EXAMINATION QUESTIONS IN BIOORGANIC CHEMISTRY

1. Bioorganic chemistry as the science, its achievements and communication with organic chemistry.
2. The theory of the structure of organic compounds.
3. Classification of organic compounds.
4. Principles of the nomenclature of organic compounds.

THEORETICAL BASES OF THE STRUCTURE AND REACTIONARY ABILITY OF ORGANIC COMPOUNDS.

1. Conjugated systems p, p - and π, p-conjugation. Energy of stabilization. The conjugated systems with the open chain (butadiene, isoprene) and features of chemical behaviour 1,3-diens.
2. The conjugated systems with the closed chain. Benzene, the electronic structure. Aromaticity and its criterions. Demonstration of aromaticity among arens: benzene, naphthalene, anthracene, phenantrene; and heterocyclic compounds: furan, thiophenes, pyrrole, imidasole, pyridine, pyrimidine, purine.
3. Bond polarization, inductive and mesomeric effects. Electronaccepting and electrondonating substituters and their influence on reactionary ability of double bonds and the aromatic nucleus. Substituters of 1 and 2 order and their orientative influence in the aromatic nucleus.
4. Acidity and basicity of organic compounds. Brensted-louri's theory. The comparative characteristic of acid properties of one - and polyatomic alcohols, phenols, thiols, carbonic acids, amines. Electronic influence of substituters on acidity.
5. Electronic structure of carboxylate-anions, as delocalysed systems. The comparative characteristics of acid properties of one - and two-basic aliphatic and aromatic acids.
6. Role of free unshared electron pair of heteroatoms in the demonstration of the basic properties of alcohols, thiols, ethers, thyoethers, amines. Dependence of basicity from electronic effects of carbon radicals.
7. The comparative characteristics of basicity in aliphatic and aromatic amines. The influence of electronic effects of substituters in benzene ring on basicity of aromatic amines.
8. Hydrogen bonds as specific feature of the acidic-basic properties.
9. Chemical reactions. Classification of reactions by the direction (addition, substitution, elimination) and on the mechanism (ionic, radical).
10. Electrophilic and nucleofilic reagents. The electronic structure of intermediate particles - carbanions, carbcations, free radicals. The factors causing their stability.

11. Reactions of radical substitution of alcanes. Free radical electronic structure. Alcanes and cycloalcanes halogenation. Regioselectivity. Chain reactions.
12. Reactions of electrofilic addition at alcenes, alcadienes and minor cycles. Hydrogenation, halogenation, hydrohalogenation (marcovnicov's rule). Hydration and the role of acidic catalysis. Specific features of electrofilic addition to the conjugated systems: hydration of α, β - unsaturated carbonic (acrylic, crotonic) acids.
13. Reactions of electrofilic substitution of arens and heterocyclic compounds (halogenation, alkylation, nitration, sulfonation). The mechanism of formation of π - and σ complexes, the catalysis necessity.
14. The influence of substituters in benzene ring and heteroatoms in aromatic heterocycles on reactionary ability. The orientative doing of substituters and heteroatoms. Pyrrole and pyridine sulfonation.
15. Reactions of nucleofilic substitution at tetragonal carbon atom among halogenalcanes as consequence of carbon-halogen bond polarization. Nucleofilic reagents. The reaction mechanism on the example of interaction of halogenalcane with alkali and primary amine.
16. The mechanism of nucleofilic substitution reactions at tetragonal carbon atom among alcohols, as consequence of carbon-oxygen bond polarization (on the example of halogenalcanes synthesis from alcohols). The role of acidic catalysis.
17. The reaction of elimination mechanism on the example of dehydrohalogenation of halogenalcanes. Dehydration of alcohols and β-oxyacids, ammonia removal from β amino acids as the consequence of CH-acid center formation.
18. Reactionary centers of carbonic acids. The reactions streaming on CH - acidic center of α - carbon atom.
19. The mechanism of nucleofilic substitution reactions (S_N) at trigonal atom of carbon in carbonic acids (on the example of reaction esterification). The role of acidic catalysis. Other reactions of acylation - formation of anhydrides, amides and opposite to them hydrolysis reactions.
20. Acilating reagents (anhydrides, carbonic acids, esters, thyoethers, halogen anhydrides), comparative activity of these reagents.
21. The mechanism of nucleofilic addition reactions to trigonal atom of carbon (aldehydes, ketons), on the example of semi-acetales, acetales synthesis. Comparison of reactionary ability of aldehydes and ketons. Cyclic acetals.
22. Reactions of carbonyl compounds with water, thiols, primary amines. The mechanism of nucleofilic addition-elimination reactions.
23. The reason of the CH-acidic center occurrence at aliphatic aldehydes. Reaction of aldol condensation, it's mechanism. The meaning of reaction. Iodoform reaction of acetone.
24. Oxidation-reduction reactions of aldehydes. Formaldehyde dismutation (Kannizzaro-Tishchenko reaction), it's mechanism.

25. Reactions of oxidation and reduction of organic compounds. Oxidation of alcenes, alcohols, thiols, aldehydes. Reduction of aldehydes, ketons, disulfides. Conception of system NAD ↔ NAD·H^+ action.

II. STEREOISOMERISM.

1. Structure of organic molecules (the structure, configuration & conformation). Configuration of sp^3, sp^2, sp- hybridized carbon atoms.
2. Conformation of open chains. Energy characteristics of conformational conditions. Newman's projective formulas.
3. Conformations of cyclic compounds (cyclohexane, α- and β-glucopyranose). Axial and equatorial bonds.
4. Stereoisomerism of molecules with one chiral center (enantiomerism).optic activity. L and D stereochemical orders of oxy- and amino-acids. Fisher's formulas.
5. Stereoisomerism of tartaric (vinic) acids. Racemates.
6. Stereoisomerism of compounds with double bonds (π - diastereoisomerism). Cis- and Trans- izomerism of alcenes, unsaturated fatty acids & dicarbonic acids (butenedioic acid).

III. HETEROFUNCTIONAL AND HETEROCYCLIC ORGANIC COMPOUNDS.

1. The chemical features of poly - & heterofunctional compounds (amphoteric character, cyclization, chelates formation).
2. Polyatomic alcohols: ethylene glycol, glycerol. Formation of chelate complexes as qualitative reaction on α - diol fragment.
3. Diatomic phenols: hydroquinone. Hydroquinone oxidation (hydroquinone - quinone system).
4. Aminoalcohols: ethanolamine (colamine). Carry out the transformation scheme: serine → colamine → choline → acetylcholine.
5. Aminophenols: dopamine, noradrenaline (norepinephrine), adrenaline (epinephrine), their synthesis from tyrosine. The biological role of compounds.
6. Hydroxyacids. Specific reactions passing while heating α, β, γ-oxy acids.
7. Amino acids. The specific reactions proceeding at heating α, β, γ-acids.
8. Aldehyde - and keto- acids: pyruvic (pyrovinic) acid, acetoacetic, oxaloacetic, α-ketoglutaric acid. Keto-enol tautomerism.
9. Reactions of ketone bodies formation from acetoacetic acid. At what disease are formed?
10. Salicylic acid and its derivatives (aspirin, methylesalicylate). Medical application.
11. Sulfanilic acid and it amide (streptocide). Synthesis from aniline. Medical usage.
12. P-aminobenzoic acid and its derivatives (benzocaine, novocaine), their usage.
13. Pyridine and its derivatives: nicotinic acid, it's amide.

14. Imidazole, its basic properties. Histidine, decarboxylation. Biological meaning.
15. Indole. Tryptophan, reactions leading to tryptamine, serotonin formation. Biological role of serotonin.
16. Purine. Uric acid (2,6,8-hydroxypurin).
17. Barbituric acid. Keto-enol and Lactam-lactimic tautomerism. Medicines on the base of barbituric acid derivatives.
18. Lactam-lactimic tautomerism of uric acid. The gout.

IV. MONO - OLIGO - POLYSACCHARIDES.

1. Classification of monosaccharides. Aldoses, ketoses, representatives.
2. Pentoses: xylose, xylulose, ribose, ribulose, 2- deoxyribose.
3. Hexoses: glucose, mannose, galactose, fructose, glucosamine.
4. Stereoisomerism and cyclo-oxo-tautomerism of monosaccharides.
5. Monosaccharides images. Fisher's and Hewthor's formulas.
6. α - and β-anomerism of monosaccharides. Tautorotation (mutorotation). Conformation of monosaccharides.
7. Chemical properties of monosaccharides. Reactions of carbonyl and hydroxyde groups.
8. Glycosidic hydroxyde group of monosaccharides. O - and n- glycosides. Synthesis and hydrolysis reactions.
9. Oxidation and reduction of monosaccharides.
10. Phosphates of monosaccharides (glucose 6-phosphate). Acylation of monosaccharides. (n- acetyl-d-glucosamine).
11. Oligosaccharides. Disaccharides. Classification. Representatives. Cyclo-oxo-tautomeriism of disaccharides.
12. Maltose, lactose, sucrose, cellobiose, the structure and properties.
13. Polysaccharides: starch, glycogen, cellulose, dextran, hyaluronic acid, chondroitin sulfates. The structure & biological role.

V. AMINO ACIDS, PEPTIDES.

1. The amino acids forming the proteins. Classification & biological role
2. Structure of amino acids. Stereoisomerism. Acidic-basic properties.
3. Chemical properties of amino acids as heterofunctional compounds. Reactions of NH_2 – and -COOH groups (reactions of esterification, acylation, amines formations).
4. Reactions of interaction of amino acids with nitrogenous acid and formaldehyde, their meaning for the amino acids analysis.
5. Reactions of oxidizing and not oxidizing deamination of amino acids.

6. Decarboxylation of α amino acids, biogenic amines formation (colamine, hystamine, triptamine, serotonin, γ-aminobutiric acid).
7. Peptides formation. The nomenclature. Electronic and spatial structure of peptyde bond.
8. The acidic-basic properties of peptydes. The isoelectric condition and the isoelectric point.
9. Hydrolysis of peptydes and aminoacid structure establishment.
10. Establishment of primary structure of peptydes (edman's method).

VI. NUCLEIC ACIDS.

1. Nucleic acids, representatives, biological role.
2. The nitrogenous bases of pyrimidine rows which are a part of nucleinic acids. Aromatic properties, lactam-lactimic tautomerism.
3. Nitrogenous bases of purine rows. Aromatic properties, lactam-lactimic tautomerism.
4. The complementarity of nitrogenous bases. Hydrogen bonds in complementary pairs of nucleic bases.
5. Nucleosides. Structure of purine and pyrimidine mononucleosides.
6. Nucleotides. The structure of mononucleotides. The nomenclature. Nucleotides hydrolysis.
7. The primary structure of nucleic acids. Phosphodiester bond.
8. The character of distinctions between DNA and RNA (in the structure and functions).
9. Secondary structure of DNA. The role of hydrogen bonds in formation of secondary structure.
10. The structure of ATP. Macroergic bonds. ATP hydrolysis. The biological role.
11. Nucleosidecyclophosphates (cyclic-AMP), the biological role.
12. Nicotinamide coenzymes. The structure of NAD. System NAD – NAD H^+, it's role in oxidation-reduction reactions (interaction with the hydride-ion).
13. The medical products, derivative the nitrogenous bases (5-fluorouracil, 6-mercaptopurin).

VII. SOAPANIFIABLE LIPIDS.

1. Neutral lipids (triglycerides). The structure & biological role.
2. The natural higher fatty acids which are a part of lipids: palmitic, stearic, oleic, linoleic, arachidonic, linolenic.
3. Plant and animal fats. The structure, properties. The analytical characteristics of fats.
4. Hydrogenation and hydrolysis of fats. The analytical characteristic.

5. Phospholipids. The structure. The biological role.
6. Phosphatidic acid. Phosphatidyl colamines (cephalins) and phosphatidyl cholines (lecithins) - structural components of cell membranes.
7. Acidic and alkalic hydrolysis of cephalines & lecithines
8. Structure and biological role sphingo - & glycolipids.
9. Peroxidation of nonsaturated fat acids in cell membranes, it's mechanism. Antioxidants.