- 4. benzyl alcohol;
- + 5. cyclohexanol.

39. Tertiary alcohols are:

- 1. 1,2,3-Trihydroxybenzen;
- + 2. 3-methylpentanol-3;
- + 3. 2-methylpropanol-2;
- 4. cyclohexanol;
- 5. butanol-2.

40. Propanol-1 has following reaction centres:

- + 1. OH-acidic;
- + 2. basic;
- + 3. CH-acidic;
- + 4. Electrophilic;
- + 5. nucleophilic.

41. Phenol has following reaction centres:

- + 1. OH-acidic;
- 2. SH-acidic;
- 3. electrophilic;
- + 4. nucleophilic;
- 5. CH-acidic.

42. Nucleophilic properties of heteroatoms are increasing in range:

- + 2. 2-methylphenol → 2-methylpropanol-1 → methylthiomethane;
- 2. 2-ethoxypropane → 2-isopropyl-5 methylphenol → thiophenol;
- 3. methylthiobenzene → methylthioethane → benzenediol-1,4;
- 4. Dioxane-1,4 → cyclohexanol → Ethoxybenzen;
- + 5. Propanol-2 → propanthiol → ethylthioethane.

43. Hydroxyl group in phenols is:

- 1. both o,p-directing and deactivating;
- + 2. both o,p-directing and activating;
- 3. both m-directing and activating;
- 4. both m-directing and deactivating;
- 5. only m-direting.

Carbonyl compounds. Aldehydes and ketones. A_N reactions.

44. The reaction centres of aldehydes are:

- + 1. electrophilic, basic, α -CH-acidic;
- 2. only nucleophilic and basic;
- 3. only nucleophilic, basic and acidic;
- 4. only electrophilic and nucleophilic;
- 5. only basic and α -CH-acidic.

45. Aromatic hydrocarbons that have oxo-group, with straight bonding to the aromatic ring have no following reaction centres:

- 1. electrophilic;
- 2. electrophilic and basic;
- 3. acidic basic, electrophilic, α -CH-acidic;
- + 4. α -CH-acidic;
- 5. basic.

46. Aldehydes and ketones are not characterized by the following reactions:

- 1. A_N ;
- 2. A_N -E;
- 3. reduction and oxidation;
- 4. reactions of α -CH-acidic centre.
- + 5. S_N .

47. The product of the addition reaction of water to the aldehyde is:

- 1. ketone;
- 2. ester;
- 3. vicinal alcohol;
- + 4. geminal hydric alcohol;
- 5. hemiacetal.

48. The mechanism of reactions of aldehydes and ketones with amines is:

- 1. A_N ;
- 2. S_N ;
- 3. E;
- + 4. A_N -E;
- 5. A_E .

49. Reactions of α -CH-acidic reaction centre are possible for the following compounds:

- 1. benzaldehyde
- + 2. ethanal
- + 3. acetone
- 4. 2,2-dimethylbutanal;

+ 5. 2-ethylpentanal.

50. The haloform reaction is possible for the following compounds:

- + 1. acetone;
- + 2. ethanal;
- 3. benzaldehyde;
- 4. formaldehyde;
- + 5. methyl phenyl ketone.

51. The following compounds form the primary alcohols as the result of the reduction reaction:

- 1. acetone;
- + 2. propanal;
- + 3. benzaldehyde;
- 4. methyl propyl ketone;
- 5. acetophenone.

52. Cupric hydroxide (II)- $\text{Cu}(\text{OH})_2$ in the basic solution (in heating) doesn't oxidate the following oxo-compounds:

- 1. formaldehyde;
- 2. propanal;
- + 3. acetone;
- + 4. 3-methylpentanon-2;
- 5. 2-methylbutanal.

53. As the result of disproportionation reaction of formaldehyde the following compounds are formed;

- 1. methanol and water;
- + 2. methanol and methanoic acid;
- 3. formic acid and water;
- 4. methanol and hydrogen;
- 5. methanol, methanoic acid, water and hydrogen.

Carboxylic acids and derivatives. S_N reactions.

54. According to the number of carboxyl groups carboxylic acids can be classified as:

- + 1. monocarboxylic;
- + 2. dicarboxylic;
- + 3. tricarboxylic;
- 4. aliphatic;
- 5. aromatic.

55. Monocarboxylic aliphatic carboxylic acids are:

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

56. The derivatives of carboxylic acids are:

- 1. ethanoic acid;
- + 2. ethanoyl chloride;
- 3. chloroethane;
- + 4. acetic anhydride;
- + 5. methyl benzoate.

57. Structure of carboxyl group is characterized by:

- + 1. sp^2 -hybridized carbon and both oxygen atoms;
- 2. sp^2 -hybridized carbon atom and one of both oxygen, and sp^3 -hybridized another oxygen;
- + 3. 3 atoms participate in the forming of conjugated system;
- 4. the absence of conjugated system;
- + 5. the plane configuration.

58. Acidity of carboxylic acids occurs in reaction centre:

- + 1. OH-acidic;
- 2. NH-acidic;
- 3. nucleophilic;
- 4. electrophilic;
- 5. basic.

59. In basic solution at room temperature is dissolved:

- 1. methyl benzoate;
- + 2. benzoic acid;
- 3. Aniline;
- + 4. phthalic acid;
- 5. methyl phenyl ether.

60. Derivates of carboxylic acids are formed as the result of the following reactions:

- 1. electrophilic addition (A_E);
- 2. nucleoplic addition (A_N);
- + 3. acyl transfer reaction;
- 4. electrophilic substitution (S_E);

+ 5. Nucleophilic substitution (S_N).

61. Thioester is formed as the result of acetic acid reaction with reagent:

- 1. alcohol/ H^+ , t;
- + 2. thiol/ H^+ , t;
- 3. NH_3 /t;
- 4. $SOCl_2$ /t;
- 5. PCl_5 .

62. Product of reaction of butanoic acid with ammonia in prolonged heating is:

- 1. ethylbutanoate;
- + 2. amide of butanoic acid;
- 3. butanoyl chloride;
- + 4. butanamide;
- 5. anhydride of butanoic acid.

63. Hydrolysis of carboxylic acid derivatives occurs in reaction centre:

- + 1. basic centre;
- 2. α -CH-acidic centre;
- 3. NH-acidic centre;
- + 4. electrophilic centre;
- 5. nucleophilic centre.

64. Which of the following compounds will be easily decarboxylated in heating:

- 1. acetic acid;
- + 2. oxalic acid (ethanedioic acid);
- + 3. malonic acid (propanedioic-1,3 acid);
- 4. propanoic acid;
- 5. butanoic acid.

Heterofunctional compounds.

65. Specific reactions of α -amino acids in heating are:

- + 1. decarboxylation;
- 2. formation of lactides;
- 3. formation of lactones;
- + 4. formation of diketopiperazines;
- 5. formation of lactams.

66. Diketopiperazines form in heating:

- + 1. 2-aminopropanoic acid;

- 2. beta-alanine;
- + 3. valine;
- 4. 4-aminobutanoic acid;
- 5. 3-aminopentanoic acid.

67. In heating beta-amino acids usually occurs:

- 1. decarboxylation;
- 2. formation of lactones;
- + 3. formation of conjugated unsaturated acid;
- 4. formation of diketopiperazines;
- 5. formation of lactams.

Carbohydrates. Monosaccharides.

68. D-fructose is:

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

69. Which of the following compounds are monosaccharides:

- 1. lactose;
- + 2. D-mannose;
- + 3. D-ribose;
- + 4. D-fructose;
- 5. starch.

70. Number of tautomeric forms of D-glucose (found in solution) is:

- 1. two;
- 2. three;
- 3. four;
- + 4. five;
- 5. possible only cyclic form of molecule.

71. Choose the carbon atom which determines the property of monosaccharide to stereochemical designation:

- 1. anomeric atom in beta-anomer molecule;
- 2. any stereocenter in monosaccharide molecule;
- + 3. highest number stereocenter;
- 4. second carbon atom in monosaccharide molecule;
- 5. no answer.

72. Deoxysugars are derivatives of monosaccharides, which have molecules with:

- 1. oxidated oxo-group;
- + 2. one or two hydroxyl-groups replaced by hydrogen atoms;
- 3. hydroxyl group (usually at the second carbon atom) replaced by amino-group;
- 4. oxidated primary hydroxyl-group;
- 5. reduced oxo-group.

73. Aminosugars are derivatives of monosaccharides which have molecules with:

- 1. oxidated oxo-group;
- 2. one or two hydroxyl-groups replaced by hydrogen atoms;
- + 3. hydroxyl group (usually at the second carbon atom) replaced by amino-group;
- 4. oxidated primary hydroxyl-group;
- 5. reduced oxo-group.

74. Trommer's test of D-glucose proceeds in the following conditions:

- 1. $[\text{Ag}(\text{NH}_3)_2]\text{OH}$, t;
- 2. $\text{Br}_2/\text{H}_2\text{O}$;
- + 3. $\text{Cu}(\text{OH})_2$, NaOH , t;
- 4. HNO_3 (dilut.);
- 5. $\text{C}_2\text{H}_5\text{OH}/\text{HCl}$.

75. Which of the following structural fragments take place in oxidation of D-glucose in D-glucuronic acid:

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

76. What information is for the structure of glycosides:

- + 1. has only cycle structure;
- 2. has open-chain and cyclic hemiacetal forms;
- 3. are oxidated by Tollen's reagent and in conditions of Trommer's test;
- + 4. are hydrolyzed at acidic solution;
- + 5. stable at basic solution.

Carbohydrates. Oligosaccharides and polysaccharides.

77. Maltose is:

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

78. Sucrose is:

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

79. Which of the following compounds are disaccharides:

- + 1. sucrose;
- 2. D-fructose;
- 3. D-glucose;
- + 4. cellobiose;
- 5. cellulose.

80. Which of the following compounds are homopolysaccharides:

- + 1. starch;
- + 2. glycogen;
- 3. lactose;
- 4. maltose;
- + 5. cellulose.

81. Which of the following compounds are reducing disaccharides:

- 1. D-glucose;
- + 2. lactose;
- 3. sucrose;
- 4. glycogen;
- + 5. maltose.

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

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

83. Which of the following information is for the properties of sucrose:

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

84. Which of the following information is for properties of maltose:

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

85. Which of the following information is for properties of glycogen:

- + 1. has structure like structure of amilopectine;
- 2. consists of alfa-D-glulactopyranose units;
- + 3. has very branching macromolecules;
- + 4. is a source of D-glucose in human organism;
- 5. is a reducing disaccharide.

86. Which of the following information is for properties of cellulose:

- + 1. consists of beta-D-glucopyranose units;
- 2. D-glucose units are chained in macromolecule beta (1,4)-glycosidic linkages;
- 3. has branching structure;
- 4. is not hydrolyzed;
- + 5. its ethers and esters, which have practical importance.

Amino acids.

87. Which of the following natural alfa-amino acid has the structure of 2S, 6-diaminohexanoic acid:

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

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

- 1. Asn;
- + 2. Met;
- + 3. Phe;

- + 4. Lys;
- 5. Ala.

89. Essential amino acids are:

- + 1. Val;
- + 2. Try;
- 3. Gly;
- 4. Cys;
- + 5. Thr.

90. Neutral alfa-amino acids are:

- + 1. Val;
- + 2. Gly;
- 3. Arg;
- + 4. Ser;
- 5. Asp.

91. Acidic alfa-amino acids are:

- 1. Thr;
- + 2. Asp;
- 3. Gln;
- 4. Cys;
- + 5. Glu.

92. Nonpolar natural alfa-amino acids are:

- + 1. Gly;
- + 2. Leu;
- + 3. Phe;
- 4. Tyr;
- + 5. Met.

93. Polar natural alfa-amino acids are:

- 1. Ala;
- 2. Val;
- + 3. Ser;
- + 4. Asn;
- 5. Glu.

94. Reaction with nitric acid ($\text{HNO}_3(\text{concd})$) occurs for alfa-amino acids:

- + 1. aromatic;
- 2. aliphatic;

- + 3. phenylalanine;
- + 4. tyrosine;
- 5. valine.

95. Qualitative reaction with $(\text{CH}_3\text{COO})_2 \text{Pb}$ occurs for:

- 1. serine;
- + 2. cysteine;
- 3. tyrosine;
- 4. proline;
- 5. asparagine.

96. Alfa-amino acid asparagin (with pI 5,41) has in solution at pH 5,41 the predominant form of:

- 1. anion;
- 2. cation;
- + 3. dipolar ion;
- 4. nonionized molecules;
- 5. statement is incorrect.

97. Alfa-amino acid threonine (with pI 5,6) has in solution at pH 10 the predominant form of:

- + 1. anion;
- 2. cation;
- 3. dipolar ion;
- 4. nonionized molecule;
- 5. statement is noncorrect.

98. Macromolecules of peptides and proteins consist of:

- 1. alfa-hydroxy carboxylic acids;
- 2. beta-oxo carboxylic acids;
- 3. dicarboxylic acids;
- 4. gamma-amino carboxylic acids;
- + 5. alfa-amino carboxylic acids.

Peptides and proteins.

99. In chemical nature peptides and proteins are:

- 1. polysters;
- + 2. polyamides;
- 3. polyglycosides;
- 4. polynucleotides;
- 5. polyterpenes.

100. Proteins and peptides differ in:

- 1. chemical nature of macromolecules;
- + 2. higher macromolecular mass;
- + 3. number of amino acid residues in molecule > 100;
- 4. number of amino acid residues < 100;
- 5. nature of peptide bond.

101. Primary structure of peptides and proteins:

- 1. show the three-dimensional structure of macromolecules;
- + 2. show the amino acid sequence in macromolecules;
- + 3. is destroyed at acidic and basic hydrolysis;
- 4. is destroyed at denaturation of proteins;
- 5. this conception makes no sense.

102. Primary structure of the tetrapeptide prolylarginylserylglycine is written in example:

- 1. Gly-Ser-Arg-Pro;
- + 2. Pro-Arg-Ser-Gly;
- 3. Glu-Asp-Ser-Gly;
- 4. Pro-Asp-Ser-Glu;
- 5. Pro-Ser-Gly.

Nucleosides. Nucleotides. Nucleic acids.

103. Purinic bases are:

- + 1. guanine;
- + 2. adenine;
- 3. uracil;
- 4. thymidine;
- 5. cytosine.

104. Products of acidic hydrolysis of ribonucleotides are:

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

105. Products of basic hydrolysis of deoxyribonucleotide are:

- + 1. deoxyribonucleoside;
- 2. heterocyclic base;
- 3. deoxyribose;
- 4. phosphoric acid;

+ 5. phosphate-ion.

106. Choose conditions for hydrolysis reaction of nucleosides:

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

107. Which of the following reaction centres form hydrogen bonds between complementary base:

- 1. nucleophilic;
- 2. electrophilic;
- + 3. acidic;
- + 4. basic;
- 5. no answer.

108. Guanine pairs with following base in DNA:

- 1. adenine;
- + 2. cytosine;
- 3. thymidine;
- 4. 6-N-methyladenine;
- 5. 1-N-methylguanine.

109. Thymidine pairs with following base in DNA:

- + 1. adenine;
- 2. cytosine;
- 3. 1-N-methylguanine;
- 4. guanine;
- 5. hypoxanthine (6-hydroxypurine).

110. DNA nucleosides are:

- 1. Guanosine 5'-monophosphate;
- + 2. 2'-Deoxythymidine;
- 3. 5'-Adenylic acid;
- + 4. 2'-Deoxycytidine;
- + 5. 2'-Deoxyadenosine.

111. RNA nucleotides are:

- + 1. 5'-Uridylic acid;
- + 2. Adenosine 5-monophosphate;
- 3. 2'-Deoxycytidine;

- + 4. Cytidine 5'-monophosphate;
- + 5. 5'-Adenylic acid.

112. DNA nucleotides are:

- + 1. 2'-Deoxythymidine 5'-monophosphate;
- 2. 2'-Deoxyguanosine;
- + 3. 2'-Deoxyadenosine 5'-monophosphate;
- 4. 2'-Deoxycytidine;
- 5. 5'-Uridylic acid.

113. Monomeric units of nucleic acids are:

- 1. Ribose;
- + 2. Ribonucleotides;
- 3. Phosphoric acid;
- + 4. Deoxyribonucleotides;
- 5. Heterocyclic base.

114. The products of the basic hydrolysis of DNA nucleotides are:

- + 1. 2'-Deoxynucleosides;
- 2. Heterocyclic bases;
- 3. 2'-Deoxyribose;
- 4. Phosphoric acid;
- + 5. Phosphate ion.

115. Hydrolysis of nucleosides undergoes in following conditions:

- 1. aqueous solution;
- + 2. acidic solution;
- 3. basic solution;
- 4. concd. base;
- 5. concd. salt solution.

116. Nucleic acids carry out:

- 1. the receptor functions;
- + 2. the storage of the genetic informations;
- 3. the energy functions;
- + 4. translation of the genetic information to proteins;
- + 5. synthesis of proteins.

117. Primary structure of RNA is represented by:

- 1. linear polypeptide chain;
- 2. helical polysaccharide chain;

- 3. double helix;
- + 4. single chain of polynucleotide;
- 5. linear polysaccharide chain.

118. Chemically nature ATP:

- 1. is polyribonucleotide;
- + 2. is nucleosidepolyphosphate;
- + 3. contains in structure anhydride linkages;
- 4. is coenzyme of oxidoreductases;
- 5. contains in structure esteric bonds.

119. ATP is:

- 1. found in nucleic acid;
- + 2. found in organism;
- + 3. important energy source;
- + 4. transfer of phosphate group;
- 5. coenzyme of oxidoreductases.

120. NAD^+ :

- + 1. is hydrolyzed in acidic and basic aqueous solutions;
- 2. is found in nucleic acid;
- + 3. is coenzyme of oxidoreductases;
- + 4. contains cation of alkylpyridine;
- 5. is nucleosidepolyphosphate.

Saponified lipids.

121. Lipids are:

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

122. Lipids are classified according to hydrolyzation into:

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

123. According to chemical structure saponified lipids are:

- 1. Isoprenoids;

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

124. Saponified lipids are:

- 1. steroids;
- + 2. waxes;
- 3. terpenoids;
- + 4. phospholipids;
- + 5. fats.

125. saponified lipids are classified into:

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

126. Simple saponified lipids are:

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

127. Complex saponified lipids are:

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

128. Most of natural fats are formed by fatty acids and:

- 1. monohydric alcohols;
- 2. dihydric alcohols glycol;
- + 3. trihydric alcohol glycerol;
- 4. heterofunctional alcohols;
- 5. any alcohols.

129. The following residues predominate in the molecules of fats:

- 1. non-saturated fatty acids;
- 2. oleic acid;

- 3. linolenic acid;
- +4. saturated fatty acids;
- 5. linoleic acid;

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

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

131. Which of the following compounds are the fats:

- +1. 3-linoleoil-2-oleoil-1-stearoilglycerol;
- 2. 1-palmitoil-2-oleoil-L-glycero-3-phosphocholine;
- 3. ethylacetate;
- 4. cetylpalmitate;
- 5. $C_{31}H_{63}OH$

132. Complex saponified lipids are the following:

- 1. fats;
- +2. glycerophospholipids;
- 3. oils;
- 4. waxes;
- 5. steroids;

133. According to chemical nature glycerophospholipids are:

- 1. Fatty acids
- 2. Polyatomic alcohols
- 3. ethers
- +4. Esters of L-phosphatidic acid
- 5. Esters of monoatomic alcohols and fatty acids

134. Mandatory components of the cellular membrane bilayer are ambivalent because of their structure. They are:

- 1. Solid fats;
- 2. Oils;
- 3. Waxes;
- 4. Terpenoids;
- +5. Glycerophospholipids;

135. The products of fats hydrolysis in basic medium are:

- 1. $C_{15}H_{31}COOH + C_{16}H_{33}ONa$;

- 2. $C_{15}H_{31}COOH + C_{16}H_{33}OH$;
- 3. $C_{15}H_{31}COONa + C_{16}H_{33}ONa$;
- 4. $C_{15}H_{31}COONa + C_{16}H_{33}OH$;
- +5. There's no correct answer;

136. Products of hydrolysis of 2-linoleoil-3-oleoil-1-stearoil-glycerol in basic medium in heating are glycerol and:

- 1. $C_{17}H_{31}COOH$, $C_{17}H_{33}COOH$, $C_{17}H_{35}COOH$;
- 2. $C_{17}H_{33}COONa$, $C_{17}H_{35}COONa$, $C_{15}H_{31}COONa$;
- 3. $C_{17}H_{33}COOH$, $C_{17}H_{35}COOH$, $C_{15}H_{31}COOH$;
- 4. $C_{19}H_{31}COONa$, $C_{17}H_{33}COONa$, $C_{17}H_{35}COOH$;
- +5. $C_{17}H_{31}COONa$, $C_{17}H_{33}COONa$, $C_{17}H_{35}COONa$

137. The product of hydrogenation of 3-lineoil-2-palmitoil-1-stearoilglycerol on the metal catalyst is:

- 1. 3-(10,13-dihydroxystearoil)-2-palmitoil-1-stearoilglycerol;
- 2. Reaction occurs in no circumstances;
- +3. 2-palmitoil-1,3-distearoilglycerol;
- 4. 1,2,3-tristearoilglycerol;
- 5. 3-lineoil-2-palmitoil-1-oleoilglycerol;

138. Saponified lipids are oxidized in mild conditions ($KMnO_4$, H_2O), if there are following residues in their molecules:

- 1. Saturated carboxylic acids;
- +2. Non-saturated carboxylic acids;
- +3. Both saturated carboxylic acids and non-saturated carboxylic acids;
- 4. Reaction occurs in no circumstances;
- 5. There's no correct answer;

139. In organism the fatty acids are oxidized by the following ways:

- 1. Hydroxylation;
- +2. Peroxide oxidation;
- +3. Enzyme-mediated oxidation;
- 4. Oxidation occurs in no circumstances;
- 5. There's no correct answer;

Non-saponified lipids. Terpenes. Steroids.

140. Non-saponified lipids are:

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

141. Non-saponified lipids are classified into:

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

142. Which the lipids according to their chemical structure are isoprenoids:

- 1. Waxes;
- 2. Fats and oils;
- 3. Phospholipids;
- +4. Terpenes and terpenoids;
- 5. Steroids;

143. Which of the following information corresponds to the isoprene rule:

- 1. Joint of the isoprene parts occurs according to the principle "tail to tail";
- 2. Addition of reagents of HX structure occurs predominantly in the direction of more stable carbocation formation;
- 3. Heteroatom hybridization type can be usually predicted by attached carbon atom state;
- +4. Joint of the isoprene parts occurs according to the principle "head to tail";
- 5. The number of stereoisomers of chiral structure usually can be predicted using the formula $N=2^n$;

144. The majority of known terpenes and terpenoids:

- 1. Are not natural compounds and are synthesized;
- 2. Are the natural compounds of animal origin;
- +3. Are the natural compounds of plant origin;
- 4. Are obtained by natural compounds modification;
- 5. Are the substances of unknown origin;

145. The number of carbon atoms of monoterpenes molecules is equal to:

- 1. 5;
- +2. 10;
- 3. 15;
- 4. 20;
- 5. 25;

146. The number of carbon atoms of diterpenes molecules is equal to:

- 1. 5;
- 2. 10;
- 3. 15;

- +4. 20;
- 5. 25;

147. The following information is true for the menthol molecule structure:

- +1. Belongs to cyclic monoterpenes;
- 2. Belongs to acyclic monoterpenes;
- 3. Joint of the isoprene parts occurs according to the principle "tail to tail";
- +4. Joint of the isoprene parts occurs according to the principle "head to tail";
- +5. Molecule is chiral;

148. The following information is true for beta-karotene:

- 1. is a vitamin of A group;
- +2. undergo in organism the oxidizing cracking into retinol;
- +3. is a precursor of vitamin A;
- +4. is the example of natural polyene compound;
- 5. the reactions of unsaturated compounds and primary alcohols are characteristic reactions;

149. The structural basis of steroids molecules is the carbon skeleton of the following compound:

- 1. Mentane;
- 2. Kamphane;
- 3. 1-methyl-4-isopropylcyclohexane;
- +4. Perhydrocyclopentanophenanthrene;
- 5. Perhydronaphthalene;

150. Structure of steroid molecules are characterized by:

- +1. Non planar structure;
- +2. Asymmetric molecule structure with several chiral centres;
- +3. Possibility for stereoisomery;
- 4. All the carbon atoms are in the same plane;
- 5. Two planes of symmetry;

151. For indication of substituents configuration in chiral centers of steroid molecule the following stereochemic nomenclature is used:

- 1. D-, L-;
- +2. alpha-, beta-;
- 3. radical-functional;
- 4. substitutive
- 5. R-, S-;

152. In molecules of natural steroids C and D rings have junction:

- 1. only trans-;
- 2. only cis-;
- 3. trans- or cis-;
- +4. commonly trans-;
- 5. commonly cis-;

153. Ancestral hydrocarbon of bile acids steroids group is:

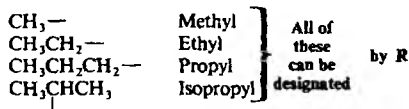
- 1. cardenolid;
- 2. estran;
- 3. cholestan;
- +4. cholane
- 5. pregnane;

154. Which of the following corresponds to steroids of bile acids group:

- 1. they are strong cardiac compounds;
- +2. glycocholic and taurocholic acids according to chemical structure may be considered as functional derivatives of cholic acid;
- +3. they are forming in liver from the sterines;
- +4. transfer the poorly soluble compounds in water solution, ameliorate the intestinal uptake;
- 5. are the estrane derivatives.

REFERENCE TABLES.

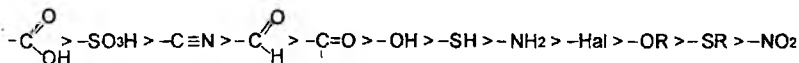
Alkyl groups



Nomenclature of the alkanes

| NAME | NUMBER OF CARBON ATOMS | STRUCTURE | NAME | NUMBER OF CARBON ATOMS | STRUCTURE |
|-------------|------------------------|--|----------------|------------------------|--|
| Methane | 1 | CH_4 | Heptadecane | 17 | $\text{CH}_3(\text{CH}_2)_{15}\text{CH}_3$ |
| Ethane | 2 | CH_3CH_3 | Octadecane | 18 | $\text{CH}_3(\text{CH}_2)_{16}\text{CH}_3$ |
| Propane | 3 | $\text{CH}_3\text{CH}_2\text{CH}_3$ | Nonadecane | 19 | $\text{CH}_3(\text{CH}_2)_{17}\text{CH}_3$ |
| Butane | 4 | $\text{CH}_3(\text{CH}_2)_2\text{CH}_3$ | Eicosane | 20 | $\text{CH}_3(\text{CH}_2)_{18}\text{CH}_3$ |
| Pentane | 5 | $\text{CH}_3(\text{CH}_2)_3\text{CH}_3$ | Heneicosane | 21 | $\text{CH}_3(\text{CH}_2)_{19}\text{CH}_3$ |
| Hexane | 6 | $\text{CH}_3(\text{CH}_2)_4\text{CH}_3$ | Docosane | 22 | $\text{CH}_3(\text{CH}_2)_{20}\text{CH}_3$ |
| Heptane | 7 | $\text{CH}_3(\text{CH}_2)_5\text{CH}_3$ | Tricosane | 23 | $\text{CH}_3(\text{CH}_2)_{21}\text{CH}_3$ |
| Octane | 8 | $\text{CH}_3(\text{CH}_2)_6\text{CH}_3$ | Triacontane | 30 | $\text{CH}_3(\text{CH}_2)_{28}\text{CH}_3$ |
| Nonane | 9 | $\text{CH}_3(\text{CH}_2)_7\text{CH}_3$ | Hentriacontane | 31 | $\text{CH}_3(\text{CH}_2)_{29}\text{CH}_3$ |
| Decane | 10 | $\text{CH}_3(\text{CH}_2)_8\text{CH}_3$ | Tetracontane | 40 | $\text{CH}_3(\text{CH}_2)_{38}\text{CH}_3$ |
| Undecane | 11 | $\text{CH}_3(\text{CH}_2)_9\text{CH}_3$ | Pentacontane | 50 | $\text{CH}_3(\text{CH}_2)_{48}\text{CH}_3$ |
| Dodecane | 12 | $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_3$ | Hexacontane | 60 | $\text{CH}_3(\text{CH}_2)_{58}\text{CH}_3$ |
| Tridecane | 13 | $\text{CH}_3(\text{CH}_2)_{11}\text{CH}_3$ | Heptacontane | 70 | $\text{CH}_3(\text{CH}_2)_{68}\text{CH}_3$ |
| Tetradecane | 14 | $\text{CH}_3(\text{CH}_2)_{12}\text{CH}_3$ | Octacontane | 80 | $\text{CH}_3(\text{CH}_2)_{78}\text{CH}_3$ |
| Pentadecane | 15 | $\text{CH}_3(\text{CH}_2)_{13}\text{CH}_3$ | Nonacontane | 90 | $\text{CH}_3(\text{CH}_2)_{88}\text{CH}_3$ |
| Hexadecane | 16 | $\text{CH}_3(\text{CH}_2)_{14}\text{CH}_3$ | Hectacontane | 100 | $\text{CH}_3(\text{CH}_2)_{98}\text{CH}_3$ |

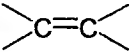
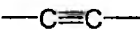

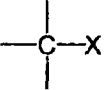
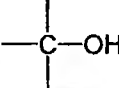
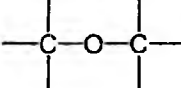
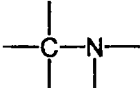
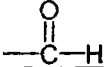
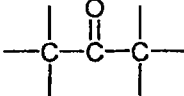
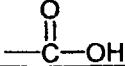
Groups seniority range



| | | | | | | | | | | | | |
|--------|-----------|----------------|----------|------|------|----------|-----------|--------|-------|---------|------------|--------|
| prefix | carboxy- | sulfo- | — | oxo- | oxo- | hydroxy- | mercapto- | amino- | halo- | alkoxy- | alkylthio- | nitro- |
| suffix | -oic acid | -sulfonic acid | -nitrile | -al | -one | -ol | -thiol | -amine | — | — | — | — |

Seniority of groups decrease from left to right

Important families of organic compounds

| Family | Specific example | IUPAC name | Common name | General formula | Functional group |
|-----------------|---|----------------|----------------|---|---|
| Alkane | $\text{H}_3\text{C}-\text{CH}_3$ | Ethane | Ethane | RH | $\begin{array}{c} \text{C}-\text{H} \\ \text{and} \\ \text{C}-\text{C} \\ \text{bonds} \end{array}$ |
| Alkene | $\text{H}_2\text{C}=\text{CH}_2$ | Ethene | Ethylene | $\begin{array}{l} \text{RCH}=\text{CH}_2 \\ \text{RCH}=\text{CHR} \\ \text{R}_2\text{H}=\text{CHR} \\ \text{R}_2\text{H}=\text{CR}_2 \end{array}$ |  |
| Alkyne | $\text{HC}\equiv\text{CH}$ | Ethyne | Acetylene | $\begin{array}{l} \text{RC}\equiv\text{CH} \\ \text{RC}\equiv\text{CR} \end{array}$ |  |
| Arene |  | Benzene | Benzene | ArH | Aromatic ring |
| Halo-alkane | $\text{CH}_3-\text{CH}_2-\text{Cl}$ | Chloroethane | Ethyl chloride | RX |  |
| Alcohol | $\text{CH}_3-\text{CH}_2-\text{OH}$ | Ethanol | Ethyl alcohol | ROH |  |
| Ether | $\text{CH}_3-\text{O}-\text{CH}_3$ | Methoxymethane | Dimethyl ether | ROR |  |
| Amine | CH_3-NH_2 | Methanamine | Methylamine | $\begin{array}{l} \text{RNH}_2 \\ \text{R}_2\text{NH} \\ \text{R}_3\text{N} \end{array}$ |  |
| Aldehyde | $\text{CH}_3-\text{C}(=\text{O})\text{H}$ | Ethanal | Acetaldehyde | $\begin{array}{c} \text{O} \\ \parallel \\ \text{RCH} \end{array}$ |  |
| Ketone | $\text{CH}_3-\text{C}(=\text{O})\text{CH}_3$ | Propanone | Acetone | $\begin{array}{c} \text{O} \\ \parallel \\ \text{RCR} \end{array}$ |  |
| Carboxylic acid | $\text{CH}_3-\text{C}(=\text{O})\text{OH}$ | Ethanoic acid | Acetic acid | $\begin{array}{c} \text{O} \\ \parallel \\ \text{RCOOH} \end{array}$ |  |

| | | | | | |
|-------|--|------------------|----------------|-----------------|---|
| Ester | $\text{CH}_3-\text{C}(=\text{O})-\text{O}-\text{CH}_3$ | Methyl-ethanoate | Methyl acetate | RCOR | $\text{---C}(=\text{O})-\text{O}-\text{C---}$ |
| Amide | $\text{CH}_3-\text{C}(=\text{O})-\text{NH}_2$ | Ethanamide | Acet-amide | RC-NHR | $\text{---C}(=\text{O})-\text{N---}$ |

Electronegativities of some of the elements.

| H 2.1 | | | | | | |
|----------|-----|-----|-----|-----|-----|-----|
| Li | Be | B | C | N | O | F |
| 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 | 4.0 |
| Na | Mg | Al | Si | P | S | Cl |
| 0.9 | 1.2 | 1.5 | 1.8 | 2.1 | 2.5 | 3.0 |
| K | | | | | | Br |
| 0.8 | | | | | | 2.8 |

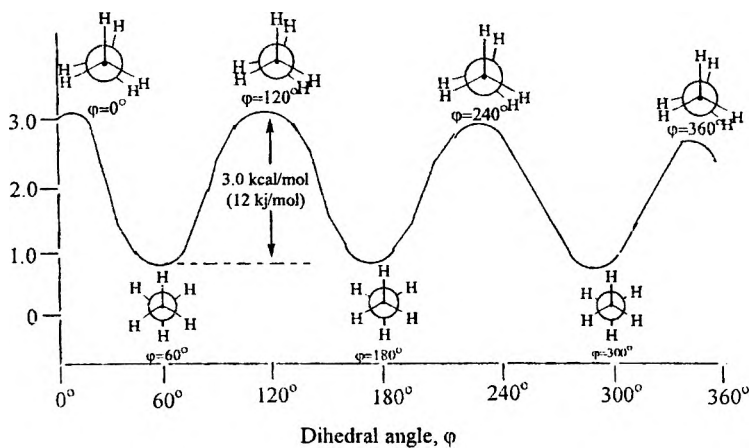
Electronic effects of substituents.

| Substituent | Inductive effect (I) | Resonance effect (M) | Electron-donating or electron - accepting group (ED*, EA**) |
|---|-------------------------|-------------------------|---|
| - Alk (- R) | | | ED |
| - CH ₃ , - C ₂ H ₅ and so on | + I | | ED |
| - O | + I | + M | EA |
| - NH ₂ (-NHR, -NR ₂) | a) - I b) - I | + M | ED (+M > -I) EA |
| - OH (-OR) | a) - I b) - I | + M | ED (+M > -I) EA |
| Halogens: | a) - I | + M | EA (-I > +M) |
| - F, - Cl, - Br, - I | b) - I | | EA |
| >C=O | a) - I b) - I | - M | EA |
| - COOH | a) - I b) - I | - M | EA |
| - SO ₃ H | a) - I b) - I | - M | EA |
| - NO ₂ | a) - I b) - I | - M | EA |
| | | | EA |

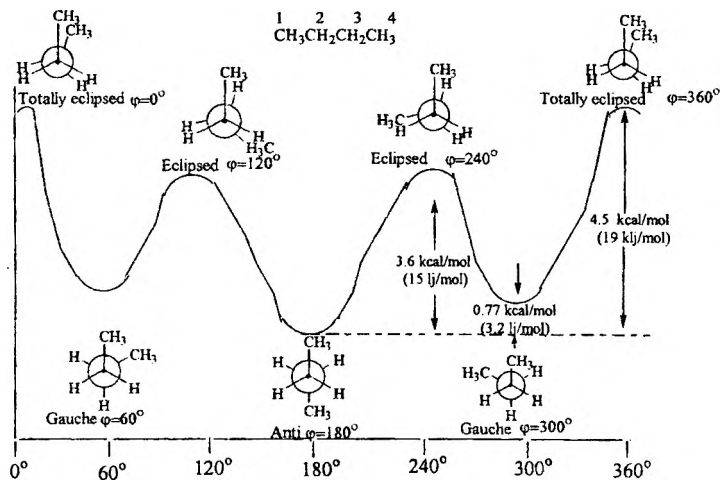
Classification of the reagents.

| Electrophilic reagents | | Nucleophilic reagents | |
|---|--|---|---|
| Positive charged ions | Neutral molecules | Negative charged ions | Neutral molecules |
| H^+ , Br^+ , $-\text{C}^+$ NO_2^+ , SO_3H^+ $\text{R}-\text{C}(=\text{O})^+$ | $\text{C}^{\delta+} \rightarrow \text{X}$ $\text{O}^{\delta-}=\text{S}^{\delta+}(\text{O})_2$ | H^- , Br^- , HO^- , RO^- HS^- , RS^- | $\text{H}_2\ddot{\text{O}}$, $\text{R}\ddot{\text{O}}\text{H}$, $\text{R}\ddot{\text{S}}\text{H}$, $\text{N}\ddot{\text{H}}_3$, $\text{R}\ddot{\text{N}}\text{H}_2$ |

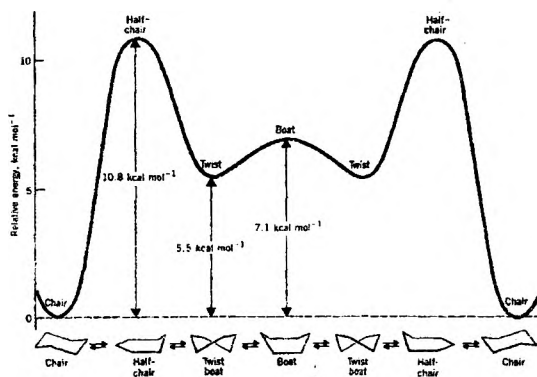
Conformations of ethane.



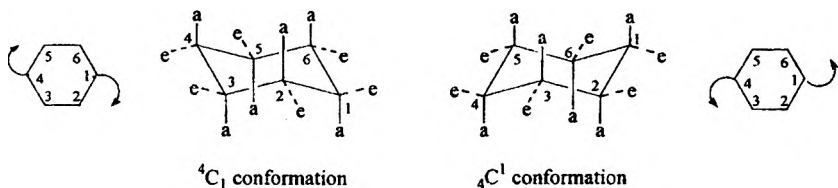
Conformations of butane.



Conformations of cyclohexane.



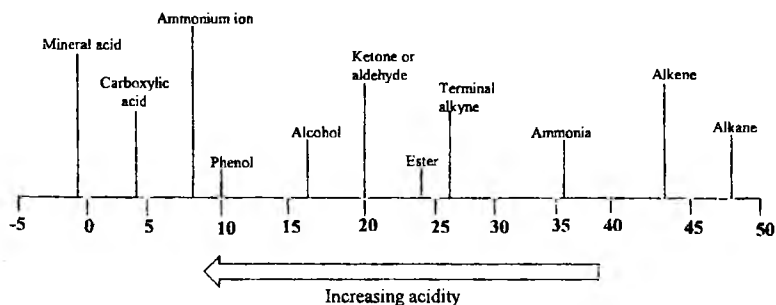
Chair conformations of cyclohexane.



Relative strength of acids and their conjugate bases.

| | ACID | APPROXIMATE pK_a | CONJUGATE BASE | |
|----------------|---|--------------------|-------------------------------------|----------------|
| Strongest Acid | HSbF_6 | > -12 | SbF_6^- | Weakest Base |
| | HI | -10 | I^- | |
| | H_2SO_4 | -9 | HSO_4^- | |
| | HBr | -9 | Br^- | |
| | HCl | -7 | Cl^- | |
| | $\text{C}_6\text{H}_5\text{SO}_3\text{H}$ | -6.5 | $\text{C}_6\text{H}_5\text{SO}_3^-$ | |
| | H_3O^+ | -1.74 | H_2O | |
| | HNO_3 | -1.4 | NO_3^- | |
| | $\text{CF}_3\text{CO}_2\text{H}$ | 0.18 | CF_3CO_2^- | |
| | HF | 3.2 | F^- | |
| | $\text{CH}_3\text{CO}_2\text{H}$ | 4.76 | CH_3CO_2^- | |
| | NH_4^+ | 9.2 | NH_3 | |
| | $\text{C}_6\text{H}_5\text{OH}$ | 9.9 | $\text{C}_6\text{H}_5\text{O}^-$ | |
| | CH_3NH_3^+ | 10.6 | CH_3NH_2 | |
| | H_2O | 15.74 | OH^- | |
| | $\text{CH}_3\text{CH}_2\text{OH}$ | 16 | $\text{CH}_3\text{CH}_2\text{O}^-$ | |
| | $(\text{CH}_3)_3\text{COH}$ | 18 | $(\text{CH}_3)_3\text{CO}^-$ | |
| | $\text{HC}\equiv\text{CH}$ | 25 | $\text{HC}\equiv\text{C}^-$ | |
| | H_2 | 35 | H^- | |
| | NH_3 | 38 | NH_2^- | |
| | $\text{CH}_2=\text{CH}_2$ | 44 | $\text{CH}_2=\text{CH}^-$ | |
| Weakest Acid | CH_3CH_3 | 50 | CH_3CH_2^- | Strongest Base |

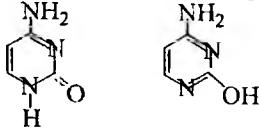
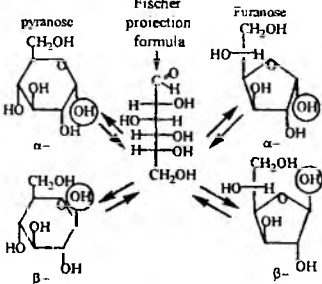
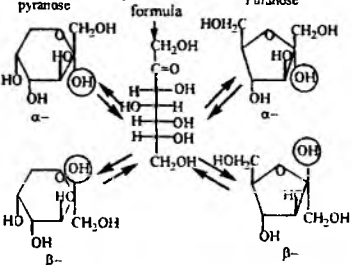
A graphical representation of pKa values for some of important categories of Bronsted-Lowry acids.



Classification of substituents according to the orientation characteristics.

| Ortho-, para-orientants | | Meta-orientants |
|---|--|---|
| Activating substituents (electron-donating groups) | | Deactivating substituents (electron-acceptance groups) |
| + I | + M > - I | - I > + M |
| - Alk (- CH ₃ , - C ₂ H ₅ and so on) | - NH ₂ - NHR - NR ₂ - NHCOR - OH - OR | - F - Cl - Br - I - C = N - COOH - COOR $\begin{array}{c} \text{O} \\ \parallel \\ \text{C} - \text{H} \end{array}$ $\begin{array}{c} \text{O} \\ \parallel \\ \text{C} - \text{R} \end{array}$ |
| | | - NO ₂ NH_3^+ NR_3^+ - SO ₃ H |

Tautomerism of organic compounds.

| Tautomerism | Tautomerism equilibrium | Example |
|---------------------------|---|---|
| Keto-enol tautomerism | $\begin{array}{c} >C-C' \rightleftharpoons >C=C' \\ \quad \quad \quad \\ H \delta^+ \quad O \delta^- \quad \quad OH \end{array}$ | $CH_3-C(=O)-CH_2-C(=O)-OC_2H_5 \rightleftharpoons CH_3-C(OH)=CH-C(=O)-OC_2H_5$ |
| Lactam-lactim tautomerism | $\begin{array}{c} \text{O} \\ \parallel \\ -N-C \rightleftharpoons -N=C \\ \quad \\ H \delta^+ \quad \quad OH \end{array}$ |  |
| Cyclo-oxo tautomerism | <p>Aldoses</p> $\begin{array}{c} C=O \\ \\ (CHOH)_n \\ \\ CH_2OH \end{array} \rightleftharpoons \begin{array}{c} C-OH \\ \\ (CHOH)_n \\ \\ CH_2 \end{array} \begin{array}{c} OH \\ \\ O \end{array}$ <p>Ketoses</p> $\begin{array}{c} CH_2OH \\ \\ C=O \\ \\ (CHOH)_n \\ \\ CH_2OH \end{array} \rightleftharpoons \begin{array}{c} CH_2OH \\ \\ C-OH \\ \\ (CHOH)_n \\ \\ CH_2 \end{array} \begin{array}{c} OH \\ \\ O \end{array}$ | <p>D-glucose</p>  <p>D-fructose</p>  |

Nomenclature of dipolysaccharides and homopolysaccharides

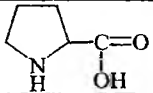
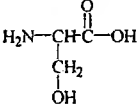
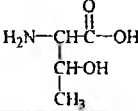
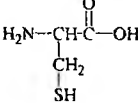
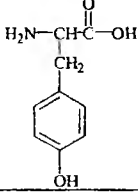
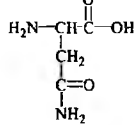
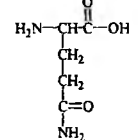
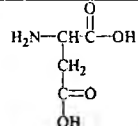
| Name | IUPAC name |
|----------------|--|
| Sucrose | α -D-glucopyranosyl-1,2 β -D-fructofuranoside |
| Maltose | 4-O-(α -D-glucopyranosyl)- α , β -D-glucopyranose |
| Cellobiose | 4-O-(β -D-glucopyranosyl)- α , β -D- glucopyranose |
| Lactose | 4-O-(β -D-galactopyranosyl)- α , β -D- glucopyranose |
| Starch | Consist of amylose and amylopectin |
| a) amylose | (α -D-glucopyranosyl-1,4) _n - α , β -D- glucopyranose |
| b) amylopectin | (α -D-glucopyranosyl-1,4) _n - α , β -D-glucopyranose with branching α , 1 \rightarrow 6 |
| Glycogen | (α -D-glucopyranosyl-1,4) _n - α , β -D- glucopyranose with branching α , 1 \rightarrow 6 |
| Cellulose | (β -D-glucopyranosyl-1,4) _n - α , β -D- glucopyranose |

Structures of heteropolysaccharides

| Polysaccharide | Monosaccharide units | | Substituents | Repeating unit |
|--|----------------------|---|-------------------------------|----------------|
| | A | B | | |
| Hyaluronate | | | $R = -C(=O)CH_3$ | |
| Chondroitin sulfates Dermatan sulfate | | | $R = -C(=O)CH_3$ | |
| | | | $R' = -H \text{ or } -SO_3^-$ | |
| Heparan sulfate and heparin | | | $R = -C(=O)CH_3$ | |
| | | | $R' = -H \text{ or } -SO_3^-$ | |
| Keratan sulfate | | | $R = -C(=O)CH_3$ | |

Structures of amino acids.

| No | Name | Structure | Abbreviation | IUPAC name | pI |
|---------------------------------|----------------|--|--------------|--------------------------------------|------|
| 1. Non polar amino acids | | | | | |
| 1. | Glycine | $\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH} \\ \\ \text{H} \end{array}$ | Gly | 2-aminoethanoic acid | 5,97 |
| 2. | Alanine | $\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH} \\ \\ \text{CH}_3 \end{array}$ | Ala | 2-aminopropanoic acid | 6,02 |
| 3. | Valine* | $\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH} \\ \\ \text{CH}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$ | Val | 2-amino-3-methylbutanoic acid | 5,97 |
| 4. | Leucine* | $\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH} \\ \\ \text{CH}_2 \\ \\ \text{CH}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$ | Leu | 2-amino-4-methylpentanoic acid | 5,98 |
| 5. | Isoleucine* | $\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH} \\ \\ \text{HC}-\text{CH}_3 \\ \\ \text{CH}_2 \\ \\ \text{CH}_3 \end{array}$ | Ile | 2-amino-3-methylpentanoic acid | 6,02 |
| 6. | Phenylalanine* | $\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH} \\ \\ \text{CH}_2 \\ \\ \text{C}_6\text{H}_5 \end{array}$ | Phe | 2-amino-3-phenylpropanoic acid | 5,98 |
| 7. | Tryptophan* | $\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH} \\ \\ \text{H}_2\text{C} \\ \\ \text{Indole ring} \end{array}$ | Trp | 2-amino-3-(indolyl-3)-propanoic acid | 5,88 |
| 8. | Methionine* | $\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH} \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{S} \\ \\ \text{CH}_3 \end{array}$ | Met | 2-amino-3-methylthiobutanoic acid | 5,75 |

| | | | | | |
|--|---------------|---|-----|--|------|
| 9. | Proline |  | Pro | Pyrrolidin-2-carboxylic acid | 6,10 |
| 2. Polar amino acids | | | | | |
| 1. | Serine |  | Ser | 2-amino-3-hydroxypropanoic acid | 5,68 |
| 2. | Threonine* |  | Thr | 2-amino-3-hydroxybutanoic acid | 6,58 |
| 3. | Cysteine |  | Cys | 2-amino-3-mercaptopropanoic acid | 5,02 |
| 4. | Tyrosine |  | Tyr | 2-amino-3-(4-hydroxyphenyl)-propanoic acid | 5,65 |
| 5. | Asparagine |  | Asn | 2-amino-3-carbamoylpropanoic acid | 5,41 |
| 6. | Glutamine |  | Gln | 2-amino-4-carbamoylbutanoic acid | 5,65 |
| 3. Negative charged amino acids | | | | | |
| 1. | Aspartic acid |  | Asp | 2-aminobutanedioic acid | 2,97 |

| | | | | | |
|--|---------------|---|-----|--|------|
| 2. | Glutamic acid | $ \begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH} \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{C}=\text{O} \\ \\ \text{OH} \end{array} $ | Glu | 2-aminopentandioic acid | 3,22 |
| 4. Positive charged amino acids | | | | | |
| 1. | Histidine | $ \begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH} \\ \\ \text{CH}_2 \\ \\ \text{N} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{CH}_3 \end{array} $ | His | 2-amino-3-(1H-imidazolyl-5)-propanoic acid | 7,58 |
| 2. | Lysine* | $ \begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH} \\ \\ (\text{CH}_2)_4 \\ \\ \text{NH}_2 \end{array} $ | Lys | 2,6-diaminohexanoic acid | 9,74 |
| 3. | Arginine | $ \begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH} \\ \\ (\text{CH}_2)_3 \\ \\ \text{NH} \\ \\ \text{C}=\text{NH} \\ \\ \text{NH}_2 \end{array} $ | Arg | 2-amino-5-guanidinopentanoic acid | 10,7 |

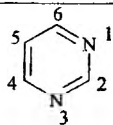
* - essential amino acids.

pKa's of Side-Chains of Acidic and Basic Amino Acids

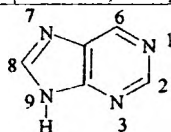
| Acidic Amino Acids | | | Basic Amino Acids | | |
|--------------------|--|----------|-------------------|---|-----------|
| Amino Acid | Side-Chain | pKa | Amino Acid | Side-Chain | pKa |
| Asp | $-\text{CH}_2\text{CO}_2\text{H}$ | 4.4 | Lys | $-(\text{CH}_2)_4\text{NH}_3^+$ | 10.2-10.5 |
| Glu | $-\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$ | 4.5 | Arg | $ \begin{array}{c} \oplus \\ \text{NH}_2 \\ \\ -(\text{CH}_2)_3\text{NH}-\text{C}-\text{NH}_2 \end{array} $ | 12.5-13 |
| Cys | $-\text{CH}_2\text{SH}$ | 7.5-9.2 | | | |
| His | $ \begin{array}{c} \text{H}^+ \\ \\ \text{N} \\ \diagup \quad \diagdown \\ \text{CH}_2- \\ \\ \text{H} \end{array} $ | 6.8-7 | | | |
| Tyr | $ \begin{array}{c} \text{—CH}_2\text{—} \text{C}_6\text{H}_4 \text{—OH} \end{array} $ | 9.9-10.3 | | | |

Nomenclature of nucleic bases

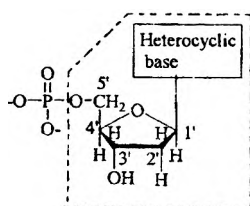
| Name | IUPAC name |
|----------|----------------------------------|
| Adenine | 6-aminopurine |
| Guanine | 2-amino-6-hydroxypurine |
| Cytosine | 4-amino-2-hydroxypyrimidine |
| Thymine | 2,4-dihydroxy-5-methylpyrimidine |
| Uracil | 2,4-dihydroxypyrimidine |



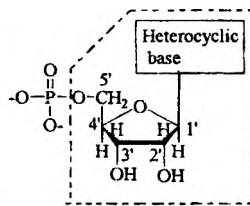
Pyrimidine



Purine



A



B

The general structure of a nucleotide found in DNA and RNA.

Nomenclature of fatty acids

| Name | Condense formula | IUPAC name |
|------------------|---|---|
| Myristic acid | (C ₁₄); C ₁₃ H ₂₇ COOH | Tetradecanoic acid |
| Palmitic acid | (C ₁₆); C ₁₅ H ₃₁ COOH | Hexadecanoic acid |
| Stearic acid | (C ₁₈); C ₁₇ H ₃₅ COOH | Octadecanoic acid |
| Palmitoleic acid | (C ₁₆); (Δ ₉); C ₁₅ H ₂₉ COOH | Cis - 9-hexadecenoic acid |
| Oleic acid | (C ₁₈); (Δ ₉); C ₁₇ H ₃₃ COOH | Cis -9-octadecenoic acid |
| Linoleic acid | (C ₁₈); (Δ _{9,12}); C ₁₇ H ₃₁ COOH | Cis,cis-9,12-octadecadienoic acid |
| Linolenic acid | (C ₁₈); (Δ _{9,12,15}); C ₁₇ H ₂₉ COOH | Cis, cis, cis-9,12,15-octadecatrienoic acid |

| R | NAME |
|--|------------|
| —H | Androstane |
| —H (with —H also replacing —CH ₃) | Estrane |
| —CH ₂ CH ₃ | Pregnane |
| —CH(CH ₃)CH ₂ CH ₂ CH ₃ | Cholane |
| —CH(CH ₃)CH ₂ CH ₂ CH ₂ CH(CH ₃)CH ₃ | Cholestane |

| Family of steroids | Name | IUPAC name |
|-------------------------|------------------------------|---|
| Estrogens | Estrone Estradiol | 3-hydroxy-1,3,5(10)-estratrien-17-one 1,3,5(10)-estratriene-3,17 β -diol |
| Androgens | Androsterone Testosterone | 3- α -hydroxy-5 α -androstan-17-one 17 β -hydroxy-4-androsten-3-one |
| Progestin | Progesterone | 4-pregnene-3,20-dione |
| Adrenocortical hormones | Cortisone Cortisol | 17 α ,21-dihydroxy-4-pregnene-3,11,20-trione 17 α , 11 β , 21-trihydroxy-4-pregnen-3,20-dion |
| Bile acid | Cholic acid | 3 α ,7 α ,12 α -trihydroxy-5 β -cholan-24-oic acid |
| Sterols | Cholesterol Ergosterol | 5-cholesten-3 β -ol 24-methyl-5,7,22-cholestatrien-3 β -oi |

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