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ABSTRACT

of the dissertation for the degree of Doctor of Science

SYNTHESIS AND STUDY OF HETEROATOM CONTAINED DERIVATIVES AND PRODUCTS OF THEIR TRANSFORMATION BASED ON ALLYL- AND PROPENYLPHENOLS

Speciality: 2314.01- Petrochemistry

Field of science: Chemistry

Applicant: **Gunay Muzakir Mehdiyeva**

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The work was performed at the Scientific laboratory "Chemistry of alkenyl phenols" of the department "Petroleum Chemistry and Chemical Technology" of Baku State University.

Scientific consultant: doctor of chemical sciences, professor
Musa Rza Bayramov

Official opponents: doctor of chemical sciences,
professor, corresponding member of ANAS
Mamed Baba Babanli
doctor of chemical sciences,
professor, corresponding member of ANAS
Tofig Abbasali Aliyev
doctor of chemical sciences,
professor, corresponding member of ANAS
Bakhtiyar Ajdar Mamedov
doctor of chemical sciences,
assistant professor
Manzar Nezameddin Amiraslanova

Dissertation council ED 1.16 of Supreme Attestation Commission under the President of the Republic of Azerbaijan operating at the Institute of Petrochemical Processes named after acad. Y.H. Mammadaliyev of the Ministry of Science and Education Republic of Azerbaijan

Chairman of the Dissertation Council: Doctor of chemical sciences, academician **Vagif Maharram Abbasov**

Scientific Secretary of the Dissertation Council: Doctor of chemical sciences, associate professor **Lala Mahammad Afandiyeva**

Chairman of the Scientific Seminar: Doctor of chemical sciences, associate professor **Fuzuli Akbar Nasirov**

GENERAL CHARACTERISTICS OF WORK

Relevance of the work and degree of development. Currently, one of the urgent problems of petrochemical science is the working out of new economically and ecologically more profitable polyfunctional surface-active heteroatom-containing organic compounds for various purposes.

In recent years, new effective processes have been implemented related to the solution of many petrochemical problems - improvement of methods for obtaining target compounds with high yields, waste disposal, reduction of emissions into the environment, etc. However, there are still unresolved economic and environmental problems.

Thus, on a global scale, more than 25-30% of metals and metal equipments under the influence of water and reservoir systems containing hydrogen sulfide, chlorides, CO_2, sulfates and other substances that enhance the corrosion and biocorrosion (under the influence of sulfate-reducing bacteria) process in the oil producing and oil refining industries corrode and become unusable.

As the analysis of scientific and technical literature of recent years shows, the working out of new corrosion inhibitors intended for wide application in the oil producing and oil refining industry based on available types of fluids is an important task. They are used not only in the operation of wells, but also in their transportation.[1]

On the other hand, to intensify oil production processes on a global scale, it is necessary to periodically clean the internal surfaces of wells using aqueous solutions of mineral acids, which necessarily contain inhibitors (without any or inhibitory composition, acid corrosion of metal occurs).[2]

Organic compounds with anticorrosive, bactericidal and other useful operational properties are mainly surface-active, they form

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[1] Migahed, M.A. Beneficial Role of Surfactants as Corrosion Inhibitors in Petroleum Industry: A Review Article // Chem. Eng. Commun., - 2009. V.196, - p. 1054–1075.

[2]Аббасов, В.М. Реагенты и продукты для нефтяной, газовой, нефтеперерабатывающей и нефтехимической промышленностей/ В.М. Аббасов, Л.И. Алиева, Е.Ш. Абдуллаев, [и др.]/ Монография, Издательство “Элм”, - 2017, - 436 с.

chemisorbed layers on the metal, which helps to reduce the corrosion rate. Although various corrosion inhibitors consisting of structural and functional fragments and heteroatoms (O, N, S, P) are known, the number of organic compounds that simultaneously possess anticorrosive, bactericidal (SRB) and other important operational properties is very limited and the demand for them is constantly growing.

From this point of view, derivatives of phenols, alkyl and alkenyl phenols containing various functional groups and heteroatoms in their structures are used as inhibitors of acid corrosion of non-ferrous and ferrous metals, bactericides (SRB), additives to petroleum products, medicines and other valuable products. It is also known that the role of phenolic compounds and their various derivatives is important when used as antimicrobial, antioxidant, anticorrosive, viscosity-temperature additives to oils and fuels. Another urgent problem of petrochemical science is also the search for effective polyfunctional sorbents from phenolic compounds for cleaning water systems, including domestic and industrial wastewater from heavy metals, radionuclides and other harmful substances. Although in recent years many studies have been conducted in this area and various cleaning methods have been proposed, using ion exchangers, sorption materials, etc., many problems associated with their reuse have not been solved to a sufficient extent, which indicates the importance of continuing targeted work. A special place is occupied by modified (cross-linked) structures containing hydroxyl, amine, amide, nitrile, carboxyl and other reactive fragments, due to which it is possible to carry out sorption of harmful substances from oil and water systems in "mild" conditions.

Particular attention in the world is also paid to solving the problem associated with increasing the light and heat resistance of oligomeric and polymeric materials for various purposes by chemically modifying their structure at the synthesis stage (inclusion of stabilizing monomeric and polymeric units of phenolic comonomers in growing polymer chains). This allows us to significantly improve the performance properties of the resulting copolymers and increase their service life.

In the last 25-30 years, interest in the chemical transformations of phenols and their derivatives has increased sharply, as evidenced by publications concerning the study of natural phenolic compounds, the development of convenient methods for extracting them from plants, using them as antitumor drugs, etc.

Special attention should be paid to the condensation products of alkenylphenols with aldehydes and amines (by Mannich). Despite the study of the Mannich reaction and the successes achieved, using a primary amine instead of a secondary amine in the Mannich reaction, it is possible to direct the condensation towards the formation of alkenyl substituted 1,3-benzoxazine - a valuable new precursor, which allowed it to be used in further reactions to implement previously unknown transformations in order to create new valuable industrial materials with unique properties. Taking into account the solution of the above problems, the presented dissertation work, devoted to the topic: "Synthesis and study of heteroatom-containing compounds and products of their transformations based on allyl and propenylphenols", devoted to the synthesis of new heteroatom-containing derivatives of allyl and propenylphenols, products of their transformation, study of their structures and patterns of change in the areas of their practical application (as corrosion inhibitors, biocides, reagents for the transformation of SRB growth, additives, antioxidants, etc.) depending on their structure, is very relevant and is of interest from both theoretical and practical points of view.

Object and subject of work. The object and subject of the study were heteroatom-containing compounds based on allyl and propenylphenols and the study of their practical application.

The purpose and objectives of the dissertation work. Synthesis of heteroatom-containing compounds based on 2-allyl-, 2-propenyl- and 4-isopropenylphenols, study of their antioxidant, viscosity-temperature and antimicrobial properties. In addition, the goal was to study them as inhibitors of steel corrosion in acidic, hydrocarbon-containing environments, in formation water saturated with hydrogen sulfide and carbon dioxide, as well as reagents for suppressing the growth of SRB. Using various modifying agents in the reactions of structuring benzoxazines and co-oligomers, materials were obtained that are

capable of sorbing radioactive and heavy metals from water systems, oil formation waters, etc. To achieve the given goal, the following problems were solved:

- study of the triple condensation reaction of 2-allyl-, 2-propenyl- and 4-isopropenylphenols with formaldehyde and primary amines in order to obtain alkenyl-substituted 1,3-benzoxazines on their basis;
- study of the triple condensation reaction of 2-allylphenol with benzaldehyde and primary or secondary amines;
- study of the structure and thermal properties of the obtained compounds;
- obtaining quaternary ammonium salts;
- obtaining propargyl-containing derivatives of allyl- and propenylphenols, as well as 1,3-benzoxazines;
- synthesis of condensation products of 2-allylphenol, formaldehyde and ethylenediamine and study of the sorption properties of the obtained materials on its basis;
- study of the reaction and condensation products of 2-allylphenol, formaldehyde (or benzaldehyde) and urea (or thiocarbamide);
- study of the anticorrosive properties of 1,3-benzoxazines and ammonium salts in a water-salt hydrocarbon-containing medium saturated with hydrogen sulfide;
- study of the anticorrosive properties of ammonium salts of synthesized compounds in petroleum formation water saturated with hydrogen sulfide and CO_2;
- study of the anticorrosive properties of synthesized compounds in a sulfuric acid medium;
- study of synthesized ammonium salts as reagents for suppressing the growth of SRB during oil production;
- study of the antioxidant properties of condensation products of 2-allyl and 2-propenylphenols;
- study of viscosity-temperature properties of condensation products of 2-allyl- and 2-propenylphenols in a composition in I-12A oil;

- study of the antimicrobial properties of 1,3-benzoxazines, aminomethyl derivatives and their ammonium salts in M-8 oil, in water and DMSO.

Research methods. Triple condensation of 2-allyl-, 2-propenyl- and 4-isopropenylphenols with aldehydes, as well as the transformation of the resulting products and the production of ammonium compounds were carried out under laboratory conditions. Their structures were studied using NMR, IR, elemental analysis, scanning electron microscopy, γ-spectrometer, etc.

The main provisions defended. The condensation products obtained based on 2-allyl-, 2-propenyl- and 4-isopropenylphenols, as well as ammonium compounds based on them, have anticorrosive properties in acidic environments under various conditions, biocidal properties in relation to SRB, antimicrobial, antioxidant and other properties. While studying the condensation products as precursors in further transformations, modifiers with functional groups are obtained that are capable of adsorbing radioactive and heavy metals from aqueous systems and oil formation waters.

Scientific novelty of the dissertation. For the first time, scientific principles have been worked out the synthesis of functionally substituted heteroatom-containing compounds based on 2-allyl-, 2-propenyl- and 4-isopropenylphenols with conjugated and non-conjugated double bonds with the aromatic ring, possessing a number of valuable operational properties (corrosion inhibitors, reagents for suppressing the growth of SRB, antioxidant, antimicrobial, sorption) depending on their structure, which can be applied in oil extracting and petrochemical industry.

Theoretical and practical value of the work. Systematic studies were conducted to identify areas of practical application of the synthesized aminomethyl derivatives of 2-allyl-, 2-propenyl- and 4-isopropenylphenols, as well as 1,3-benzoxazines of various structures based on them, and the following conclusion was made regarding their properties:

- in order to identify the anticorrosive properties of the synthesized compounds in various systems: in a water-salt hydrocarbon-containing medium saturated with hydrogen sulfide, in a sulfuric acid

medium, as well as in oil formation water saturated with hydrogen sulfide and carbon dioxide, the dependence of the operational properties of functionally substituted heteroatom-containing compounds, as well as their ammonium salts on the structure was revealed;

- the dependence of the biocidal properties of the synthesized ammonium salts based on functionally substituted heteroatom-containing compounds on their structure was studied. It was found that the synthesized ammonium salts in low concentrations have 100% suppression of SRB growth;

- antioxidant properties of synthesized heteroatom-containing compounds soluble in oils were studied, and the relationship between their structure and properties was established;

- antimicrobial activity of synthesized 1,3-benzoxazines and their ammonium salts against microorganisms (Staphylococcus aureus, Escherichia coli, Candida albicans, Shigella flexneri, Salmonella enterica, Pseudomonas aeruginosa, Aspergillus niger) was revealed. A correlation was established between the bactericidal and fungicidal properties of the tested compounds and their structure;

- a new approach to obtaining environmentally friendly, light- and thermal-stable monomeric and polymeric stabilizers based on aminomethyl derivatives of alkenylphenols was identified;

- it has been established that the condensation products of 2-allylphenol with formaldehyde and ethylenediamine have high sorption properties in relation to uranyl ions and heavy metals in aqueous systems and in oil formation waters.

Approbation and publication. The research results were reported and discussed at the following International and Republican scientific conferences: the 2nd International Scientific Conference dedicated to the 105th anniversary of Academician Hasan Aliyev on the topic "Ecology: problems and challenges" (Baku, November 7-8, 2012); the International Scientific and Technical Conference for the 75th anniversary of Academician Valery Legasov (Tula, 2012); the 1st International Chemical and Chemical-Technological Conference dedicated to the 90th anniversary of National Leader Heydar Aliyev (Baku, April 17-21, 2013); the International Scientific and Methodological Conference "Integration of Science and Education in

Universities of the Oil and Gas Profile -2014", Ufa; VIII Republican Scientific Conference "Kimyanın aktual problemləri" dedicated to the 91st anniversary of National Leader Heydar Aliyev (Baku, May 7-8, 2014); IX Republican Scientific Conference dedicated to the 92nd anniversary of National Leader Heydar Aliyev (Ganja, May 7-8, 2015; Baku, 2015); International Scientific Conference "Müasir kimya və biologiyanın aktual problemləri" dedicated to the 93rd anniversary of National Leader Heydar Aliyev (Ganja, May 12-13, 2016); International Scientific Conference "Actual problems of modern chrmistry" dedicated to the 90th anniversary of Academician Yu.G.Mammadaliyev (Baku, October 2-4, 2019); III and IV International Conferences of Students and Young Scientists dedicated to the 97th, 98th, 99th, 100th and 101st Anniversaries of National Leader Heydar Aliyev (April 6-16, 2020; May 25-26, 2021; April 18-29, 2022; Baku, May 4-05, 2023; Baku, 2024); I International Scientific Conference "Recent Scientific Investigation" (Oslo, Norway, December 6-8, 2020); Republican Scientific Conference (Baku, December 12, 2020); IV International Novruz Conference of Scientific Research (Karabakh, March 18-21, 2021); International Conference "Modern Problems of Theoretical and Experimental Chemistry" dedicated to the 90th anniversary of Academician Rafiga Aliyeva (Baku, September 29-30, 2022); II International Scientific and Practical Conference "Innovative Development in the Global Science" (Boston, USA, June 26-28, 2023); II International Scientific and Practical Conference "Diversity and Inclusion in Scientific Area" (Warsaw, January 26-28, 2023); VIII International Scientific and Practical Conference "Global and Regional Aspects of Sustainable Development" (Copenhagen, March 26-28, 2023); VI International Scientific and Practical Conference "Scientific Community In" (Hamburg, July 6-8, 2023); Republican Scientific Conference "Kimya və kimya texnologiyasında müasir yanaşmalar", dedicated to the 80th anniversary of the Department of Petroleum Chemistry and Chemical Technology (Baku, December 14, 2023); Republican Scientific Conference “Oil, Polyfunctional Monomers, Oleomers, and Synthetic Polymers” dedicated to the 90th anniversary of Academician S.M. Aliyev (Baku, June 23, 2023); I International Book Publication of the Commonwealth of Independent States “Best

Researcher - 2023" (Astana, 2023); International Scientific Conference "Modern Problems of Macromolecular Compound Technology" (Baku, April 25-26, 2024); XI International Scientific and Practical Conference "Science, Education, Innovation: Topical Issues and Modern Aspects" (Tallinn, Estonia, November 16-18, 2024); International Scientific Conference "Scientific Advances and Innovative Approaches", Tokyo, Japan (2024), etc.

Based on the results of the dissertation work, 82 scientific works were published, including 33 articles (29 of them with international indexation), 43 abstracts, 1 monography, and 5 Azerbaijani Patents.

The name of the institution where the dissertation work was performed. The dissertation work was completed in the research laboratory "Chemistry of Alkenylphenols" at the Department of "Chemistry of Oil and Chemical Technology" of Baku State University. The studies presented in the dissertation are one of the planned research works carried out at Baku State University.

The total volume of the dissertation indicating the volume of structural sections. The dissertation consists of an introduction, 6 chapters, conclusions, a list of references including 542 titles, an appendix consisting of 2 test reports, and spectra. The material is presented on 400 pages, contains 49 tables and 186 figures.

The **Introduction** briefly and clearly provides information about the relevance of the completed dissertation, the stated goal, the object of research to achieve the stated goal, the methods and subjects of research, the scientific novelty of the results obtained and testing, as well as the structure and volume of the dissertation work.

The first chapter provides a comprehensive analysis of the current state of research on new methods for the synthesis of various alkenylphenols, their transformations at the multiple bond, benzene ring and OH group in the presence of catalysts and initiators, as well as areas of their practical application. The review also provides comprehensive information on the syntheses of cyclic heteroatom-containing phenol derivatives - 1,3-benzoxazines, their transformations and application in various fields of the national economy and technology. In addition, the review clearly analyzes the possibility of using heteroatom-containing organic compounds.

The second chapter is devoted to the methodology of experimental work on syntheses and studies of the structures of the obtained compounds, description of the methods for analyzing the structures of the studied compounds, as well as methods for conducting corrosion, biocidal, antioxidant, antimicrobial studies of the properties of the obtained compounds. The second chapter also presents ^{1}H and ^{13}C NMR, IR spectra, elemental analysis (Carlo Erba EA 1108, G10 GSM6610RV and JEOL JSM-6610LV, ICP MS 7700e, RFY-1 method AR2092_0721), TGA and DTA of the synthesized compounds. The second chapter also provides a method for determining the molecular weight of oligomers, determining the sorption capacity of modified oligomers (HPGe γ-spectrometer), and conducting antimicrobial studies (Leica EMUC7 ultramicrotome, Zeiss microscope (Primo Star) with an EOS D650 digital camera, TEM JEM-1400).

The third chapter is devoted to a discussion of the results of the synthesis of heteroatom-containing compounds and their transformation products, establishing the influence of the nature of the reagents taken on the yields of target compounds, and studying their thermal properties.

The fourth chapter discusses the results of syntheses and studies of the structures of the obtained products based on 2-allyl- and 4-isopropenylphenols with aldehydes and diamines, and identifies areas of application for their modified derivatives.

The fifth chapter discusses the importance and results of syntheses of propargyl derivatives of 2-allyl-, 2-propenyl- and 4-isopropenylphenols, their nitrogen-containing derivatives, as well as 8-allyl- and 8-propenyl-substituted 1,3-benzoxazines.

The sixth chapter is devoted to the discussion of the results of studies of alkenyl-substituted 1,3-benzoxazines, aminomethyl derivatives of alkenylphenols, various ammonium salts based on them as inhibitors of acid corrosion of metals in aqueous, aqueous-salt hydrocarbon environments, oil reservoirs, as biocides against SRB in oil production, antioxidant, antimicrobial, viscosity-temperature additives to oils, as well as drugs and identifying patterns between the performance properties and structure of the synthesized compounds.

The Conclusions section provides the scientific novelty of the research results, which are important from both a scientific-methodological and chemical point of view.

At the end of the dissertation, **a list of references (source)** is given, formatted during its writing in accordance with the requirements.

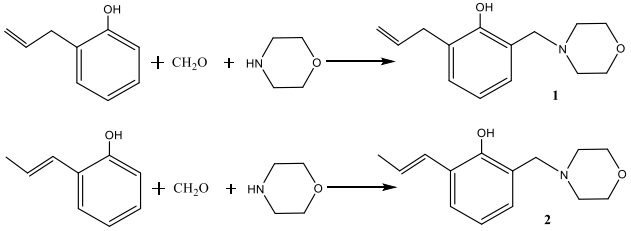
The total volume of the dissertation consists of 369186 characters, where the introduction is 17403, the first chapter is 90319, the second chapter is 75104, the third chapter is 55458, the fourth chapter is 39225, the fifth chapter is 6767, the sixth chapter is 78998, and the conclusions are 5912.

The applicant's personal contribution to the research conducted. When completing a dissertation according to the topic, when analyzing a literature review of recent years, when conducting experiments, analyzing NMR and IR spectra, etc., writing articles and when conducting all other studies, they are done by the applicant himself.

THE MAIN CONTENT OF THE WORK

Synthesis and study of condensation products of 2-allyl- and 2-propenylphenols with formaldehyde and morpholine

In order to develop previously conducted studies in the field of triple condensation of alkenylphenols with formaldehyde and amines (according to the Mannich reaction), a reaction of 2-allyl and 2-propenylphenols with formaldehyde and morpholine was carried out and aminomethyl derivatives containing multiple bonds in the structures were obtained according to the following scheme:



The obtained compounds **1** and **2** were synthesized as precursors with yields of 70.8 and 80.7%, respectively.

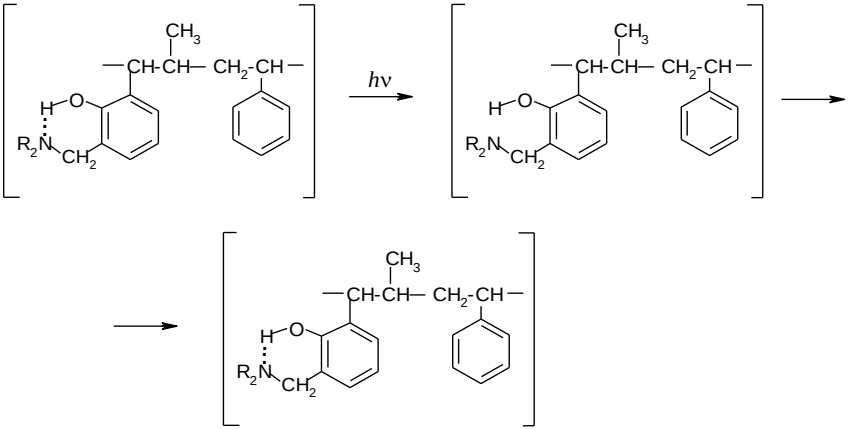
From the NMR spectra of the compounds it is evident that the protons of the OH group are detected in a weak field: for compound **1** – 7.5 ppm, for compound **2** – 10.5 ppm. The obtained results indicate the formation of an intramolecular hydrogen bond between the nitrogen of the morpholinomethyl fragment and the hydrogen of the OH group of phenol.

A study of the structures of aminomethylated derivatives of 2-allyl- and 2-propenylphenols by IR and NMR spectroscopy allowed us to establish the presence of a fairly stable intramolecular hydrogen bond (up to 70 °C) due to the free electron pair of nitrogen and hydrogen of the hydroxyl group. In addition, when studying aminomethyl derivatives of alkenylphenols by NMR spectroscopy up to the boiling point of the solvent taken (CCl_4), a slight shift in the signals of the OH group protons is observed, which confirms the sufficient strength of the intramolecular hydrogen bond.

In connection with the above, we made a new approach to blocking the OH group of phenol to obtain monomeric and polymeric heat and light stabilizers.

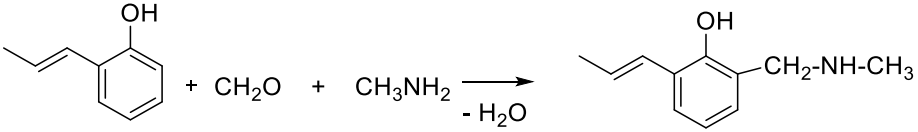
Taking into account the above and the presence of a strong intramolecular hydrogen bond, stable up to 70 ° C in aminomethyl derivatives of alkenylphenols, it was of interest to carry out the copolymerization of the latter with styrene in the presence of a low-temperature initiator (diniz). This is where the idea arose to use the possibility of eliminating the inhibitory effect of phenolic hydroxyl on the course of the process of radical copolymerization of aminomethylated derivatives of alkenylphenols at relatively low temperatures (60 °C), due to the presence of a strong intramolecular hydrogen bond in the latter, stable up to 70 °C in the presence of low-temperature initiators - azo compounds, in particular azobutyric acid dinitrile. The effect of temperature (from 60 to 900 °C) on the yield of the copolymer was studied at a phenolic monomer:styrene ratio of 1:2 (mol), initiator concentration of 0.2-1.0% (based on the monomer mixture) and reaction time from 5 to 40 hours. The thermal stability and light-stabilizing properties of the synthesized copolymers were studied using differential thermal analysis (DTA) and thermogravimetric analysis (TG). The improvement of the light-stabilizing properties in the copolymers of

aminomethyl derivatives of alkenylphenols can be explained by the presence of an aminomethyl substituent in the ortho-position relative to the phenolic hydroxyl, where the intramolecular hydrogen bond in the stabilizer monomer, preserved after copolymerization, leads to the formation of a six-membered quasi-aromatic cycle with a benzene ring. The latter, in turn, helps to slow down the aging of the copolymer due to the rupture of the H-bond upon absorption of UV rays and the subsequent restoration of the original structure:



Thus, the obtained research results make it possible to use the synthesized compounds (**1** and **2**) as high-polymer environmentally friendly stabilizers, and aminomethyl derivatives of alkenylphenols - as monomer stabilizers of industrial polymers.

The reaction of 2-propenylphenol with formaldehyde and methylamine also was carried out at equimolar ratios of the initial reagents according to Mannich at a temperature of 65-70 °C with the formation of product 3 of the following structure:



3 (82%)

It is evident from the scheme that when carrying out the reaction of 2-propenylphenol, formaldehyde and methylamine in equimolar ratios, the reaction product is compound 3 (as expected) with a

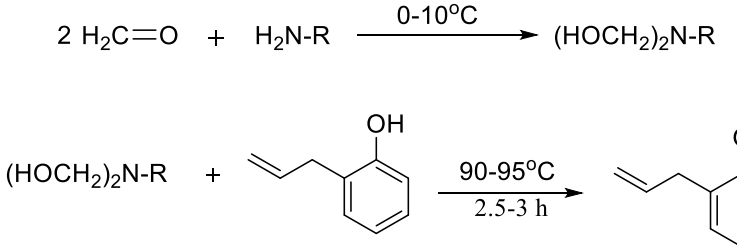
yield of 82%. The formation of compound 3 is confirmed by the presence of signals of OH- protons (6.26 ppm), NH-group (3.52 ppm).

The obtained aminomethyl derivatives (**1-3**) were used in further studies as precursors. The operational properties of compound **3** were also investigated.

Synthesis of allyl- and propenyl-substituted 1,3-benzoxazines

We set the goal of synthesizing 1,3-benzoxazines based on 2-allyl-, 2-propenyl- and 4-isopropenylphenols and studying the properties of the obtained products, previously not described in the scientific and technical literature.

Condensation of 2-allylphenol with formaldehyde and primary amines was carried out in the absence of a solvent according to the following reaction scheme:



15-21 62-73%

R = CH_3 (**15**), n-C_3H_7 (**16**), n-C_6H_{13} (**17**), n-C_8H_{17} (**18**), C_6H_5 (**19**), $C_6H_5CH_2$ (**20**), Br-C_6H_4- (**21**)

As can be seen from the scheme, the reaction of formaldehyde with primary amines occurs first at a low temperature range (0-10 °C). In the case of bromoaniline, its reaction with formaldehyde was carried out at a temperature of 25-30 °C due to its relatively low reactivity at lower temperatures (0-10 °C).

As for the reactivity of the amines taken in the work in the condensation reaction, in this case it is possible to draw a conclusion based on the yields of the target products, as well as on the theoretical foundations of the properties of amines. Based on the results of the experimental data and yields, as well as judging by the rate of the

reaction of formaldehyde with aliphatic amines, the activities of the amines taken can be arranged in the following sequence:

methylamine > n-propylamine > n-hexylamine > n-octylamine.

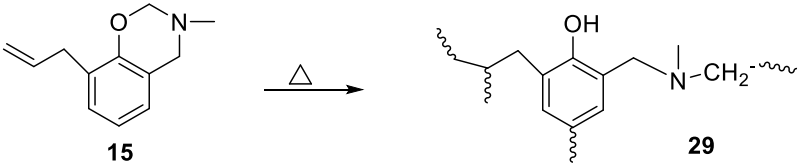
In aromatic primary amines, on the contrary, the basicity of the amines is relatively low and their activities in this case, judging by the yields of 1,3-benzoxazines, can be represented as follows:

benzylamine > aniline > bromoaniline.

The structures of the synthesized compounds were studied by IR and NMR spectroscopy.

It was found that the reaction of formaldehyde with primary amines in most cases, even at room temperature, leads to the formation of oligomeric and polymeric compounds. However, at the indicated temperature, the intermediate product of the reaction is the corresponding aminodicarbinol. The first stage of the reaction is carried out for 0.5 h. Then 2-allylphenol is added dropwise to the reaction mass and the reaction is carried out under the conditions shown in the scheme.

When the synthesized compound **15** – 8-allyl-3-methyl-3,4-dihydro-2H-benzo[e][1,3]oxazine is heated to 180°C, the product undergoes a thermal transformation with the opening of the oxazine ring, resulting in polymerization due to the oxazine ring and the double bond of the allyl group with the formation of polybenzoxazine **29** according to the following reaction scheme:



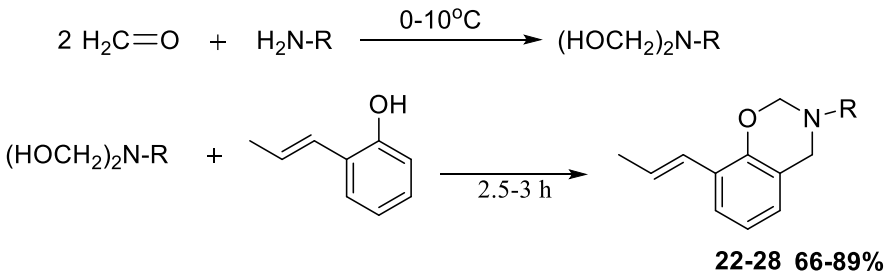
15 **29**

It is known that in the absence of a multiple bond in 1,3-benzoxazines, linear polymers are obtained. However, in the presence of an 8-substituted multiple bond (in our case, an allyl group) in 1,3-benzoxazine, a polybenzoxazine of a cross-linked structure is obtained (**29**). The resulting cross-linked polybenzoxazine (**29**) was purified by repeatedly washing it in dimethyl sulfoxide and dried under vacuum until a constant weight was achieved. Comparing the IR spectrum of compound **15** with the spectrum of polybenzoxazine **29**, it can be said that the

region related to the multiple bond is changed, and in the latter case, absorption bands of the OH group are also revealed, which confirms the opening of the benzoxazine ring, as well as cross-linking at the multiple bond. However, the remaining absorption bands can be said to coincide. Thermal and sorption properties of the obtained polybenzoxazine **29** were studied. The results of thermal analysis confirm the sufficient stability of polybenzoxazine (up to ~560 °C) **29**. It was established that the maximum degree of sorption is ~ 69% at pH 7.

The presence of a multiple bond in the structures of benzoxazines should contribute to their higher reactivity, and therefore, products obtained on the basis of alkenyl-substituted phenols obviously possess several useful properties at the same time. Therefore, in the indicated direction for the synthesis of a new series of benzoxazines, it is very expedient to carry out targeted reactions of phenols containing in the structures a multiple bond conjugated with an aromatic ring.

Therefore, for the first time the condensation reaction of 2-propenylphenol with formaldehyde and primary amines was carried out according to the following scheme:



22-28 66-89%

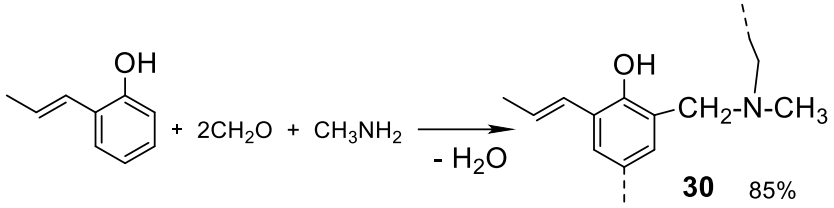
R = CH_3 (**22**), n-C_3H_7 (**23**), n-C_6H_{13} (**24**), n-C_8H_{17} (**25**), C_6H_5 (**26**), $C_6H_5CH_2$ (**27**), Br-C_6H_4- (**28**)

As can be seen from the obtained data, the reaction products in the case of 2-propenylphenol are obtained with comparatively high yields (66-89%). This can be explained by the comparatively high reactivity of the 2-propenylphenol molecule. As in the case of 2-allylphenol, in this case the yields also vary depending on the amine used. The maximum result (89%) can be achieved when using hexylamine as the amine. Product **28**, containing an N-bromophenyl-substituted substituent in the structure, is obtained with a comparatively lowest yield (66%). It should be noted that the reaction of formaldehyde

with methylamine, propylamine, hexylamine, octylamine, aniline and benzylamine occurs very quickly. Therefore, in this case, the reaction was carried out by cooling the initial reagents (formalin and the above primary amines) to 10°C for 0.5 h.

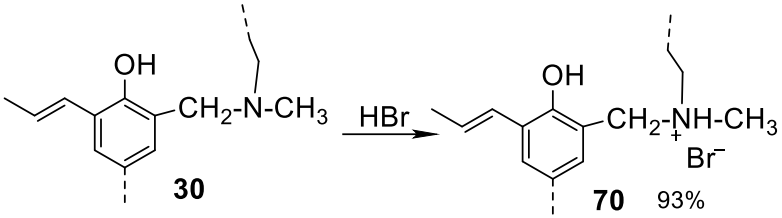
It is also important to note that in the scientific and technical literature, 1,3-benzoxazines obtained from phenols, substituted phenols, bis-phenols, etc. are synthesized in a solvent medium, for example, in a dioxane medium, which contributes to some difficulties in purifying the target product. However, the 1,3-benzoxazines synthesized by us based on 2-allyl- and 2-propenylphenols, due to the homogeneity of the initial reaction mixture, are carried out in the absence of a solvent, which leads to relatively high yields of the target products.

It was found that under identical conditions of formation of 1,3-benzoxazines, i.e. when carrying out a reaction of 2-propenylphenol with formaldehyde and methylamine at a ratio of 1:2:1 mol, respectively, and a temperature of 90-95 °C, an oligomeric compound is obtained - polybenzoxazine (**30**) of the following structure:

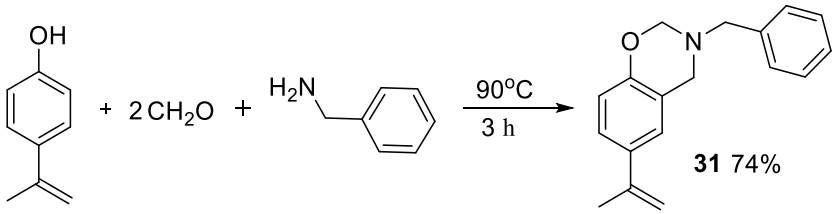


30 85%

The comparatively high reactivity of methylamine in comparison with other primary amines is also confirmed experimentally in its reaction with formaldehyde at 0-10°C, where the reaction proceeds with comparatively high exothermicity, as a result of which in this case the yield of benzoxazines is low in comparison with previously obtained results using other aliphatic and aromatic amines. Therefore, in order to obtain 1,3-benzoxazine based on methylamine, the reaction was carried out at a temperature of 70-75°C. In order to obtain a water-soluble polymer based on the condensation product **30**, it was treated with HBr and the corresponding ammonium salt **70** was obtained according to the following reaction scheme:



The obtained water-soluble polymer was investigated as a corrosion inhibitor for Ct. 3 steel in a water-salt hydrocarbon medium saturated with hydrogen sulfide at 25°C for 5 hours. The process of synthesis of 6-isopropenyl-substituted 1,3-benzoxazine (compound **31**) was carried out by condensation of 4-isopropenylphenol with formaldehyde (37% of its aqueous solution - formalin) and benzylamine at a temperature of 900°C, their ratio of 1:2:1 mol, respectively, and for 3 hours according to the following scheme:

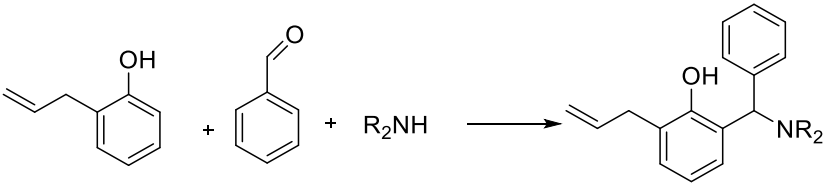


The ^{1}H NMR spectrum of compound **31** clearly revealed signals of protons of the CH_2 groups of the 1,3-oxazine ring (4.02 and 4.97 ppm). The NMR spectrum of compound **31** also revealed signals of protons of the multiple isopropenyl bond.

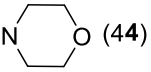
Synthesis of products of the condensation reaction of 2-allylphenol with benzaldehyde and primary or secondary amines

We also carried out for the first time the condensation reactions of 2-allylphenol with benzaldehyde and primary or secondary amines according to the Mannich reaction and studied the regularities of the process of formation of the final products. The primary amines n-propylamine, n-hexylamine, n-octylamine, aniline, benzylamine, and the secondary amines were diethylamine, diethanolamine, and morpholine were used. The triple condensation of 2-allylphenol with benzaldehyde and secondary amines (according to the Mannich reaction) was

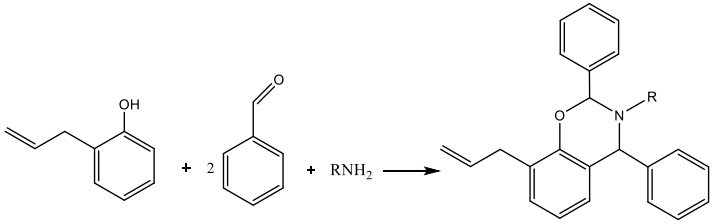
carried out at equimolar ratios of the reagents taken, a temperature of 80-85 °C, and a reaction time of 4 hours according to the following scheme:



42-44

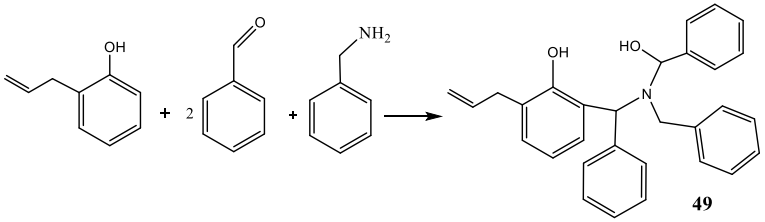
R = C_2H_5 (**42**), C_2H_4OH (**43**), R_2N=  (**44**)

The products obtained with yields of 66, 69 and 80%, respectively, are highly viscous compounds of dark brown color. The reaction of 2-allylphenol with benzaldehyde and primary amines was carried out primarily by interaction of benzaldehyde and primary amine at a temperature of 5-10 °C and stirring for 0.5 h with subsequent addition of calculated amounts of 2-allylphenol to the reaction medium. Then the mixture was stirred for 3-3.5 h at 90-95 °C according to the following reaction scheme:



45-48

R = methylamin (**45**), n-propylamine (**46**), n-hexylamine (**47**), n-oktylamine (**48**).



49

Based on the results of spectral analyses and schemes, it can be said that the triple condensation reaction of 2-allylphenol with benzaldehyde and primary aliphatic amines (propylamine, hexylamine and octylamine) proceeds with the formation of 1,3-benzoxazine.

However, under identical conditions, when using benzylamine, the reaction in the direction of the formation of the 1,3-oxazine ring does not proceed, which can presumably be explained by the steric factor. The presence of a 1,3-benzoxazine ring in the case of aliphatic amines is confirmed by the presence of signals of the protons of the CH groups in the oxazine ring (5.28 and 5.9 ppm in the case of propylamine, 5.35 and 5.98 ppm in the case of hexylamine), as well as the absence of signals of the OH group of 2-allylphenol. The shift of the singlets of the protons of the CH groups to a weak field is apparently due to the presence of substituted aromatics in the structure. In this case, the aromatic ring is located close to the protons of the CH groups, and, apparently, their deshielding occurs here.

Study of the thermal properties of synthesized alkenyl substituted 1,3-benzoxazines and aminomethyl derivatives of 2-allylphenol

The thermal stability of the synthesized unsaturated 1,3-benzoxazines and other Mannich bases was studied in a NETZSCH STA 449F3 device in an inert environment. The results of the analyses are shown in Figure 1.

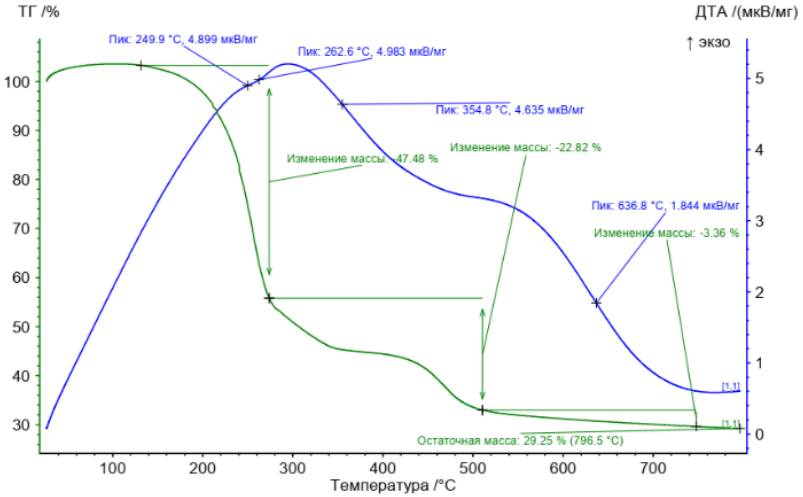


Figure 1. Results of TG and DTA analysis of 8-allyl-3-propyl-3,4-dihydro-2H-benzo[e][1,3]oxazine (16)

As can be seen from the derivatogram, the process is exothermic due to the transformations occurring within the 1,3-benzoxazine molecule. This state can be explained by the opening of the benzoxazine ring and the formation of an oligomeric structure with its subsequent transformation into high-molecular polybenzoxazine. Here, the opening of the multiple allyl bond cannot be ruled out. Initially, a sharp loss of mass (up to 47%) occurs from a temperature of 140 °C, then it stabilizes in the temperature range of 320-440 °C, and then a 20% loss of mass of the sample occurs again.

Similar results are also observed in the case of compounds **16** and **17**, which differ in structure only by the number of methylene units. However, in the presence of an N-hexyl substituent in the molecule of allyl-substituted 1,3-benzoxazine, a comparatively high thermal stability is observed. The presence of a comparatively long alkyl substituent in compound **18** does not exert a special effect on the change in the thermal stability of the product. Almost all thermograms of the samples show an exothermic peak before the loss of sample mass. In all studies, this indicates intramolecular addition.

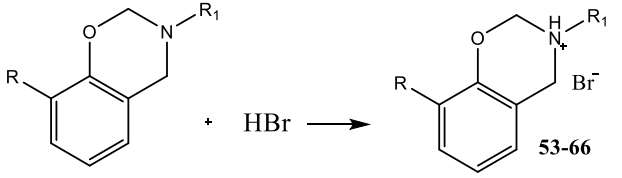
In order to compare the thermal properties of the triple condensation products - 8-alkenyl-substituted 1,3-benzoxazines (compounds **16-19, 23-25, 27**), comparative studies of the condensation products of 2-allylphenol with benzaldehyde (instead of formaldehyde) and amines (compounds **42**, **44**, **45**) were carried out. Based on the results of the thermal studies, it can be concluded that 1,3-benzoxazines and other synthesized Mannich bases are sufficiently stable, which allows them to be used at higher temperatures as corrosion inhibitors, bactericides, viscosity-temperature additives to petroleum products, etc. It has been shown that among the compounds studied, compounds with an additional aromatic ring, i.e. compounds obtained on the basis of 2-allylphenol, benzaldehyde and amines, have comparatively high thermal properties.

Preparation of 8-allyl- and 8-propenyl-substituted 1,3-benzoxazinium bromides and hydrobromides of aminomethyl derivatives of 2-allyl- and 2-propenylphenols

In order to compare the performance properties of the compounds we obtained, ammonium compounds **53-70** were also

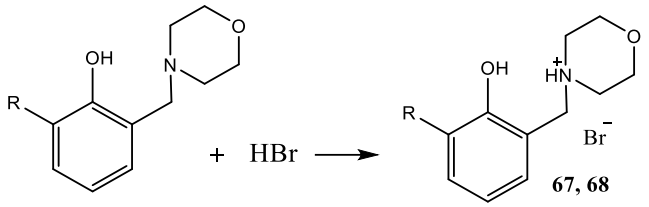
synthesized on their basis and their anticorrosive and bactericidal properties were studied in comparison with the initial products.

Ammonium salts were obtained by the interaction of the synthesized allyl and propenyl-substituted 1,3-benzoxazines, as well as Mannich bases, with hydrogen bromide at room temperature for 0.5 h according to the following schemes:



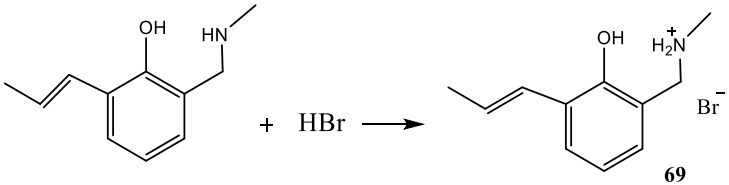
53-66

R = CH_2-CH=CH_2: R_1 = CH_3 (**53**), C_3H_7 (**54**), C_6H_{13} (**55**), C_8H_{17} (**56**), C_6H_5 (**57**), CH_2-C_6H_4 (**58**), C_6H_4-Br (**59**);
R = CH=CH-CH_3: R_1 = CH_3 (**60**), C_3H_7 (**61**), C_6H_{13} (**62**), C_8H_{17} (**63**), C_6H_5 (**64**), CH_2-C_6H_4 (**65**), C_6H_4-Br (**66**)



67, 68

R = CH_2-CH=CH_2 (**67**), CH=CH-CH_3 (**68**)



69

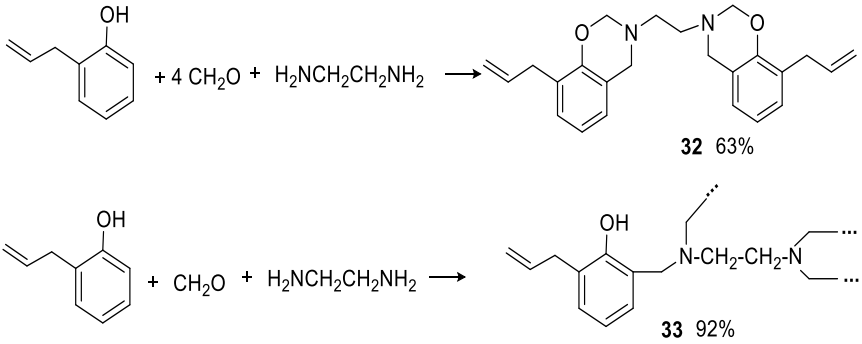
According to the characteristics of the synthesized ammonium salts, their yields are high and amount to 69-94%. The highest yields (88-94%) are possessed by compounds containing propenyl, hexyl, benzyl and bromophenyl substituents in the structures. All synthesized ammonium salts are solid powder or crystalline compounds of white, yellow, light green, orange, light brown colors, well soluble in water, alcohols, chloroform, dimethyl sulfoxide. In the ^{1}H NMR spectra of

ammonium compounds, signals of NH-group protons are clearly revealed within 4.0 ppm. In the IR spectra of ammonium compounds, in comparison with the initial 1,3-benzoxazines, as well as aminomethyl derivatives, stretching vibrations of the absorption band of the NH group, as well as absorption bands of Br ions are revealed.

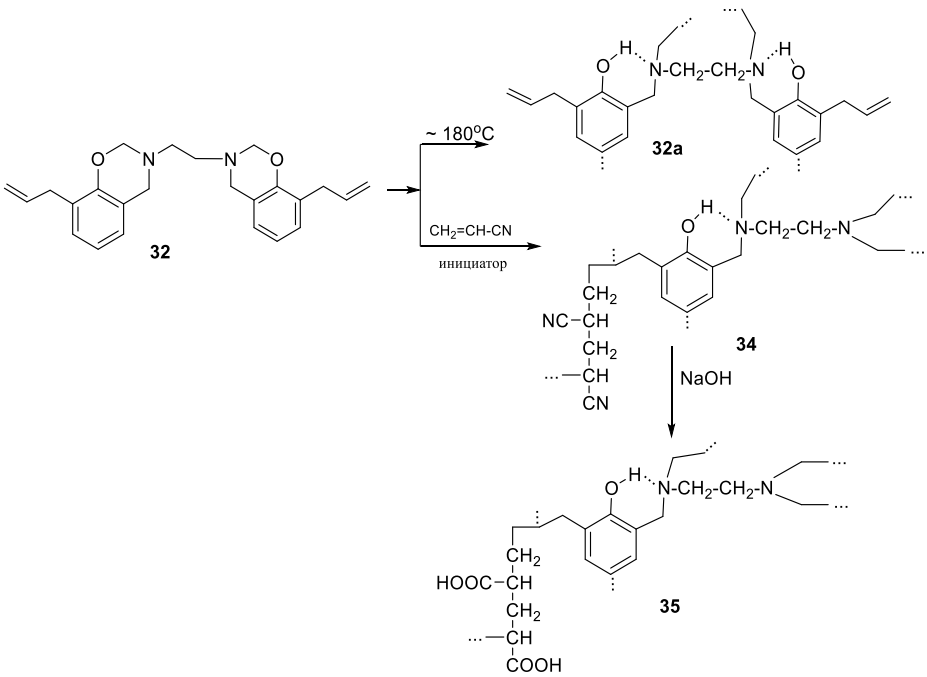
Triple condensation of 2-allylphenol with formaldehyde and ethylenediamine and transformations of reaction products

To compare the properties and structure of the obtained products, we carried out a triple condensation of 2-allylphenol, formaldehyde and ethylenediamine in two ratios: 1) 1:2:0.5 (mol) (under the conditions for obtaining benzoxazine - 1,2-bis(8-allyl-2H-benzo [e][1,3]oxazin-3(4H)-yl)ethane (**32**) and 2) 0.5:4:1 (mol) (to obtain oligomer **33**), respectively.

It was found that with a molar ratio of 2-allylphenol, formaldehyde and ethylenediamine of 1:2:0.5 (mol), benzoxazine **32** is obtained with a yield of 63%, and with a ratio of 0.5:4:1, co-oligomer **33** is obtained with a yield of 92% according to the following scheme:



The study of the structure of the synthesized benzoxazine - 1,2-bis(8-allyl-2H-benzo[e][1,3]oxazin-3(4H)-yl)ethane (**32**) by NMR and IR spectroscopy showed that 1,3-benzoxazine fragments are formed. Heating of benzoxazine **32** to 180 °C experimentally led to the formation of product **32a** according to the scheme:



As can be seen from the scheme, in the self-structuring product (**32a**), in comparison with the initial benzoxazine **32**, an absorption band of the OH group is revealed, a multiple bond (1638 cm^{-1}, 994 cm^{-1}) is preserved, and a hydrogen bond is formed, which is confirmed by the IR spectral data by a wide absorption band (3400 cm^{-1}).

The structure of compound **32** was also modified with acrylonitrile in the presence of an initiator and the hydrolysis of the resulting product 34 with sodium hydroxide was carried out to obtain polymer **35**, which contains carboxyl groups in the structure. When compound **32** is structured with acrylonitrile (**34**), an absorption band of the nitrile group (2240 cm^{-1}) appears in the IR spectrum.

The thermal properties of the hydrolysis product (**35**) were studied by the derivatographic method. As can be seen from the results of thermal studies (Fig. 2), the initial temperature of mass loss of polybenzoxazine **35** begins at ~410°C.

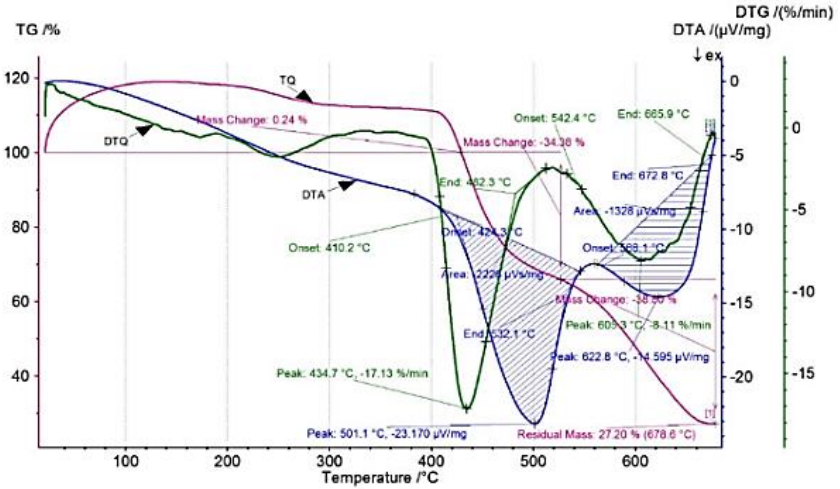


Figure 2. Results of thermogravimetric and differential thermal analysis of cross-linked copolymer 35

The effect of pH of the medium on the degree of sorption of uranyl ions and on the sorption capacity of the **35** modifier was studied under statistical conditions (temperature 25°C, initial concentration of uranyl ions in water 134.5 mg/l, holding time 24 h).

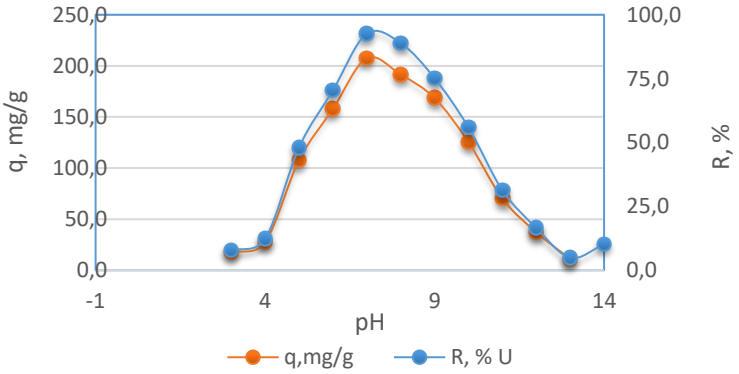


Figure 3. Dependence of the degree of sorption (R) of uranyl ions and the sorption capacity (q) of the sorbent (35) on the pH of the solution

Sorption studies were carried out at the National Center for Nuclear Research under the Ministry of Digital Development and Transport. From Figure 3 it is evident that a high degree of extraction of uranyl ions (R) from the aqueous medium (92.6%) is achieved at pH 7. In this case, the sorption capacity (q) is ~207.5 mg/g.

The sorption capacity of polybenzoxazine **35** is confirmed by IR spectra before and after sorption. A clear change and shift of the signals of the carbonyl (1776 cm^{-1}) and OH groups is observed in the spectrum.

The effect of the duration of sorption of polybenzoxazine **35** on the degree of sorption of uranyl ions was studied. Maximum sorption of uranyl ions is achieved in 1440 min (24 h). The degree of sorption in this case is 92.6%, q ~ 207.5 mg/g.

Table 1

Results of studies on the extraction of microelements from oil formation waters A and B by sorbent 35

Microelements in oil formation water	Sorption degree of microelements from oil formation water A, %	Sorption degree of microelements from oil formation water B, %
K	96.6	~99.9
Na	~100	~100
Ca	99.0	~99.2
Ba	97.6	96.5
Zn	100	~100
Cd	-	94.6
Cu	100	100
Hg	99.7	100
Fe	95.5	96.0
Cr	100	100
Mn	100	100
As	100	98.9
Se	99.0	99.1
Ni	-	90.0

It should be noted that when studying the sorption properties of polybenzoxazine **34**, which contains a nitrile group in its structure, the degree of extraction of uranyl ions at pH = 7 is 69.4%, q ~ 156.8 mg / g. Comparatively low sorption properties can be explained by the absence of a carboxyl group in copolymer **34**, which confirms the importance of the hydrolysis process of the nitrile group.

Studies were also conducted to extract microelements from oil field waters of two fields (A and B): Lokbatan (Karadag district) (well 260) (A) and Bibieybat (Sabail district) (well 748) (B). First of all, microelements were determined by a quantitative flame ionization method using an ICP MS 7700e apparatus manufactured by Agilent, USA. As can be seen from the results of comparative studies (Table 1), the structure of the modified oligomer used as a sorbent has a significant effect on the process of extracting microelements from the formation water environment. As can be seen from Table 1, 100% sorption is achieved in formation water A for Na, Zn, Cu, Hg, Cr, Mn and As. For K, Ca, Ba, Fe and Se, the degree of sorption by sorbent 35 is slightly lower than 100% (96.6-99.7%). Similar results were achieved in the case of oil reservoir B.

Synthesis, transformation and study of co-oligomer 33 based on 2-allylphenol, formaldehyde and ethylenediamine

The results of the IR spectra analysis showed that despite the amount of formaldehyde taken in sufficient quantity (4 mol), co-oligomer **33** is formed of a linear structure, i.e. electrophilic substitution in this case is carried out mainly in the ortho-position of 2-allylphenol, based on the presence of absorption bands of deformation vibrations of the C-H tri-substituted aromatic ring in the IR spectrum (749 cm^{-1}).

The molecular weight of co-oligomer **33** was determined by chromatography.

In order to confirm the results of thermal studies of co-oligomer **33**, self-structuring was carried out at a temperature of 280 ° C according to the following scheme:

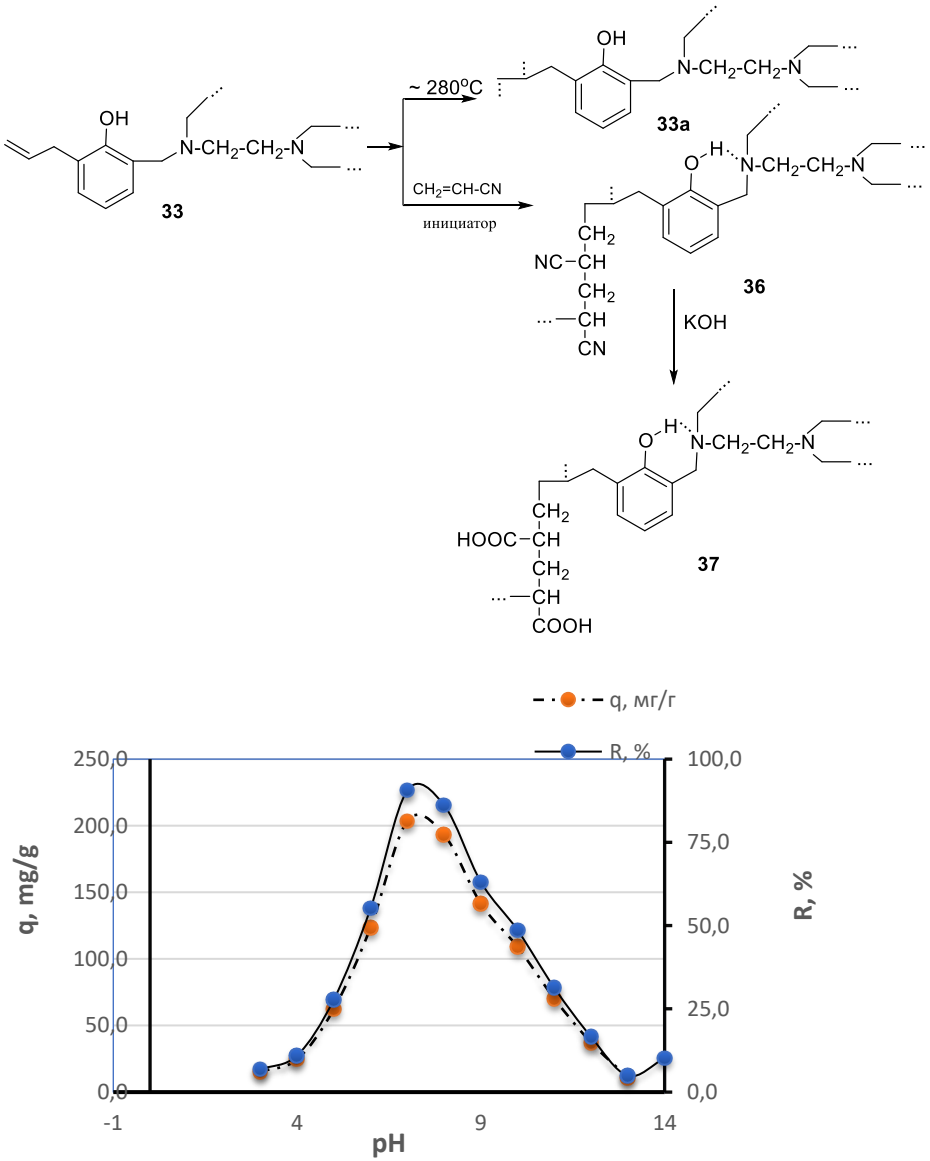


Figure 4. Dependence of the degree of sorption (R) of uranyl ions and the sorption capacity (q) of sorbent 37 on the pH of the solution

As can be seen from the scheme, the obtained product **33a** does not contain a multiple bond. The absence of a multiple bond is confirmed by the IR spectra. As shown in the above scheme, the modification of co-oligomer **33** with acrylonitrile was carried out in the presence of 2% initiator (based on the sum of the taken amounts of co-oligomer and acrylonitrile) - benzoyl peroxide (BPO), at 80^0C, for 10 hours. The cross-linked polymer **36** obtained with a yield of 94% is insoluble and yellow. Hydrolysis of the acrylonitrile-structured co-oligomer (**36**) was carried out in the presence of a 10% aqueous solution of sodium hydroxide by boiling for 10 h. It can be seen from Figure 4 that a high degree of extraction of uranyl ions (R) from an aqueous medium (90.8%) is achieved at pH 7. In this case, the sorption capacity (q) is ~204 mg/g.

The sorption properties of sorbent **37** are also confirmed by the results of IR spectra (Figure 5), EDX (Figure 6) and scanning electron microscopy (SEM) (Figure 7). As can be seen from Figures 6 and 7, the elemental composition of polymer **37**, as well as the sorbed uranyl ions, are clearly revealed. The data obtained once again confirm the implementation of the uranium sorption process by polymer **37**. In addition, Figure 7 1-4 shows a uniform distribution of the sorbent **37** granule after the sorption of uranyl ions, where the uranium signals are clearly revealed (Figure 7-4). Based on the results, a conclusion was made about the sorption process occurring both on the surface and in the volume (in granules) of sorbent **37.**

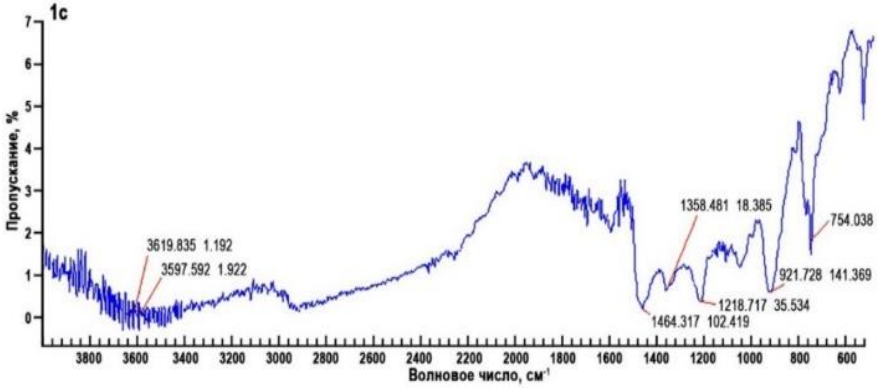


Figure 5. IR spectrum of copolymer 37 after sorption

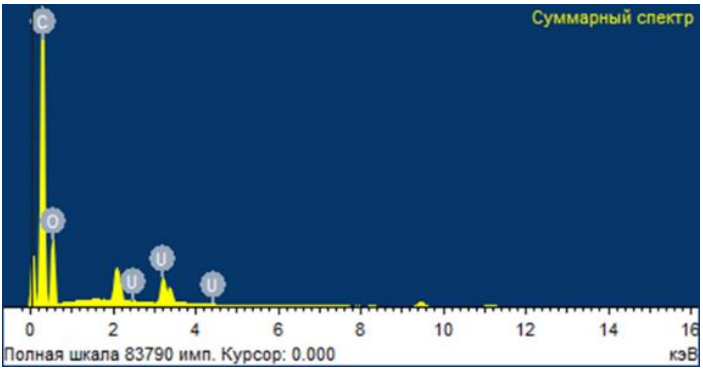


Figure 6. EDX spectrum of the sorbent 37

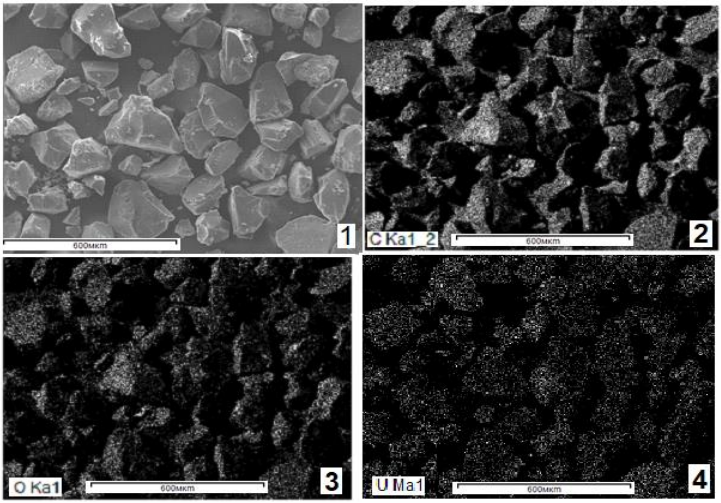


Figure 7. SEM images of a sample of modified oligomer 37 after sorption: 1 - image of a sample of polymer 37 under a microscope, 2 - presence of carbon in sample 37, 3 - presence of oxygen in 37, 4 - presence of uranium in 37

To study the possibility of regenerating sorbent **37**, desorption of bound uranyl ions (100 mg/g) with solutions of nitric and hydrochloric acids was studied. It was found that as the concentration of both acids increases, the desorption of uranium from the sorbent increases. Maximum desorption occurs at a concentration of mineral acids equal to 0.5 M. It was found that during desorption of uranyl ions

with nitric acid, the degree of desorption is 90.3%, and during desorption with hydrochloric acid - 91.2%.

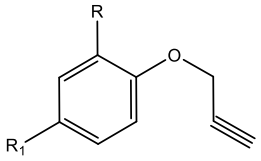
For comparison, sorption studies were also conducted on a co-oligomer based on 4-isopropenylphenol and maleic anhydride structured with ethylenediamine and formaldehyde, and its effectiveness with respect to uranyl ions and heavy metals was revealed.

Thus, the oligomers obtained on the basis of 2-allyl and 4-isopropenylphenol, polybenzoxazines and their modified derivatives have sufficiently high thermal stability, and the modified derivatives have sufficiently high sorption properties for trapping uranyl ions from aqueous systems, as well as for extracting heavy metals from oil formation waters of Azerbaijan fields.

Synthesis of propargyl derivatives of 2-allyl-, 2-propenyl-, 4-isopropenylphenols and alkenyl-substituted 1,3-benzoxazines

In order to synthesize propargyl derivatives of allyl- and propenylphenylphenols, as well as alkenyl-substituted 1,3-benzoxazines, reactions of propargyl bromide with the above compounds were carried out in order to compare and identify their inhibitory, biocidal and other properties.

The production of propargyl ethers of alkenylphenols of the following structures was carried out by reaction with propargyl bromide at a temperature of 80-85 °C, for 4 hours in the presence of an alcoholic (isopropyl alcohol) solution of KOH in an isopropyl alcohol medium:



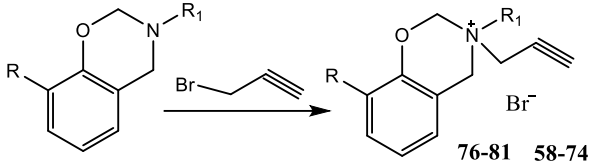
71-75

R = -CH=CH-CH_3, R_1=H (**71**)
R = -CH=CH-CH_3, R_1=CH_3 (**72**)
R = -CH_2-CH=CH_2, R_1=H (**73**)
R = -CH_2-CH=CH_2, R_1=CH_3 (**74**)
R = H, R_1 = CH_3-C(=CH_2)- (**75**)

The products obtained in yields of 84-96% are viscous compounds from dark yellow to dark brown in color. Comparatively high yields are obtained for the compounds in the case of propargyl ethers of alkenylphenols themselves.

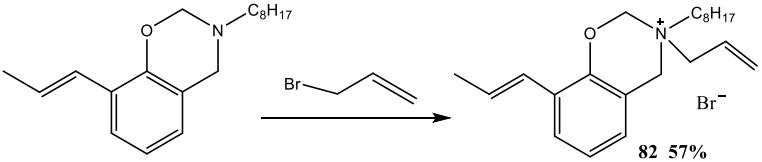
From the ^{1}H NMR spectra of compounds **71-75**, signals of CH≡ protons at 2.34-2.8 ppm in the form of triplets, signals of CH_2 protons in the form of singlets at 3.9-4.87 ppm are clearly revealed.

The values of the signals change depending on their structure. These signals confirm the formation of propargyl ethers of alkenylphenols and their derivatives. The synthesis of water-soluble ammonium salts (**76-83**) was carried out in a benzene medium at a temperature of 45-50°C for 3 hours at a molar ratio of substrate: propargyl bromide (or allyl bromide) of 1:1.2 according to the following schemes:

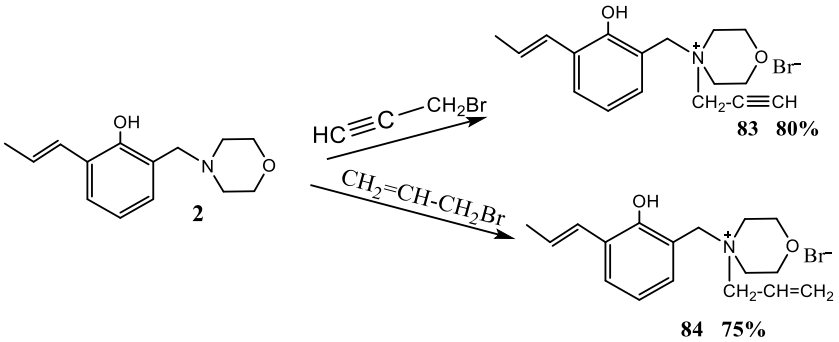


76-81 58-74%

R = -CH_2-CH=CH_2, R_1 = C_3H_7 (**76**); R = -CH_2-CH=CH_2, R_1 = C_6H_{13} (**77**);
R = -CH_2-CH=CH_2, R_1 = C_6H_5 (**78**); R = -CH_2-CH=CH_2, R_1 = -CH_2-C_6H_4 (**79**);
R = -CH_2-CH=CH_2, R_1 = C_6H_4-Br (**80**); R = -CH=CH-CH_3, R_1 = C_6H_5 (**81**)



82 57%



2

83 80%

84 75%

The maximum yield can be achieved by using the morpholinomethyl derivative of 2-propenylphenol (comp. **2**) as a substrate, where the yields of compounds **83** and **84** are 80 and 75%, respectively.

Spectral data have proven that the 1,3-oxazine ring is preserved when obtaining propargyl and allylated salts. For example, in

compound 81, singlets of protons of the CH_2 groups in the oxazine ring are clearly detected at 4.6 and 5.4 ppm. In the synthesized compounds, protons of the propargyl and allyl fragments are also clearly detected. Thus, we have obtained esters and water-soluble ammonium salts based on alkenylphenols and their derivatives of various structures, as well as allyl- and propenyl-substituted 1,3-benzoxazines and morpholinomethyl derivative of 2-propenylphenol, containing in their structures simultaneously fragments with C=C and C≡C bonds and other functional groups. The ways of practical application of the synthesized multifunctional compounds have been studied and a correlation of their operational properties depending on their structure has been given.

Study of 2-allyl- and 2-propenylphenol derivatives, 1,3-benzoxazines as corrosion inhibitors in aqueous, salt and hydrocarbon environments saturated with hydrogen sulfide

In order to identify the anticorrosive properties of the synthesized heteroatom-containing functionally substituted compounds, systematic studies of their inhibitory properties of the synthesized compounds in water-salt hydrocarbon systems in the presence of various acids (H_2SO_4, H_2S, etc.) were carried out and a correlation was established between the anticorrosive properties and the structure of the compounds under study.

Anticorrosion studies were carried out in an aqueous-salt kerosene-containing environment saturated with hydrogen sulfide, in a sulfuric acid solution, as well as in formation water saturated with hydrogen sulfide and carbon dioxide, and a conclusion was made about the properties of the studied products depending on their structures, concentrations, and conditions of corrosion tests. Corrosion testing of synthesized ammonium salts (**64, 65, 82, 83**) in their concentrations of 50 and 100 mg/l was carried out in a medium of 3% NaCl and kerosene (with a ratio of aqueous solution and kerosene of 9:1 vol.), saturated with hydrogen sulfide. As can be seen from Table 2, the studied ammonium salts **67, 68, 83, 84** have an anticorrosive effect in a water-salt, kerosene-containing medium saturated with hydrogen sulfide. From the results it is evident that the highest inhibitory activity is

possessed by compounds containing in the structures, in addition to the propenyl substituent in the aromatic ring, also fragments with an allyl and propargyl substituent at the nitrogen atom of the morpholinomethyl group. It was revealed that the specified compounds (**83** and **84**) at their concentration of 50 and 100 mg/L have a degree of protection against corrosion of 89.3 and 91.9% in the case of a compound with an allyl fragment (**83**), 93.4 and 96.9% - with a propargyl substituent (**84**), respectively.

Table 2

Results of anticorrosive studies of ammonium salts in a water-salt-hydrocarbon medium saturated with hydrogen sulfide. Conditions: temperature 25 ° C, time 5 hours

Compound	Consentration, mg/L	Corrosion rate, g/m^{2}hour	Protection degree, %
4-(3-Allyl-2-hydroxybenzyl)morpholine-4-ium bromide **(67)**	50	1.3631	69.3
	100	1.1366	74.4
(E)-4-(2-Hydroxy-3-(prop-1-en-1-yl)benzyl)morpholin-4-ium bromide **(68)**	50	1.1722	73.6
	100	0.5949	86.6
(E)-4-(2-Hydroxy-3-(prop-1-en-1-yl)benzyl)-4-(prop-1-en-1-yl)morpholin-4-ium bromide **(83)**	50	0.4751	89.3
	100	0.3596	91.9
(E)-4-(2-Hydroxy-3-(prop-1-en-1-yl)benzyl)-4-(prop-1-in-1-yl)morpholine-4-ium bromide **(84)**	50	0.2931	93.4
	100	0.1376	96.9
Without inhibitor	-	4.44	-

It is also evident from Table 2 that ammonium salts based on the morpholinomethyl derivative of 2-allyl- (**67**) and 2-propenylphenols (**68**) also have an inhibitory effect. Compounds **67** and **68** in identical concentrations have a degree of protection of 69.3 and 74.4% for **67**, 73.6 and 86.6% for **68**, respectively. Based on the results of the studies, the compounds can be arranged in the following sequence according to their inhibitory activity: **84**>**83**>**68**>**67**. The presence of multiple bond fragments, N-substituted functional substituents, quaternary ammonium groups and Br-anions in the structures of

compounds **16-21** and **54-59** allows them to be considered as potential corrosion inhibitors, biocides in oil production, etc.

Table 3 shows that the studied 1,3-benzoxazines **16-21** in concentrations of 50, 100 and 150 mg/L have inhibitory properties. Compounds **57-59** with an aromatic substituent have the highest inhibitory activity, where at a concentration of 150 mg/L the maximum degree of protection is 94%). Among them, the compound with a bromophenyl substituent (**21**) has the highest degree of protection. Among 1,3-benzoxazines with alkyl substituents, compound **18**, which contains an octyl substituent in its structure (at a concentration of 150 mg/L, the degree of protection is 82.8%), has the highest degree of protection.

In order to identify the effect of a multiple allyl bond on the anticorrosive properties of the studied compounds **16-21**, 1,3-benzoxazine was synthesized by an identical method based on phenol, formaldehyde and aniline, which was studied as an inhibitor of hydrogen sulfide corrosion of steel at a concentration of 150 mg/L. It was shown that the studied compound without an allyl substituent at a concentration of 150 mg/L has an inhibitory effect of 50.3%.

The obtained research results allow us to emphasize the importance of the allyl fragment in the 1,3-benzoxazine molecule in anticorrosive studies. The presence of electron density in the allyl fragment apparently results in additional adsorption on the metal surface.

Taking into account the high inhibitory properties of the synthesized 1,3-benzoxazines with an aromatic substituent (**19-21**), the goal was to study their anticorrosive properties at a relatively low concentration (50 mg/L) (Table 3). It was revealed that the studied compounds **19-21** at the specified concentration have a degree of protection of 65, 81 and 88%, respectively.

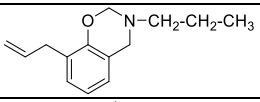
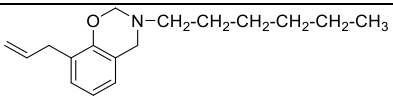
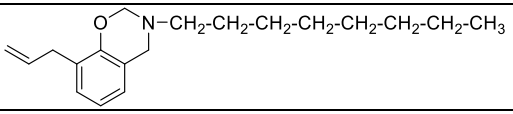
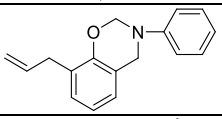
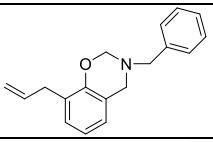
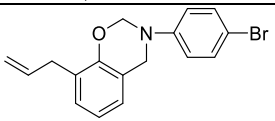
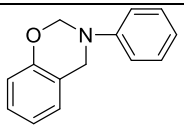
Thus, when replacing the N-alkyl substituent with an N-aromatic substituent in allyl substituted 1,3-benzoxazines, the increase in inhibitory properties is explained by the additional content of the π system in the molecule, due to which adsorption on the metal surface occurs.

In continuation of the studies, ammonium salts were obtained based on allyl substituted 1,3-benzoxazines, which are of great interest

from both a practical and theoretical point of view. As can be seen from Table 4, when passing from 1,3-benzoxazines **16-21** to their ammonium salts **54-59**, an increase in the inhibitory activity of the studied compounds is observed.

Table 3

Results of anticorrosion studies of compounds 16-21 in a water-salt-hydrocarbon medium saturated with H_2S

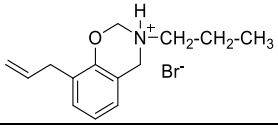
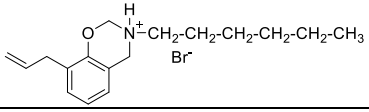
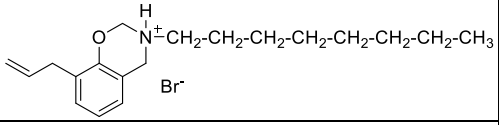
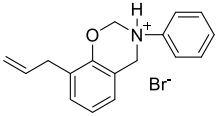
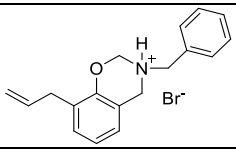
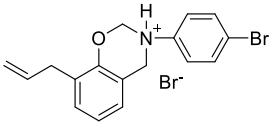
№	Compounds	Concentration, mg/L	K, g/m^2h	Z, %
16		100 150	2.1720 1.9802	51.3 55.6
17		100 150	1.6368 0.8940	63.3 79.9
18		100 150	1.5119 0.7651	66.1 82.8
19		50 100 150	1.5592 0.7209 0.3897	65.0 83.8 91.3
20		50 100 150	0.8295 0.4906 0.3129	81.4 89.0 93.0
21		50 100 150	0.5352 0.4460 0.2480	88.0 90.0 94.4
		150	2.2166	50.3
	Without inhibitor		4.46	

To confirm the results of the conducted anticorrosion studies, as well as the sorption capacity of the studied compounds on the

surface of steel St.3, analyzes were carried out using elemental analysis, scanning electron microscopy (SEM) and EDX on the surface of steel St.3 before and after corrosion.

Table 4.

Results of anticorrosion tests of compounds 54-59 in a water-salt-hydrocarbon (kerosene) environment saturated with hydrogen sulfide

	Compound	Cons., mg/L	K, g/m^{2}h	Z, %
51		50 100	1.6234 1.2934	63.6 71.0
52		50 100	1.3826 0.8920	69.0 80.0
53		50 100	1.6769 0.7804	62.4 82.5
54		50 100	0.6289 0.2944	85.9 93.4
55		50 100	0.4460 0.2007	90.0 95.5
56		50 100	0.3523 0.1383	92.1 96.9
	Without inhibitor	–	4.46	–

As can be seen from the results of the analysis of steel plates after corrosion (Table 5 and Figures 8 and 9), almost the complete elemental composition of the plates is revealed, as well as the sorbed substance (**21**) on its surface. From Table 5 it is clear that all elements of the adsorbed substance on the surface of steel St.3 are revealed. The

results (Table 5) also show that in the absence of compound **21**, the same absence of nitrogen and a relatively small amount of carbon and oxygen are observed.

As can be seen from the SEM results (Figure 9), in the absence of inhibitor **21** (A), a corrosion process is observed on the surface of the steel plate St.3, where a change in the smooth surface of the sample occurs after corrosion and cracks are formed. However, in the presence of compound **21**, obvious adsorption is detected on the steel surface. The data obtained once again confirm the inhibitory effect of compound **21**.

The surface of the steel plate after the corrosion process in the presence of compound **59** was analyzed in a similar manner. The results of the analysis are shown in the SEM image (Figure 10) and EDX (Figure 11).

Table 5

Elemental composition of the surface of steel St.3 after corrosion in the absence and presence of compound 21

Element	Weight, %	Atomic, %	Element	Weight, %	Atomic, %
In the absent of compound **21**			In the presence of compound **21**		
C K	15.77	45.54	C K	41.63	71.07
			N K	1.92	2.81
N K	0.00	0.00	O K	5.84	7.49
O K	1.39	3.01	Si K	0.13	0.09
Mn K	0.46	0.29	Mn K	0.27	0.10
Fe K	82.38	51.16	Fe K	48.61	18.44
			Br K	1.60	1.28
Total	100.00		Total	100.00	

The obtained data once again confirm the anti-corrosion properties of the synthesized compounds, as well as their adsorption properties on the surface of the steel plate.

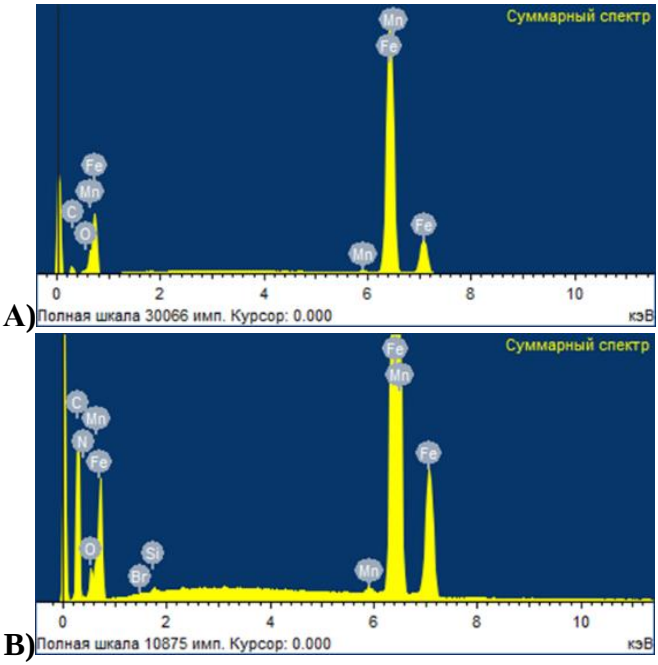


Figure 8. EDX of the plate surface after corrosion in the absence (A) and presence (B) of compound 21

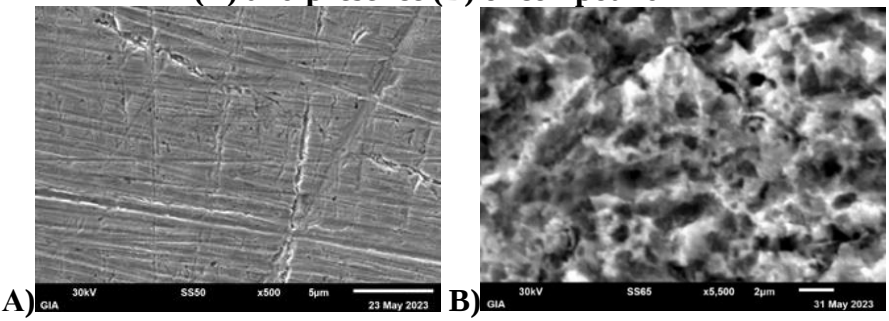


Figure 9. SEM images of the surface of a steel plate before (A) and after (B) corrosion in the presence of compound 21

Condensation products of 2-propenylphenol, formaldehyde and methylamine in concentrations 50 and 100 mg/L were studied as inhibitors of corrosion of St.3 steel in a water-salt hydrocarbon medium saturated with hydrogen sulfide at a temperature of 25°C and a time of 5 h.

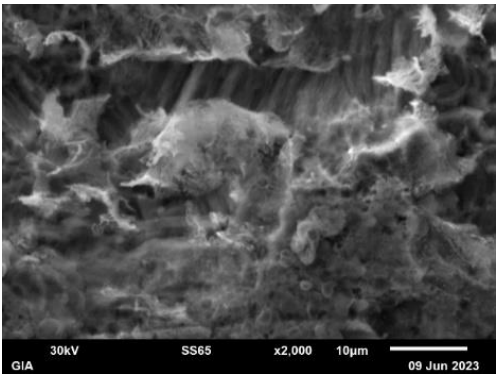


Figure 10. SEM images of the surface of the steel plate after corrosion in the presence of compound 59

As can be seen from the results (Figures 10 and 11), in the corrosion process in the presence of compound **59**, obvious adsorption occurs on the surface of the steel plate St.3.

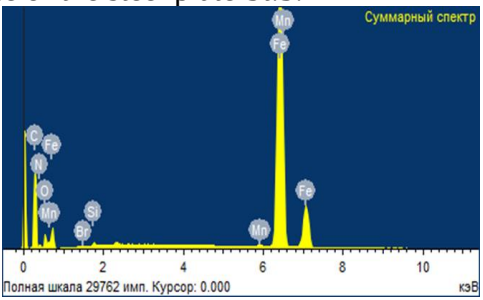


Figure 11. EDX of the plate surface after corrosion in the presence of compound 59

It was established that the studied 1,3-benzoxazines (**22,60**), aminomethyl derivatives (**3,69**) and ammonium salt of polybenzoxazine (**70**) have inhibitory properties in concentrations of 50 and 100 mg/L. Compounds **60, 69** and **70** have the maximum inhibitory activity. This is probably due to their good solubility in water, as well as the presence of an ammonium fragment, as well as a bromine anion. This is probably also due to their high chemisorption properties on the surface of steel St.3.

Tables 6 and 7 present the results of anticorrosive tests of functionally substituted derivatives of allyl and propenylphenols containing fragments with C=C and -C≡C bonds in their structures (compounds **71-75**).

As can be seen from the results of anticorrosive tests (Tables 6 and 7), all compounds that we studied have protective properties with respect to unalloyed steel St.3 in model aqueous systems containing 3% NaCl, various hydrocarbons (kerosene) and hydrogen sulfide (500 mg/L). In the structures of these compounds, substituents with mobile π-electrons (C=C and C≡C) are present in the aromatic ring (Table 6).

Table 6

Results of anticorrosive tests of compounds 71-75 in a water-salt kerosene-containing medium saturated with hydrogen sulfide

Формула соединения	Concentration, mg/L	25^0C		40^0C	
		Corrosion rate, g/m^{2}hour	Protection degree, %	Corrosion rate, g/m^{2}hour	Protection degree, %
(E)-1-(Prop-1-en-1-yl)-2-(prop-2-in-1-yloxy)benzene (**71**)	50 100	0.6467 0.5352	85.5 88.0	1.014 0.8467	80.0 83.3
(E)-4-Methyl-2-(prop-1-en-1-yl)-2-(prop-2-in-1-yloxy)benzene (**72**)	50 100	0.7983 0.6021	82.1 86.5	1.3486 0.9937	73.4 80.4
1-Allyl-2-(prop-2-in-1-yloxy)benzene (**73**)	50 100	0.8831 0.6868	80.2 84.6	1.4703 1.0495	71.0 79.3
1-Allyl-2-(prop-2-in-1-yloxy)benzene (**74**)	50 100	0.9812 0.8028	78.0 82.0	1.5717 1.2574	69.0 75.2
1-(Prop-1-en-2-yl)-4-(prop-2-in-1-yloxy)benzene (**75**)	50 100	0.5352 0.4371	88.0 90.2	0.9177 0.6946	81.9 86.3
(Prop-2-in-1-yloxy)benzene (for comparing)	50 100	1.2666 1.4183	68.2 71.6	2.8189 2.0787	44.4 59.0
Without inhibitor		4.46	-	5.07	-

To identify the inhibitory effect of the double and triple bond, corrosion studies were carried out under identical conditions and concentrations in the presence of propargyl ether of phenol, a compound obtained using an identical method for comparing anticorrosive properties. It was found that in the absence of an alkenyl substituent, the inhibitory property sharply decreases to 71% at a concentration of 100 mg/L. For comparative studies of the anticorrosive activity of compounds **71-75**, tests were carried out under identical conditions for compounds **76-82** –

quaternary ammonium salts, i.e. propargylated derivatives of 1,3-benzoxazines at a concentration of 50 mg/L. The results of the studies are given in Table 7.

Table 7

Results of anticorrosion tests of compounds 76-82 in a water-salt, kerosene-containing environment saturated with hydrogen sulfide

Соединение	Consentration, mg/L	Corrosion rate, g/m^{2}hour	Protection degree, %
8-Allyl-3-(prop-2-in-1-yl)-3-propyl-3,4-dihydro-2H-benzo[e][1,3]oxazine-3-ium bromide (**76**)	50	0.6958	84.4
8-Allyl-3-hexyl-3-(prop-2-in-1-yl)-3,4-dihydro-2H-benzo[e][1,3]oxazin-3-ium bromide (**77**)	50	0.4460	90,0
8-Allyl-3-phenyl-3-(prop-2-in-1-yl)-3,4-dihydro-2H-benzo[e][1,3]oxazin-3-ium bromide (**78**)	50	0.8028	82,4
8-Allyl-3-benzyl-3-(prop-2-in-1-yl)-3,4-dihydro-2H-benzo[e][1,3]oxazin-3-ium bromide (**79**)	50	0.4192	90,6
8-Allyl-3-(4-bromophenyl)-3-(prop-2-in-1-yl)-3,4-dihydro-2H-benzo[e][1,3]oxazin-3-ium bromide (**80**)	50	0.2364	97,6
(E)-3-Phenyl-8-(prop-1-en-1-yl)-3-(prop-2-in-1-yl)-3,4-dihydro-2H-benzo[e][1,3]oxazin-3-ium bromide (**81**)	50	0.6422	85,6
(E)-3-Octyl-8-(prop-1-en-1-yl)-3-(prop-2-in-1-yl)-3,4-dihydro-2H-benzo[e][1,3]oxazin-3-ium bromide (**82**)	50	0.3568	92,0
Без ингибитора	-	4,46	-

As can be seen from the results of the studies, all synthesized ammonium compounds **76-82**, containing in the structures in addition to 1,3-benzoxazine and alkenyl fragments also an N-propargyl substituent and a bromine anion, have good anticorrosive properties in an aggressive hydrogen sulfide aqueous-salt medium containing kerosene. The positive results obtained can be explained by the presence

of double (C=C) and triple (C≡C) bonds, quaternary nitrogen, a bromine anion, and an aromatic ring in their structures.

It was found that ammonium salts with N-benzyl (**79**, 90.6%), N-bromophenyl (**80**, 97.5%), N-hexyl (**77**, 90%) and N-octyl (82, 92%) substituents have the highest degrees of protection. As can be seen, among them the highest value of the degree of protection was found for compound **80** with an N-bromophenyl substituent (97.6%), which can be explained by the additional presence of a bromine atom in the N-bromophenyl fragment.

In addition, the detection of relatively high anticorrosive properties in low concentrations (50 mg/l) in compounds **76-82** once again confirms the importance of the presence of the propargyl fragment.

The reliability of the results obtained is also confirmed by elemental analysis, EDX and SEM of the plate surface after corrosion.

Study of anticorrosive properties of synthesized ammonium compounds based on 1,3-benzoxazines and 2-propenylphenol derivatives in oil formation water

At the Oil and Gas Research and Design Institute at SOCAR, corrosion studies were conducted on water-soluble ammonium salts at a concentration of 200 mg/dm^3 (200 mg/L) in formation water saturated with hydrogen sulfide and carbon dioxide. The tests were carried out at room temperature and for 24 hours on steel St.20.

It was found that for 24 hours test the compounds exhibited a protection level of 59.0-96.8% depending on the nature of the compounds (Table 8).

Among the benzoxazinium compounds, the highest protection level (more than 90%) was exhibited by compounds with N-phenyl (**64**), N-benzyl (**65**) and propenyl substituents, where their protection level was 92.8 and 94.5%, respectively. In the presence of N-alkyl substituents (propyl, hexyl and octyl) in propenyl-substituted 1,3-benzoxazinium bromides, the protection level was comparatively low (59.0-89.6%). In this case, the compound with the N-hexyl substituent exhibited comparatively high anticorrosive properties (89.6%).

Table 8

Results of anticorrosion studies of ammonium salts in oil formation water

Compounds	Weight loss, g	Corrosion rate, g/m^{2}hour	Protection degree, %
Without inhibitor	0.1826	1.3585	-
8-Allyl-3-propyl-3,4-dihydro-2H-benzo[e][1,3]oxazin-3-ium bromide (**54**)	0.0771	0.4280	68.5
8-Allyl-3-hexyl-3,4-dihydro-2H-benzo[e][1,3]oxazin-3-ium bromide (**55**)	0.0758	0.4211	69.0
8-Allyl-3-octyl-3,4-dihydro-2H-benzo[e][1,3]oxazin-3-ium bromide (**56**)	0.0734	0.4076	70.0
88-Allyl-3-phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazin-3-ium bromide (**57**)	0.0632	0.4702	65.4
8-Allyl-3-benzyl-3,4-dihydro-2H-benzo[e][1,3]oxazin-3-ium bromide (**58**)	0.0636	0.3532	74.6
8-Allyl-3-(4-bromophenyl)-3,4-dihydro-2H-benzo[e][1,3]oxazin-3-ium bromide (**59**)	0.0384	0.2133	84.3
(E)-8-(prop-1-en-1-yl)-3-propyl-3,4-dihydro-2H-benzo[e][1,3]oxazin-3-ium bromide (**61**)	0.0444	0.3301	75.7
(E)-3-hexyl-8-(prop-1-en-1-yl)-3,4-dihydro-2H-benzo[e][1,3]oxazin-3-ium bromide (**62**)	0.0190	0.1412	89.6
(E)-3-octyl-8-(prop-1-en-1-yl)-3,4-dihydro-2H-benzo[e][1,3]oxazin-3-ium bromide (**63**)	0.1443	0.5570	59.0
(E)-3-phenyl-8-(prop-1-en-1-yl)-3,4-dihydro-2H-benzo[e][1,3]oxazin-3-ium bromide (**64**)	0.0132	0.0978	92.8
(E)-3-benzyl-8-(prop-1-en-1-yl)-3,4-dihydro-2H-benzo[e][1,3]oxazin-3-ium bromide (**65**)	0.010	0.0747	94.5
8-Allyl-3-hexyl-3-(prop-2-in-1-yl)-3,4-dihydro-2H-benzo[e][1,3]oxazin-3-ium bromide (**77**)	0.0826	0.4591	66.2
8-Allyl-3-phenyl-3-(prop-2-in-1-yl)-3,4-dihydro-2H-benzo[e][1,3]oxazin-3-ium bromide (**78**)	0.0782	0.4347	68.0
8-Allyl-3-benzyl-3-(prop-2-in-1-yl)-3,4-dihydro-2H-benzo[e][1,3]oxazin-3-ium bromide (**79**)	0.0269	0.1494	89.0
(E)-4-(2-Hydroxy-3-(prop-1-en-1-yl)benzyl)-4-(prop-2-in-1-yl)morpholin-4-ium bromide (**84**)	0.0078	0.0435	96.8

Due to the presence in the structure of 1,3-benzoxazine of substituents with a multiple bond conjugated with the aromatic ring, as well as an N-substituted propargyl fragment, the inhibitory properties

are noticeably improved in comparison with hydrobromides, i.e. in the presence of a fragment with a C≡C bond, the degree of protection increases, which once again confirms the importance of the propargyl fragment in ammonium compounds (**77-79, 84**).

Compound **84**, which contains phenolic hydroxyl, morphlinium and propargyl fragments, as well as a bromine anion in its structure, was also studied under identical test conditions. It was found that with the presence of a phenolic OH group in compound **84**, the anticorrosive activity increases and amounts to 96.8%.

Study of anticorrosive properties of ammonium salts of morpholinomethyl derivatives of 2-allyl- and 2-propenylphenols in sulfuric acid medium

The aim of this study was a comparative study of water-soluble derivatives of 2-allyl- and 2-propenyl-6-morpholinomethylphenols obtained by their reactions with HBr, allyl bromide and propargyl bromide as corrosion inhibitors of unalloyed steel St.3 in 0.5 H H_2SO_4 at a compound concentration of 10, 20 and 50 mg/L and for 3 h.

It was found that all the studied ammonium salts have anticorrosive activity, especially ammonium salts based on 2-propenylphenol (compounds **68, 83, 84**). The degrees of their protection are 80.3-97.8% depending on their quantities taken. Among the derivatives of 2-propenylphenol (**68,83,84**), the best anticorrosive properties are exhibited by ammonium compounds with an N-allyl substituent (90%). The obtained results once again confirm the importance of the presence of the N-allyl and N-propargyl fragments in ammonium compounds. The obtained results also show the comparative importance of the presence of the 2-propenyl substituent in the aromatic ring.

Study of the biocidal properties of ammonium compounds based on alkenylphenol derivatives in oil production

This work presents the results of studies of the biocidal properties of ammonium salts of functionally substituted 1,3-benzoxazines, various derivatives of Mannich bases and other derivatives containing a bulky cation with allyl, propenyl and other groups in the 1,3-benzoxazine ring and a Br anion in the structures of oil production.

Bactericidal studies were also conducted at the Scientific Research Oil Project Institute at SOCAR.

Table 9

Results of biocidal studies of compounds 67,68,83,84. Concentration of compounds 200 mg/L

Compounds	N, SRB cells/ml	S,%
Distilled water	10^8	-
67	10^4	50.0
68	10^1	90.0
83	10^1	89.5
84	10^0	100.0

As can be seen from Table 9, the studied ammonium compounds at a concentration of 200 mg/L have a bactericidal effect on SRB. The results show that compound **84** - (E)-4-(2-Hydroxy-3-(prop-1-en-1-yl)benzyl)-4-(prop-2-yn-1-yl)morpholine-4-ium bromide, which contains in its structure a propenyl, N-substituted propargyl and other fragments conjugated with an aromatic ring, as well as a bromine anion, has 100% suppression of SRB growth. It is also clear that ammonium compounds with a propenyl fragment have high bactericidal properties compared to an allyl fragment.

Compounds **54-59** at a concentration of 200 mg/L (Table 10) also have bactericidal properties against SRB growth. As can be seen from the results of the studies (Table 10), the highest degree of inhibition of SRB growth (100%) is possessed by compound **59**, which contains in its structure, in addition to the bromine anion and other functional groups, also a bromophenyl substituent.

Table 10.

Results of bactericidal studies of compounds 54-59 (conc. 200 mg/L)

Compounds	N, SRB cells/ml	*S*, %
Distilled water	10^8	–
54	10^1	87.5
55	10^2	75.0
56	10^5	37.5
57	10^4	50.0
58	10^1	87.5
59	10^0	100.0

From the results of the studies (Table 10), it is evident that compounds **54**, **58** and **59** have comparatively high activity.

Therefore, the aim was to study the above compounds at lower concentrations (50, 100 and 150 mg/L). The results of the studies make it possible to use the studied compounds as effective reagents that can be used in the oil industry.

High biocidal properties (the degree of SRB suppression is approximately 100%) were also revealed in compounds **79** and **80** with a propargyl substituent at the quaternary nitrogen atom with N-benzyl (**79**) and N-bromophenylnyl (**80**) substituents. Compound **77**, containing an allyl and N-phenyl fragment in its structures, has 90% suppressibility.

Thus, the results of the studies showed that the studied derivatives of 1,3-benzoxazines, aminomethyl and other derivatives of 2-allyl- and 2-propenylphenols possess both inhibitory and bactericidal properties and, it can be said, are not inferior in properties to the indicators of the traditional inhibitors and bactericides used, and in many cases even surpass them.

Study of the antioxidant properties of the synthesized compounds

The antioxidant activity of the synthesized nitrogen-containing derivatives (new Mannich bases), as well as 1,3-benzoxazines based on 2-allyl- and 2-propenylphenols, containing in the structures simultaneously fragments with a multiple bond, OH, benzoxazine ring and other substituents, was studied and their pattern of change in properties depending on their structures was studied.

According to the values of the induction periods found from the kinetic curves of cumene autoxidation in the presence of the studied compounds (**3,16,18,19,20,25,26,42**), it was established that they have high antioxidant activity and, according to the above-mentioned property, significantly exceed 2,6-di-tert-butylphenol (ionol), which is widely used in industry as an antioxidant.

It was established that the antioxidant properties of compounds with N-propyl and N-octyl fragments (**16, 18**) are higher than those of compounds containing N-phenyl and N-benzyl substituents (**19, 20**).

When the double bond in the propenyl radical is located toward the benzene ring (i.e. conjugated with the aromatic ring), the antioxidant properties of the compounds (compounds **25** and **26**) are reduced compared to compounds **16** and **18**, which contain N-propyl (**16**) and N-octyl (**18**) fragments in their structures and an allyl substituent in the benzoxazine molecule.

Study of viscosity-temperature properties of some compounds in I-12A oil

Considering the temperature stability of the above-mentioned compounds **33, 42, 44, 46**, they were studied in compositions in I-12A oil. The use of compounds **33, 42, 44, 46** in a composition with double copolymers of decyl methacrylate and dicyclopentadiene (1:1 wt) in lubricating distillate oil I-12A (in concentrations of 4 and 6%) allows increasing its kinematic viscosity at 100°C from 3.8 to 8.0 mm^2/s. At the same time, the viscosity-temperature properties of the compiled lubricating compositions are improved. The viscosity index (VI) increases from 90 to 100-115 at their concentration of 4% and to 110-125 - at 6%.

Study of the antimicrobial properties of the synthesized compounds

Antimicrobial studies of the synthesized compounds were carried out in the Sanitary and Quarantine Center in the Microbiology laboratory of the Ministry of Health. The aim of this work is to study the synthesized heteroatom-containing derivatives of 2-allyl-, 2-propenyl- and 4-isopropenylphenols as antimicrobial preparations, as well as antimicrobial additives to oils, and to develop scientific foundations for identifying patterns of antimicrobial properties depending on their structure. The following microorganisms were used in the studies of the antimicrobial properties of the synthesized compounds: *Staphylococcus aureus, Escherichia Coli, Shigella flexneri, Salmonella enterica, Pseudomonas aeruginosa, Candida albicans and Aspergillus niger*.

As can be seen from Table 11, the studied 8-allyl-1,3-benzoxazines and their ammonium derivatives at concentrations 15 and 30 mg/L exhibit bactericidal and fungicidal activity with respect to all the

microorganisms used. Among compounds **16-19** and **54-57**, ammonium salts **54-57** exhibit the highest antimicrobial activity, which at a concentration of 15 mg/L are approximately twice as effective as the original compounds **16-19**.

The TEM study suggests that 3-hexyl-substituted 8-allyl-1,3-benzoxazinium bromide (**55**) exerts its effect by passing through the cell walls of bacteria. Figure 12 shows an E. coli cell without treatment with compound **55** and amoxicillin. Figure 13 shows the ultrastructural characteristics of the change in an E. coli cell in the presence of the standard (amoxicillin). As can be seen, the cell wall and cell membrane (shown by a single black arrow) of the E. coli cell are damaged. In this case, bacterial growth stops and they lose the ability to reproduce.

Table 11.

Results of antimicrobial activity of compounds 16-19 and 54-57

Compounds	**Concentration, mg/L**	**Diameter of the microorganism suppression zone, mm**					
		S.aureus	***E.coli***	***S.flexneri***	***S.enterica***	***C.albicans***	***A.niger***
16	15	15	19	17	14	6	7
	30	29	39	33	26	15	15
17	15	11	24	14	12	6	5
	30	24	41	29	25	14	11
18	15	10	22	13	10	9	12
	30	26	27	22	19	17	21
19	15	13	22	10	10	4	5
	30	25	38	20	21	11	13
51	15	16	24	14	10	15	10
	30	31	42	27	21	29	23
52	15	22	28	18	15	13	12
	30	43	45	38	31	28	25
53	15	16	23	19	13	18	16
	30	31	38	32	29	33	32
54	15	19	27	20	14	12	10
	30	34	45	36	30	25	22
Amoxicillin	30	14	9	10	9	-	-
Fluconazole	30	-	-	-	-	29	22

Figure 14 clearly shows that both the inner and outer layers of the membrane are destroyed in all bacterial cells and complete destruction of the *E. coli* bacterium is observed by compound **55**.

As can be seen from Table 12, the studied compounds **23,24,26,27** at a concentration of 35 mg/L have antimicrobial activity against the microorganisms used in the work. Compound **27**, with a 3-benzyl substituent, has antimicrobial activity against all microorganisms used in the work, and especially against *Escherichia Coli, Candida albicans and Aspergillus niger,* where the diameter of the zone of inhibition of their growth at a concentration of 35 mg/L is 28, 31 and 27 mm, respectively.

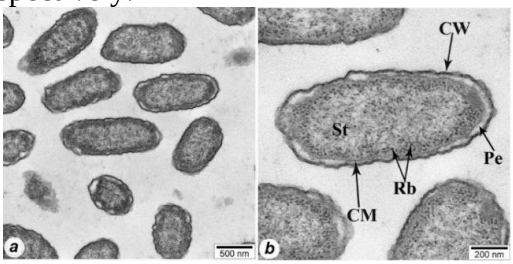


Figure 12. TEM images of untreated E. coli bacteria. a - overview, b - bacterial ultrastructure. Staining: uranyl acetate and Pb-citrate. St-cytoplasm, CM-cell membrane or plasma membrane, CW-cell wall, Rb-ribosome, Pe-peptideglycan

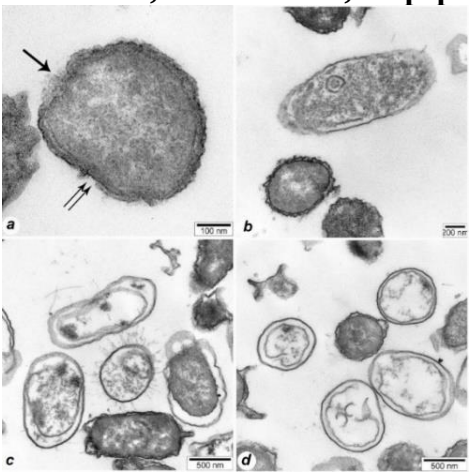


Figure 13. TEM images of damaged *E. coli* bacteria treated with amoxicillin

The results of the antimicrobial activity studies using the zonal diffusion method and the serial dilution method (35 mg/L, 3.5 mg/L, 0.35 mg/L and 0.035 mg/L) allowed us to identify their antimicrobial efficacy and the minimum inhibitory concentration (MIC) of the test compounds. Thus, for compound **24**, the minimum bactericidal activity (MBC) upon dilution of concentrations is 0.01 ml (0.35 mg/L), for **26** and **23** 0.001 ml (0.035 mg/L), for **27** the MBC and minimum fungicidal activity (MFA) are 0.001 ml (0.035 mg/L).

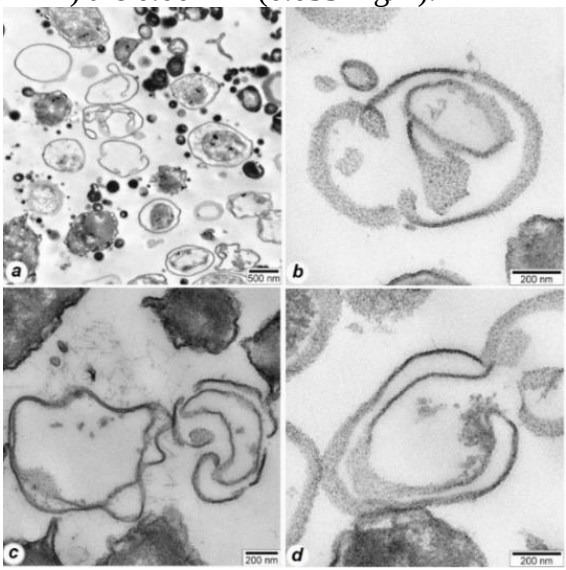


Figure 14. TEM micrographs of killed E. coli bacteria treated with 3-hexyl-substituted 8-allyl-1,3-benzoxazinium bromide 55

1,3-Benzoxazines **20, 21, 28** and their water-soluble ammonium salts **58, 59, 66** in concentrations of 20, 30 and 50 mg/L also exhibit antimicrobial activity against the following microorganisms: S. aureus, E. coli, C. albicans, Sh. flexneri, S. enterica and A. niger. Compound **58** is particularly effective against strains of E. coli and Sh. flexneri, where at a concentration of 50 mg/L the diameter of the inhibition zone of the indicated bacteria is 40 and 39 mm, respectively.

Studies have shown that compound **58** in dilutions of concentrations of 1:10 (5 mg/L), 1:100 (0.5 mg/L) and 1:1000 (0.05 mg/L) exhibits comparatively high effectiveness against bacteria, especially E. coli. However, the minimum fungicidal activity of compound **58** is

manifested at 1:100. Thus, the minimum bactericidal activity (MBA) of 58 is 0.05 mg/l, and the minimum fungicidal activity (MFA) is 0.5 mg/L.

Table 12.

Results of antimicrobial efficacy of compounds 23,24,26,27

Compounds	Concentration, mg/L	Diameter of the microorganism suppression zone, mm					
		S.aureus	*E.coli*	*S.flexneri*	*S.enterica*	*C.albicans*	*A.niger*
23	15	8	6	6	5	0	0
	35	12	10	11	10	4	4
24	15	6	9	11	8	0	0
	35	10	13	18	11	0	2
26	15	4	6	10	4	0	0
	35	6	10	16	8	2	3
27	5	7	6	5	4	8	6
	15	12	13	11	10	14	12
	35	21	28	20	22	31	27
Amoxicillin	35	15	10	9	9	-	-
Fluconazole	35	-	-	-	-	29	22

The antimicrobial activity of the synthesized compounds was also studied in M-8 motor oil by the disk-diffusion method according to GOST 9.023-74 in the Sanitary and Quarantine Center of the Ministry of Health. To conduct studies in M-8 oil at concentrations of 30 and 50 mg/l against bacteria Stafilococcus aureus, Escherichia coli and fungi Pseudomonas aeruginosa, Candida albicans, Aspergillus niger, the following compounds were used: **1-3, 16-21, 23-28** and **42**.

As can be seen from Tables 13 and 14, all the studied compounds - 8-allyl- (Table 13) and 8-propenyl-substituted (Table 14) 1,3-benzoxazines (**16-21, 23-28**) at concentrations of 30 and 50 mg/L in M-8 oil have bactericidal and fungicidal properties in relation to the microorganisms used in the work.

It is evident from Table 13 that the studied compounds are not inferior in antimicrobial activity to the standard taken for comparison - 8-hydroxyquinoline, and in many cases even surpass it.

Table 13.

Results of antimicrobial activity of compounds 16-23 in M-8 oil

Compounds	**Concen-tration , mg/L**	**Diameter of the microorganism suppression zone, mm**				
		S.aureus	*E.coli*	*Pseudomonas aeruginoza*	*C.albicans*	*A.niger*
16	30	19	21	25	16	13
	50	24	26	29	18	19
17	30	12	14	11	13	12
	50	23	24	24	15	16
18	30	10	12	9	6	5
	50	19	27	26	10	9
19	30	22	25	24	16	14
	50	28	30	29	19	18
20	30	21	24	25	15	16
	50	30	32	31	20	22
21	30	20	23	24	14	13
	50	28	29	30	25	22
8-hydroxy-quinolin	50	20	24	18	+	+
Масло М-8 (без добавки)	-	+	+	+	+	+

Table 14.

Results of antimicrobial activity of compounds 23-28 in M-8 oil

Compounds	**Con-cen-tration , mg/L**	**Diameter of the microorganism suppression zone, mm**				
		S.aureus	*E.coli*	*Pseudomonas aeruginoza*	*C.albicans*	*A.niger*
23	30	20	24	23	16	14
	50	26	29	28	18	16
24	30	16	18	15	12	10
	50	24	26	23	16	14
25	30	12	18	16	8	6
	50	21	26	22	12	10
26	30	24	29	26	17	15
	50	30	33	32	23	21
27	30	26	28	27	18	16
	50	32	36	34	27	25
28	30	28	30	28	20	18
	50	34	36	35	29	25

Among the 8-propenyl-substituted 1,3-benzoxazines with an aromatic substituent at the nitrogen atom, the compound **27** - (E)-3-benzyl-8-(prop-1-en-1-yl)-3,4-dihydro-2H-benzo[e][1,3]oxazine with a benzyl substituent has the highest antimicrobial activity. Thus, a series of heteroatom-containing compounds were synthesized by triple condensation of allyl and propenylphenols with aldehydes and various amines (by the Mannich reaction) that can find application in the oil industry as acid corrosion inhibitors, antimicrobial, antioxidant, viscosity-temperature additives to petroleum products, biocides in the oil-producing industry, medical preparations, etc.

In addition, the synthesized compounds containing both multiple bonds and heteroatoms can be successfully used as precursors in obtaining monomeric and polymeric light and heat stabilizers for polymeric materials, as well as in obtaining modified polymeric materials for the purpose of extracting radioactive compounds and heavy metals from water systems and formation waters. It was found that when including a propargyl fragment in the molecule of alkenylphenol derivatives or alkenyl-substituted 1,3-benzoxazines, their operational properties are significantly improved.

Based on the obtained research results, the synthesized compounds can be recommended for use as corrosion inhibitors, biocides, antimicrobial, antioxidant additives, drugs, etc.

CONCLUSION

1.Scientific foundations have been developed for systematic studies on the synthesis of 84 numerous functionally substituted heteroatom-containing compounds based on alkenylphenols (2-allyl, 2-propenyl and 4-isopropenylphenols) and the study of their chemical and operational (thermal, anticorrosive, biocidal, antioxidant, antimicrobial, viscosity-temperature) properties depending on their structure [3,4,13,16,23].

2. The triple condensation reaction of 2-allyl, 2-propenyl and 4-isopropenylphenols with aldehydes (formaldehyde and benzaldehyde) and primary or secondary amines (aliphatic, cyclic, aromatic) (according to Mannich) has been systematically studied. It was found that

depending on the nature, ratio of the initial reagents, reaction temperature, etc., products of various structures are obtained: 1,3-benzoxazines, aminomethyl derivatives, oligomers, polybenzoxazines [34,41-44,64,67].

3. Thermogravimetric and differential thermal methods were used to study the thermal stability of the synthesized alkenyl-substituted 1,3-benzoxazines and other derivatives of alkenylphenols. It was found that the synthesized benzoxazines have thermal stability up to a temperature of ~200 ° C (depending on their structure). It was shown that up to the decomposition temperature of the product (~200 ° C), thermal opening of the 1,3-oxazine ring occurs with the formation of polybenzoxazine [44,66,69].

4. Based on the synthesized functionally substituted ethers of alkenylphenols, 8-alkenyl substituted 1,3-benzoxazines, and aminomethyl derivatives of alkenylphenols, ammonium compounds were obtained with yields of 60-92% and melting points of 111-204 °C. Spectral data showed that as a result of the reaction, a multiple bond is preserved in the reaction products and a +N-H bond is formed [41-43,49].

5. Based on 2-allyl-, 2-propenyl-, and 4-isopropenylphenols, their methyl-substituted derivatives, and alkenyl-substituted 1,3-benzoxazines, their propargyl derivatives were obtained with yields of 57-96%. A correlation was revealed between their operational properties depending on their structure. It was found that the introduction of a propargyl substituent into the structures of the synthesized compounds significantly improves their operational (anti-corrosion and biocidal) properties [68,76].

6. Triple condensation of alkenylphenols and their derivatives with aldehydes (formaldehyde and benzaldehyde) and primary diamines (ethylenediamine, urea, thiocarbamide) yielded a series of functionally substituted heteroatom-containing compounds (yield 58-96%) with a number of valuable properties. It was found that, depending on the reaction conditions, nature, and ratio of the initial reagents, various products are obtained (1,3-benzoxazines, polybenzoxazines, oligomers). The resulting products were used as precursors in obtaining materials for the extraction of radioactive elements and heavy metals

from aqueous media (the degree of extraction of uranyl ions is 90.8-92.6%) and oil formation waters of Azerbaijan oilfields [65,66,73-75].

7. Synthesized alkenyl-substituted 1,3-benzoxazines, aminomethyl derivatives of 2-allyl-, 2-propenylphenols, their ammonium salts, as well as propargylated derivatives based on 2-allyl-, 2-propenyl- and 4-isopropenylphenols, their aminomethyl derivatives and alkenyl-substituted 1,3-benzoxazines in concentrations of 50, 100, 150 mg/l exhibited anticorrosive properties in a water-salt, kerosene-containing medium saturated with hydrogen sulfide (the degree of protection is 51.0-98.3%). It was found that among the studied compounds, ammonium salts of 1,3-benzoxazines with a propargyl fragment and an N-bromophenyl substituent have the highest anticorrosive properties. At a concentration of the specified compound of 50 mg/L, the degree of protection is 97.6% [9,16,23,35,40,41,71,72].

8. Ammonium salts based on synthesized 8-alkenyl substituted 1,3-benzoxazines, as well as aminomethyl derivatives of alkenylphenols at a concentration of 200 mg/dm^3 (200 mg/L) in mineralized formation water saturated with hydrogen sulfide and carbon dioxide, have an inhibitory effect (the degree of protection is 59.0-96.8%). The highest rates are shown by salts of 8-propenyl-1,3-benzoxazines with N-phenyl and N-benzyl substituents (the degree of protection is 92.8 and 94.5%, respectively), as well as the propargyl salt of the morpholinomethyl derivative of 2-propenylphenol (the degree of protection is 96.8%) [76].

9. In a study of ammonium salts of aminomethyl derivatives of alkenylphenols, as well as some 1,3-benzoxazines and their ammonium salts at concentrations of 10, 20, 50, 100, 150 and 200 mg/L in a 0.5 N sulfuric acid medium, it was found that the highest inhibitory properties in this case are possessed by ammonium salts based on morpholinomethyl derivatives of 2-allyl- and 2-propenylphenols, where at a concentration of 50 mg/L their degree of protection is 74.9-99.0%. It was found that the highest results can be achieved in combination with a propargyl substituent [49,76].

10. When studying the synthesized functionally substituted compounds as reagents for suppressing the growth of SRB in their concentrations of 50, 100, 150 and 200 mg/L, their high biocidal properties

(the degree of suppression up to 100%) were revealed. It was found that the synthesized compounds can be used not only as corrosion inhibitors, but also as reagents for suppressing the growth of SRB, i.e. the compounds are reagents of complex action for preventing biocorrosion during oil production [16,23,41,49].

11. Synthesized alkenyl substituted 1,3-benzoxazines and their ammonium salts also showed antimicrobial action in M-8 oil, DMSO, in water, and in alcohol against the following microorganisms: Staphylococcus aureus, Escherichia coli, Candida albicans, Shigella flexneri, Salmonella enterica, Pseudomonas aeruginosa, and Aspergillus niger (isolate obtained from water) and are not inferior to the standards taken for comparison (amoxicillin, cefazolin and fluconazole), and in many cases even surpass them. It was found that the bactericidal properties of the studied compounds are more pronounced than the fungicidal ones. It was found by the dilution method that some of the studied compounds also exhibit activity even in low concentrations (30-35 μg/L). The obtained images of Escherichia coli under a microscope in the presence of the synthesized compounds once again confirmed the antimicrobial efficiency of the compounds [41-43,77].

12. As a result of complex studies of the antioxidant properties of the synthesized compounds, their high activity was established. It was found that the condensation products of 2-allyl- and 2-propenylphenols with aldehydes and various amines have an inhibitory property with respect to the oxidation of hydrocarbons and surpass the standard (ionol) in antioxidant activity. It was found that compounds with phenolic hydroxyl and 1,3-benzoxazines with N-propyl and N-octyl substituents have the highest antioxidant properties. Thus, the induction period of oxidation in the presence of these compounds is 350, 320 and 300 min [78].

The main results of the dissertation were expressed in the following publications:

1. Bayramov, M.R. 1,4-Bis[2-(prop-1-en-1-yl)phenoxy]butane / Musa Bayramov, Abel Maharramov, Gunay Mehdiyeva, Shahnaz Hoseinzadeh, Rizvan Askerov // Acta Cryst., - 2011. E67, - p. 01478
2. Maharramov, A.M. 1,10-Bis[2-(prop-1-enyl)phenoxy]decane / Abel Maharramov, Musa Bayramov, Gunay Mehdiyeva, Shahnaz Hoseinzadeh, Bahruz Rashidov // Acta Cryst., - 2012. E68, - p. 0266
3. Magerramov, A.M. Inhibitors of hydrogen sulfide corrosion of steel in oil water-salt solutions / A.M. Magerramov, M.R. Bayramov, H. Farhadi, G.M. Mekhtieva // PPOR, - 2012. V.13, N.2(50), - p. 139-143
4. Magerramov, A.M., Study of radical copolymerization of aminomethylated derivatives of alkenylphenols with styrene/ Abel Magerramov, Musa Bayramov, Gunay Mehdiyeva, Mahira Agayeva// Polymer science, Ser.B, - 2012. V.54, N.7-8, - p.399-406
5. Magerramov, A.M., Bayramov, M.R., Mekhtieva, G.M., Alieva, S.G., Bayramova, G.M., Gasimova, Sh.Z. Alkenyl phenol derivatives as reagents for suppressing the growth of sulfate-reducing bacteria in oil production // II International Scientific Conference dedicated to the 105th anniversary of Academician Hasan Aliyev, - Baku: - November 7 - 8, - 2012, - s. 430-431
6. Bayramov, M.R., Magerramov, A.M., Khoseinzade, Sh.B., Mekhtiyeva, G.M., Agaeva, M.A., Aliyeva S.G. New inhibitors of sulfur-carbon corrosion// International scientific and technical conference "Sustainable development. Rational nature management. Health technologies", dedicated to the 75th anniversary of academician Valery Legasov, - Tula,- 2012, - c. 92
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