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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

SYNTHESIS AND RESEARCH OF BIOLOGICAL ACTIVITY OF AMINOMETOXY DERIVATIVES BASED ON C5 FRACTION OF LIQUID PRODUCTS OF PYROLYSIS

Speciality: 2314.01 – Petrochemistry

Field of science: Chemistry

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The work was performed at laboratory of "Studies of antimicrobial reagents and biodeterioration" of the Institute of Petrochemical Processes named by acad. Y.H. Mammadaliyev of National Academy of Sciences of Azerbaijan

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GENERAL CHARACTERISTICS OF THE WORK

The relevance of the work. It is known that the chemical and petrochemical industries are among the basic branches of the republican industry. It is in demand by all other sectors of the economy, and the level of national competitiveness, the rate of economic growth, and the well-being of the country depend on its state and development. In this regard, the development of new effective economically viable and environmentally friendly methods for obtaining valuable substrates of modern organic and petrochemical synthesis on the basis of available raw materials of national importance is of wide scientific and practical interest. In this regard, the C_5 fraction of liquid pyrolysis products should be especially noted, which is a large-tonnage by-product of the EP-300 Sumgait pyrolysis plant and contains chemically valuable and highly reactive diene hydrocarbons (isoprene, piperylene, dicyclopentadiene). The isolation of these dienes, their use in the diene synthesis reaction and the production of important multifunctional derivatives of unsaturated hydrocarbons of the cyclohexene and norbornene series on their basis, their subsequent use in various chemical processes to obtain polyfunctional organic substrates largely determines the relevance of the presented dissertation work.

Since the last century, derivatives of the norbornene series have become the object of close attention of researchers in various countries. The uniqueness of the structure of this bicyclic olefin, the presence of a hydrocarbon framework with a fairly rigid conformation, the presence of additional functionalities in the molecules of these derivatives (ether, amino, hydroxy, aminomethoxy groups), the establishment of a relationship between the structure of norbornene derivatives and their biological and others operating properties creates the prerequisites for extensive research in the field of synthesis, study of properties and determination of new areas of application of derivatives of the bicyclo[2.2.1]-hept-5-ene series.

The relevance of the work lies in the fact that by synthesizing aminomethoxy derivatives of compounds of the norbornene series, it

is possible to enhance existing properties, as well as to obtain new compounds with the required properties**.**

Subject and object of research. In the presented dissertation work, the object of research was norbornene-containing Mannich bases synthesized by a three-component reaction of thermal and catalytic aminomethylation with the participation of norbornenylmethanol, aliphatic and aromatic aldehydes, as well as secondary aliphatic, ali- and heterocyclic amines. The paper studies the properties of these compounds and defines the areas of their practical application. For research, dicyclopentadiene (DCPD), isolated from the C_5 fraction of liquid pyrolysis products, which is a large-tonnage by-product of the EP-300 Sumgait pyrolysis plant, was used as the main raw material resource.

The purpose and objectives of the work. The purpose of the presented dissertation work is to obtain new aminomethoxy derivatives of norbornene, to determine the optimal conditions for their synthesis, to study their physicochemical properties, to confirm their composition and structure, as well as to study the areas of their application.

To achieve this goal, the following specific tasks were solved:

- ✓ separation of cyclopentadiene (CPD) from liquid pyrolysis products;
- ✓ on the basis of CPD and allyl alcohol in an autoclave at high temperature and pressure, the Diels-Alder (D-A) reactions were carried out to obtain racemic norbornenyl-methanol, which is the main precursor for further syntheses;
- ✓ in the presence of a chiral catalyst, the reaction of CPD and allyl alcohol in a metal ampoule carried out asymmetric reactions D-A to obtain optically active norbornylmethanol;
- ✓ new Mannich bases (MBs) were synthesized based on racemic norbornylmethanol, formaldehyde and secondary amines (aliphatic and cyclic); in order to increase the yield of the target products, the same reactions were carried out in the presence of catalysts, and the optimal conditions for the reaction were found;
- ✓ new MBs were obtained on the basis of racemic norbornylmethanol, benzaldehyde and secondary amines (aliphatic

and cyclic), and to increase the yield of reaction products, they were additionally carried out in the presence of catalysts;

- ✓ optical forms of aminomethoxy derivatives of norbornene based on optically active norbornylmethanol, formaldehyde and secondary amines (aliphatic and cyclic) were synthesized, their optical activity was determined;
- ✓ the physicochemical properties of all the obtained compounds have been studied, and their composition and structure have been confirmed by modern physical methods;
- ✓ the antimicrobial activity of some synthesized compounds has been studied in comparison with known bactericidal preparations widely used in medical practice;
- ✓ the minimum inhibitory concentration (MIC) and the minimum bactericidal concentration (MBC) of the compounds under study have been determined;
- ✓ some obtained MBs were investigated as inhibitors against SRB, for comparison of bactericidal properties a complex of 5-morpholinomethoxymethylbicyclo[2.2.1]-hept-2-ene with hexyl bromide was obtained;
- ✓ some synthesized aminomethoxy derivatives of bicyclo[2.2.1]-hept-2-ene have been investigated as antimicrobial additives to oils and fuels.

Research methods. The starting racemic and optically active norbornenylmethanol were synthesized by the thermal and asymmetric reaction D-A, respectively. Aminomethoxy derivatives of norbornylmethanol were obtained by the thermal Mannich reaction (RM), catalytic RM, and the optical forms of some of them were synthesized by asymmetric RM.

Antimicrobial activity was investigated by the method of serial dilutions at the Azerbaijan Medical University at the Department of «Microbiology and Immunology».

The bactericidal-inhibiting properties were analyzed, respectively, by OST 39-151-83 at the Institute of Petrochemical Processes of ANAS.

At the Institute of Additives Chemistry of ANAS, the obtained compounds were tested by the zonal diffusion method as

antimicrobial additives to oils and fuels.

Accuracy of results. The physicochemical properties, composition and structure of the new MBs were studied by modern physical research methods: IR, ^{1}H and ^{13}C NMR spectroscopy, as well as mass spectrometry.

The optical activity of chiral aminomethoxy derivatives of bicyclo[2.2.1]-hept-2-ene was determined with a polarimeter at the Azerbaijan Medical University at the Department of Pharmaceutical Chemistry.

Mass spectrometric analysis and NMR spectra of some compounds were taken at the Institute of Organoelement Compounds named after Academician A.N. Nesmeyanov (INEOS) RAS.

Main provisions of protection:

✓ synthesis of new MBs based on norbornenylmethanol, formaldehyde and secondary amines have been carried out and repeat reaction have been carried out in the presence of catalysts;

✓ new optical forms of aminomethoxy derivatives of norbornylmethanol based on reaction of chiral norbornenylmethanol, formaldehyde and secondary amines have been obtained;

✓ physicochemical parameters of synthesized compounds have been determinated, as well as proof of their composition and structure;

✓ antibacterial, antifungal and bactericidal properties of the obtained compounds have been studied; the possibility of their use as antimicrobial substances is shown.

Scientific novelty:

✓ synthesized novel aminomethoxy derivatives of norbornylmethanol on the basis of norbornylmethanol, formaldehyde (benzaldehyde) and secondary amines;

✓ in the presence of isopropyl alcohol, a complex of 5-morpholinomethoxymethylbicyclo[2.2.1]-hept-2-ene with hexyl bromide was obtained;

✓ it have been implemented novel catalytic RMs based on norbornylmethanol, formaldehyde (benzaldehyde) and secondary amines;

✓ novel optical forms of aminomethoxy derivatives of

norbornenyl methanol were obtained using chiral norbornenylmethanol, formaldehyde and secondary amines;

✓ 26 new compounds were synthesized;

✓ target products have been investigated as antimicrobial substances;

✓ MIC and MBC of the investigated compounds were determined;

✓ the synthesized compounds and the resulting complex were studied as inhibitor-bactericides against SRB;

✓ the obtained new aminomethoxy derivatives of norbornenylmethanol were tested as antimicrobial additives to oils and fuels.

Theoretical and practical value. To obtain norbornylmethanol, which is a precursor in the synthesis of target products, we used CPD isolated from the C_5 fraction of pyrolysis products. These products, obtained in large quantities at the EP-300 unit in the city of Sumgait, are by-products, the expedient use of which meets the tasks of "green chemistry".

In the synthesis of RM end products, unreacted reagents, as well as used solvents and catalysts, can be washed, purified, distilled and reused in subsequent reactions, which ensures environmentally friendly production with minimal waste.

The investigated compounds at very low concentrations are capable of completely suspending or inhibiting the growth of SRB, exhibiting strong antimicrobial properties for a short time and at very low concentrations; they also showed good results as antibacterial and antifungal additives to lubricating oils and fuels. The synthesized compounds can be proposed as inhibitors and bactericides against SRB, antimicrobial substances for use in medicine and antimicrobial additives to oils and fuels.

Approbation and application of the work. According to the dissertation work, 37 works have been published, 19 of which are articles, and 18 of them are abstracts of reports from international and republican scientific conferences.

The results of the dissertation work were announced and discussed at the III Republican fair of innovative ideas of young

scientists (Baku, September 16–20, 2013); conference dedicated to the 91st anniversary of the birth of the national leader H. Aliyev (GSU, Ganja, May 12–13, 2014); scientific-practical conference "Actual problems of modern chemistry and biology" dedicated to the 92-th anniversary of the birth of the national leader H. Aliyev (GSU, Ganja, May 5–6, 2015); IX republican scientific conference of doctoral students, masters and young researchers "Actual problems of chemistry", dedicated to the 92-nd anniversary of the birth of national leader H. Aliyev (BSU, Baku, May 6–7, 2015); republican scientific conference "Lubricants, fuel, special fluids, additives and reagents" dedicated to the 50th anniversary of the formation of the ICA (ICA, Baku, October 13–14, 2015); republican scientific conference dedicated to the 90-th anniversary of academician T. Shakhtakhtinsky (ICIC, Baku, October 22, 2015); the international scientific conference "Actual Problems of Modern Chemistry and Biology" dedicated to the 93-rd anniversary of the birth of the national leader H. Aliyev (GSU, Gandja, May 12–13, 2016); cluster of conferences on organic chemistry, "Org Chem-2016" (St. Petersburg, June 27 – July 1, 2016); IX Baku international Mammadaliyev conference on petrochemistry (IPCP, Baku, October 3–5, 2016); XII international conference of young scientists in petrochemistry (Zvenigorod, September 17–21, 2018); republican scientific and technical conference of students and young scientists on the theme "Youth and scientific innovations", dedicated to the 95th anniversary of the birth of the national leader of the Azerbaijani people H. Aliyev (ATU, Baku, May 3–5, 2018); international scientific conference "Actual problems of modern natural and economic sciences" (GSU, Ganja, May 2–3, 2019); XIII republican scientific conference of doctoral students, masters and young researchers "Actual problems of chemistry", dedicated to the 96-th anniversary of the birth of the national leader H. Aliyev (BSU, Baku, May 15–16, 2019); international scientific conference "Actual Problems of Modern Chemistry" dedicated to the 90-th anniversary of the Institute of Petrochemical Processes named after Academician Y.Mammadaliev of ANAS (IPCP, Baku, October 2–4, 2019); Republican scientific conference "Modern view of chemistry" (NSU,

Nakhichevan, October 8, 2019); international scientific conference "Prospects for the innovative development of chemical technology and engineering" (SSU, Sumgayit, November 28–29, 2019); republican scientific-practical conference "Problems and trends in the development of modern chemistry" (Baku, December 12, 2020).

Place of the dissertation work. The research presented in this dissertation was carried out according to the program of research work of the Institute of Petrochemical Industry of ANAS 12/2007, 2012–2014. (State registration number 0107 Az 00259), 14/2015, 2015–2017. (State registration number 0115 Az 2126), 14/2018, 2018–2021. The work was carried out on the basis of agreement No. 1/18 dated April 12, 2018 on scientific and technical cooperation between INEOS RAS and IPCP ANAS. Optical and antimicrobial activity, MIC and MBC of compounds were determined at the Azerbaijan Medical University. The analysis of MBs as antimicrobial additives to oils and fuels was studied at the Institute of Additive Chemistry of ANAS.

The structure and scope of the thesis. The dissertation work is presented on 200 pages of computer text and consists of an introduction – 8 pages (13246 symbols); four chapters: literary review – 37 pages (37997 symbols), experimental part – 26 pages (38440 symbols), discussion of the results (3 and 4 chapters) – 81 pages (76404 symbols); conclusions – 2 pages (3470 symbols); list of used literature, consisting of 164 bibliographic titles – 20 pages (32259 symbols). The thesis includes 32 tables and 25 figures, as well as an appendix on page (symbols). The total volume of the thesis is 174417 symbols (without tables, figures, bibliography and applications).

The introduction provides information about the relevance, goals, objectives, scientific novelty, practical value of the dissertation work.

The first chapter is a literary review, which discusses the current state of research in the field of synthesis and application of OM as biologically active substances.

The second chapter contains information on the starting products, on the methods of obtaining the initial alcohol, target

products and some catalysts, apparatuses and methods used in the analysis of intermediate and final compounds, on the data obtained as a result of the reactions carried out and physical methods of analysis.

The third chapter discusses the results obtained in the course of the work carried out, shows the optimal conditions for carrying out the reactions, and studies in detail the IR, ^{1}H, ^{13}C NMR and mass spectra of the synthesized compounds.

In the fourth chapter, possible fields of application of the synthesized compounds are considered based on the data obtained as a result of studying the antimicrobial activity and inhibitory properties of these compounds.

Conclusions, bibliography and applications are presented at the end of the dissertation.

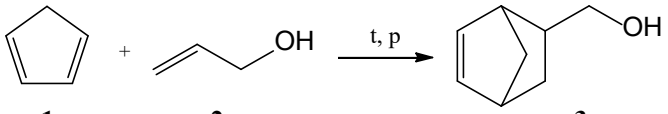
Personal contribution of the author. Statement of problems, collection and generalization of literature data, development and implementation of experiments, preparation of samples for further research, systematization of results, compilation of articles and abstracts, as well as interpretation and generalization of data from physicochemical analyzes were performed mainly by the author**.**

MAIN CONTENT OF WORK

Trends in the development of modern petrochemical and organic synthesis put forward the development of new economically and ecologically effective methods for obtaining valuable organic compounds on the basis of available raw materials. In this regard, the C_5 fraction of liquid pyrolysis products should be especially noted, which is a multi-tonnage by-product of the ethylene-propylene production of the EP-300 unit in the city of Sumgait. This fraction contains valuable highly reactive diene hydrocarbons (isoprene, piperylene, dicyclopentadiene) and can serve as a feedstock for the production of a number of industrially important petrochemical products. In the presented dissertation, DCPD, isolated from the C_5 fraction of liquid pyrolysis products, was used for further production of norbornene containing Mannich bases and the subsequent determination of their areas of application [5, 6].

Synthesis of racemic and chiral bicyclo[2.2.1]-hept-2-en-5-ol

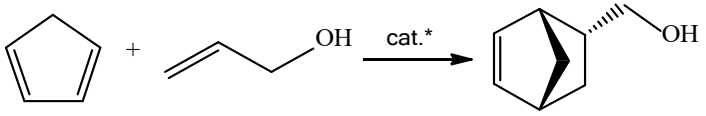
The starting racemic bicyclo[2.2.1]-hept-2-en-5-ol (**3**) was synthesized from DCPD and allyl alcohol (**2**) in an autoclave. An autoclave with a capacity of 1000 ml, equipped with a manometer and a thermometer, was loaded with DCPD and allyl alcohol (**2**) in a ratio of 1:2.4. The reaction proceeds for 9 hours at a temperature of 170–180°C and a pressure of 4–5 atm. At high temperature and pressure, DCPD monomerizes in the CPD, and as a result, the reaction proceeds according to scheme 1:



1 **2** **3** (**1**).

The mixture was distilled under vacuum. Target product yield – 74%, $T_{boil.}$ – 82–83ºC (10 mm Hg), n_D^{20} – 1.4970, ρ – 1027.0 кg/m^3.

In the presence of a chiral catalyst – BBr_3·MentOEt [20], (+)-norbornenylmethanol (3*) was synthesized by the D-A reaction[1] from CPD (1) and allyl alcohol (2). The reaction was carried out in a metal ampoule, in benzene, at a temperature of 78–80°C, for 3 hours according to scheme 2.



1 **2** **3*** **(2),**

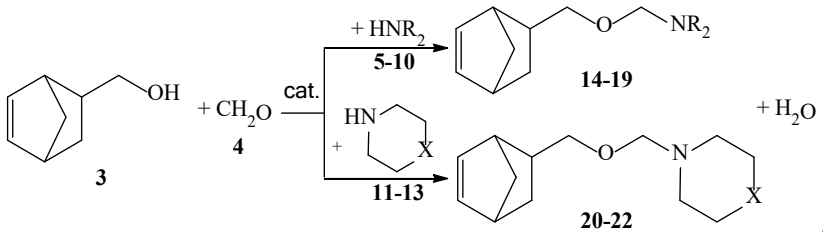
where cat. * = BBr_3·MentOEt.

[1]Klabunovskii, E.I. Asymmetric Diels-Alder reactions of cyclopentadiene in the synthesis of chiral norbornene derivatives / E.I.Klabunovskii, E.G.Mamedov // Russian Journal of Organic Chemistry, – 2008. V. 44, № 8, – p. 1097-1120.

The reaction mixture was distilled under vacuum. The yield was 79%. The physicochemical properties of the obtained optically active norbornenylmethanol (**3***) coincide with the data on the physicochemical properties of racemic norbornenylmethanol (**3**) [1]. The angle of rotation is [α] (+)-38.51° (EtOH, c 2.5).

Thermal and catalytic reactions of aminomethylation of norbornenylmethanol with formaldehyde and secondary amines

Thermal [**7–9, 11, 12, 14, 16, 19**] and catalytic [**25, 29, 35**] Mannich condensation based on norbornenylmethanol (**3**), formaldehyde (**4**) and secondary amines [diethylamine (**5**), dipropylamine (**6**), dibutylamine (**7**), dipentylamine (**8**), dihexylamine (**9**), diisobutylamine (**10**), piperidine (**11**), morpholine (**12**), azepane (**13**)] proceeded according to the following scheme 3:



(**3**),

where R = C_2H_5 (**5**, **14**); C_3H_7 (**6**, **15**); C_4H_9 (**7**, **16**); C_5H_{11} (**8**, **17**); C_6H_{13} (**9**, **18**); *i*-C_4H_9 (**10**, **19**); X = CH_2 (**11**, **20**); O (**12**, **21**); CH_2–CH_2 (**13**, **22**); cat. = without catalyst; CuCl; $Sm(NO_3)_3 \cdot 6H_2O$; *N*-methylpyrrolidonium hydrogen sulfate (**23**); 1,4-dimethylpiperazine dihydrosulfate (**24**).

The concentration of the catalyst is 1 mol.%. The reactions were carried out in a benzene solution at 78–80°C for 4–5 h (without cat.) and 0.5–1.0 h (in the presence of cat.) At a molar ratio of reagents: norbornenylmethanol (**3**), formaldehyde (**4**), and amines (**5–13**) – 1:2:1, respectively. The physicochemical data of the synthesized compounds were determined (Table 1).

Table 1. Physicochemical properties of compounds (14–22)

№	$T_{boil.}$, °C (p, mm Hg)	n_D^{20}	ρ, кg/m^3	Brutto-formula	Founded / Calculated, %		
					C	H	N
14	102–104 (4)	1.4672	939.5	$C_{13}H_{23}NO$	74.56 / 74.59	10.86 / 11.07	6.61 / 6.69
15	119–122 (4)	1.4670	922.8	$C_{15}H_{27}NO$	75.82 / 75.90	11.56 / 11.46	5.77 / 5.90
16	135 (2)	1.4660	910.0	$C_{17}H_{31}NO$	75.60 / 76.92	10.84 / 11.77	5.36 / 5.28
17	114–117 (5)	1.4596	873.1	$C_{17}H_{31}NO$	76.71 / 76.92	11.80 / 11.77	5.15 / 5.28
18	185 (13)	1.4680	905.7	$C_{19}H_{35}NO$	77.66 / 77.76	12.07 / 12.02	4.63 / 4.77
19	192–194 (6)	1.4645	885.4	$C_{21}H_{39}NO$	77.68 / 78.44	12.31 / 12.23	4.24 / 4.36
20	138–141 (8)	1.4958	984.5	$C_{14}H_{23}NO$	75.98 / 75.97	10.81 / 10.47	6.13 / 6.33
21	155–158 (4)	1.4942	1038.9	$C_{13}H_{21}NO_2$	70.65 / 69.92	9.92 / 9.48	5.28 / 6.27
22	148 (10)	1.5010	987.5	$C_{15}H_{25}NO$	75.61 / 76.55	10.80 / 10.71	5.39 / 5.95

The yields of compounds (**14–22**) are presented in table 2. The obtained compounds (**14–22**) are liquids with a characteristic odor, insoluble in water, readily soluble in organic solvents (ethanol, acetone, benzene, CCl_4, $CHCl_3$, etc.). The composition and structure of the obtained compounds (**14–22**) were confirmed using the data of elemental analysis (Table 1), IR (Table 3), ^{1}H (Table 4), ^{13}C NMR spectroscopy and mass spectrometry.

Table 2. Yields of compounds (14–22) in the present of different catalysts with concentration 1 mol. %

Catalysts	Compounds yield, %								
	14	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**
Without catalyst	51	43	49	71	64	46	45	50	49
CuCl	83	72	79	90	89	–	71	77	76
$Sm(NO_3)_3 \cdot 6H_2O$	79	70	76	89	87	–	69	76	74
23	87	80	87	94	90	–	78	87	86
24	86	77	84	93	91	–	75	82	82

Table 3. Data of IR-sprectroscopic analysis of compounds (14–22) (cm^{-1})

№	=C–H	C–H	C=C	C–N	C–O–C	CH_2
14	3057, 978–816	2961, 2858, 1460, 1359	1629	1215	1057	715
15	3059, 983–903	2957–2868, 1463–1343	1685	1202	1091–1048	717
16	3059, 984–904	2955–2803, 1459–1343	1685	1272–1190	1070, 1048	717
17	3057, 986–820	2951–2787, 1467–1312	1687	1277, 1206	1172–1112	718
18	3059, 984–903	2956–2862, 1462–1343	1686	1252–1192	1069, 1050	718
19	3058, 987, 839	2927, 2857, 1459, 1361	1635	1221, 1172	1063	717
20	3058, 987–781	2931–2780, 1446–1313	1629	1228, 1048	1184, 1127	715
21	3056, 911–791	2952, 2853, 1452, 1356	1629	1257, 1067	1109	716
22	3058, 968–829	2923, 2856, 1449–1340	1643	1234, 1069	1188, 1141	715

Table 4. Indices of ^1H NMR spectras of compounds (14–22) (δ, m.h.)

№	C^1H	C^2H	C^3H	C^4H	C^5H	C^6H_2	C^7H_2	C^8H_2	$C^{10}H_2$	NCH_2
14	2.80 m	5.94 m	6.10 m	2.80 m	2.80 m	1.35 m	1.78 d.d.d	3.42 d	4.17 s	3.36 m
15	2.57 d.d	5.94–6.11 m		2.77 d.d	1.26–1.46 m		1.81 m	3.02 m	4.07 s	3.02 m
16	2.47 d.d	5.93 5 m	6.10 5 m	2.63 d.d	1.34–1.50 m		1.79 d.d.d	3.055 m	4.07 s, 4.09 s	3.055 m
17	2.202 d	5.93–6.08 m		2.20 d	1.635–1.771 m			2.93 d	3.274 s	2.06 m
18	1.425 m	5.94–6.12 m		1.33–1.52 m			1.79 d.d.d	3.17 m	4.08 s, 4.09 s	3.17 m
19	2.47 d.d	5.94–6.11 m		2.63 d.d	1.40–1.53 m		1.79 d.d.d	3.06 m	4.08 s, 4.09 s	3.06 m
20	2.465 m	5.94 d.d	6.10 d.d	2.35–2.58 m		1.26–1.54 m		3.005 m	3.94 d.d, 4.00 d.d	2.99–3.02 m
21	2.19–2.32 m	5.88 d.d	6.00 d.d	2.34–2.51 m		1.33–1.47 m	1.57–1.72 m	3.01–3.12 m	3.78 d.d, 3.80 d.d	2.80–3.00 m
22	2.57–2.70 m	5.94 d.d	6.01 d.d	2.72–2.88 m		1.20–1.29 m	1.34–1.42 m	2.88–3.02 m	4.04 d.d, 4.08 d.d	3.04–3.16 m

The ^{1}H NMR spectrum of 5-piperidinomethoxymethylbicyclo-[2.2.1]-hept-2-ene (**20**) and the mass spectrum of 5-morpholinomethoxymethyl-bicyclo[2.2.1]-hept-2-ene (**21**) are shown in Figures 1 and 2, respectively.

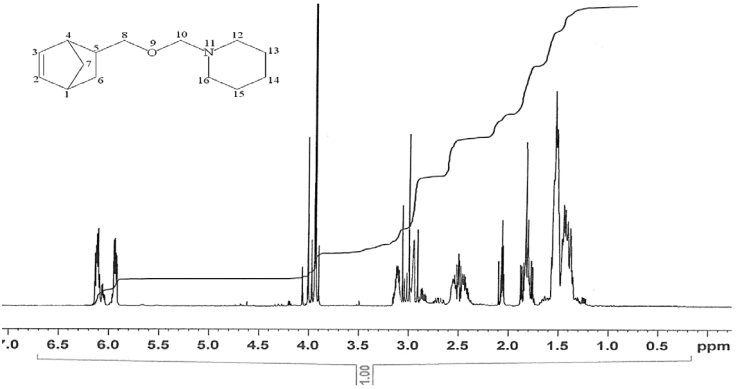


Fig. 1. ^{1}H NMR spectra
5-piperidinomethoxymethylbicyclo[2.2.1]-hept-2-ene (20)

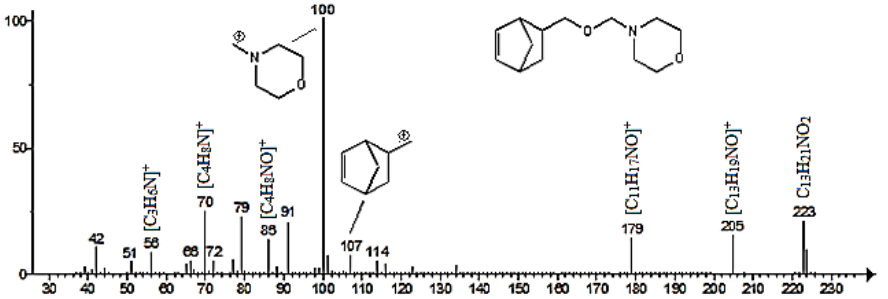
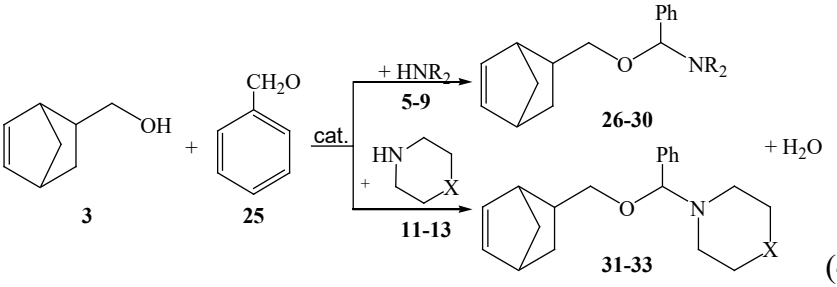


Fig. 2. Mass spectra
5-morpholinomethoxymethylbicyclo[2.2.1]-hept-2-ene (21)

Thermal and catalytic reactions of aminomethylation of norbornenylmethanol with benzaldehyde and secondary amines

Three-component thermal [24, 28, 34] and catalytic [35] aminomethylation reaction based on norbornenylmethanol (**3**), benzaldehyde (**25**) and secondary amines (**14–16, 18–22**) synthesized new aminomethoxy derivatives of norbornene according to scheme 4.



(**4**),

where R = C_2H_5 (**5**, **26**); C_3H_7 (**6**, **27**); C_4H_9 (**7**, **28**); C_5H_{11} (**8**, **29**); C_6H_{13} (**9**, **30**); X = CH_2 (**11**, **31**); O (**12**, **32**); CH_2–CH_2 (**13**, **33**); cat. = without cat.; CuCl; $Sm(NO_3)_3 \cdot 6H_2O$; cat. **(23)**; cat. **(24)**.

The concentration of the catalyst is 1 mol.%. The reactions were carried out in a benzene solution at 78–80°C for 6–7 h (without cat.) and 1.0 h (with cat.). At a molar ratio of reagents: norbornenylmethanol (**3**), benzaldehyde (**25**), and amines (**5–9, 11–13**) – 1:1:1, respectively. The physicochemical properties of the synthesized compounds were determined (Table 5).

Table 5. Physicochemical properties of compounds (26–33)

№	T_{boil}, °C (p, mm Hg)	n_D^{20}	ρ, кг/м^3	Brutto-formula	$\frac{\text{Founded}}{\text{Calculated}}$, %		
					C	H	N
26	60 (9)	1.5160 (24)	944.1	$C_{19}H_{27}NO$	79.67 / 79.95	9.76 / 9.53	4.68 / 4.91
27	177–179 (5)	1.4854 (28)	974.9	$C_{21}H_{31}NO$	79.34 / 80.46	10.62 / 9.97	4.83 / 4.47
28	190–192 (8)	1.4862 (26)	988.5	$C_{23}H_{35}NO$	79.74 / 80.88	11.01 / 10.33	5.26 / 4.10
29	196–198 (8)	1.4860 (26)	979.7	$C_{25}H_{39}NO$	80.65 / 81.24	10.98 / 10.64	4.38 / 3.79
30	232–235 (5)	1.4857 (26)	948.1	$C_{27}H_{43}NO$	80.49 / 81.55	11.76 / 10.90	4.36 / 3.52
31	179–181 (4)	1.5629 (24)	1060.5	$C_{20}H_{27}NO$	80.37 / 80.76	9.44 / 9.15	4.76 / 4.71
32	181–184 (4)	1.5235 (20)	1045.3	$C_{19}H_{25}NO_2$	76.72 / 76.22	8.69 / 8.42	4.53 / 4.68
33	142–145 (6)	1.5819 (24)	1035.5	$C_{21}H_{29}NO$	80.48 / 80.98	9.76 / 9.38	4.54 / 4.50

The yields of compounds (**26–33**) are presented in table 6. The obtained compounds (**26–33**) are liquids with a characteristic odor, insoluble in water, readily soluble in organic solvents (ethanol, acetone, benzene, CCl_4, $CHCl_3$, etc.). The composition and structure of the obtained compounds were confirmed using the data of elemental analysis (Table 5), IR (Table 7), ^1H (Table 8), and ^{13}C NMR spectroscopy.

Table 6. Yields of compounds (26-33) in the present of different catalysts with concentration 1 mol.%

Catalysts.	Compounds yield, %							
	26	**27**	**28**	**29**	**30**	**31**	**32**	**33**
Without cat..	42	69	65	70	75	41	48	38
CuCl	73	79	85	89	88	75	77	74
$Sm(NO_3)_3 \cdot 6H_2O$	71	83	82	87	88	71	75	69
23	81	88	90	92	94	83	86	82
24	78	85	88	92	93	79	82	79

Table 7. Data of IR-spectroscopic analysis of compounds (26–33) (cm^{-1})

№	$=C-H_{cycl.}$	$C-H_{ar.}$	C–H	$C=C_{cycl.}$	$C=C_{ar.}$	C–N	C–O–C	$-C_6H_5$
26	3058, 925–828	3023	2937, 2866, 1451, 1338	1650	1604, 1573	1252, 1209, 1026	1147	717, 698
27	3060, 929, 841	3027	2956–2870, 1493–1376	1650	1599	1263, 1206, 1077	1137	751–672
28	3059, 903, 832	3027	2957–2870, 1494–1376	1627	1598, 1552	1273, 1067, 1028	1172, 1112	753–671
29	3061, 963–843	3027	2955–2870, 1492–1377	1685, 1648	1601	1267, 1207, 1028	1172–1089	752–672
30	3061, 912, 849	3027	2954–2856, 1493–1301	1648	1601	1201, 1073, 1028	1165, 1116	751–671
31	3058, 968–788	3026	2932–2806, 1493–1317	1657	1612–1578	1274, 1210, 1063, 1030	1175, 1111	745–695
32	3057, 969–788	3026	2957, 2863, 1494–1317	1643	1609, 1568	1273–1179, 1061, 1031	1139, 1111	752–695
33	3060, 963–831	3026	2926, 2858, 1494–1376	1643	1599–1554	1271, 1218, 1070, 1026	1170–1110	751–693

Table 8. Indices of ^{1}H NMR spectras of compounds (26-33) (δ, m.h.)

№	$C^{1}H$	$C^{2}H$	$C^{3}H$	$C^{4}H$	$C^{5}H$	$C^{6}H_2$	$C^{7}H_2$	$C^{8}H_2$	$C^{10}H_2$	$5CH_{ap.}$
26	2.12–2.31 m	5.88–6.00 m	6.04–6.17 m	2.12–2.31 m	1.74–1.82 m	1.39–1.63 m		3.18 d.d, 3.30 d.d	4.62 s	7.19–7.45 m
27	2.51–2.70 m	5.89–6.03 m	6.06–6.19 m	2.51–2.70 m	1.76–1.97 m			3.22 d.d, 3.31 d.d	5.17 s	6.99–7.46 m
28	2.57–2.75 m	5.96–6.08 m	6.12–6.20 m	2.57–2.75 m	1.77–1.91 m			3.26 d.d, 3.38 d.d	5.18 s	6.98–7.44 m
29	2.57–2.75 m	6.08 d	6.20 d	2.57–2.75 m	1.77–2.04 m			3.75 d.d, 3.96 d.d	5.22 s	6.88–7.59 m
30	2.23–2.51 m	6.05 d		2.23–2.51 m	1.77–1.89 m	1.90–1.21 m		3.76 d.d, 3.91 d.d	5.19 s	6.88–7.59 m
31	2.18–2.50 m	5.96–5.99 m	6.12–6.15 m	2.18–2.50 m	1.75–1.88 m	1.51–1.74 m		3.27 d.d	4.90 s	6.91–7.67 m
32	2.28–2.39 m	5.87–5.94 m	6.02–6.11 m	2.28–2.39 m	1.70–1.81 m	1.13–1.31 m	1.38–1.42 m	3.15 d.d	4.78 s	7.12–7.41 m
33	2.20–2.48 m	5.80–6.25 m		2.20–2.48 m	2.179 s	1.45–1.90 m		3.20 d.d	4.88 s	6.92–7.69 m

IR spectrum of 5-(10-phenyl-11-pentyl-9-oxa-11-azanonyl)-bicyclo[2.2.1]-hept-2-ene (**29**) and ^{13}C NMR spectrum of 5-(10-phenyl-11-hexyl-9-oxa-11-azadecyl)bicyclo[2.2.1]-hept-2-ene (**30**) is shown in Fig. 3 and 4, respectively.

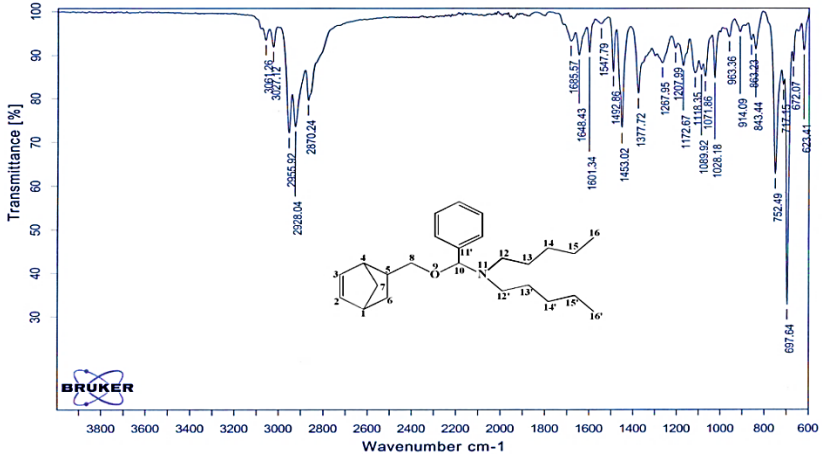


Fig. 3. IR spectrum of 5-(10-phenyl-11-pentyl-9-oxa-11-azanonyl) bicyclo[2.2.1]-hept-2-ene (29)

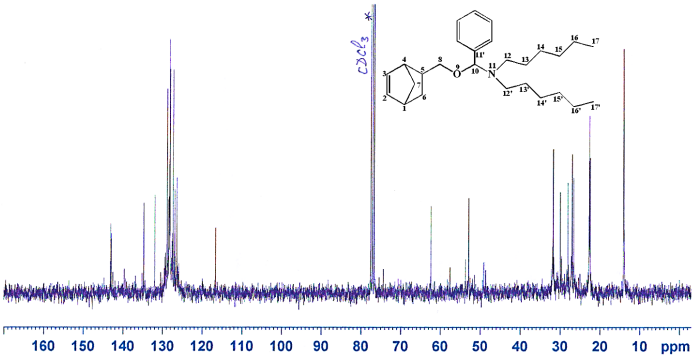


Fig. 4. ^{13}C NMR spectrum of 5-(10-phenyl-11-hexyl-9-oxa-11-azadecyl)bicyclo[2.2.1]-hept-2-ene (30)

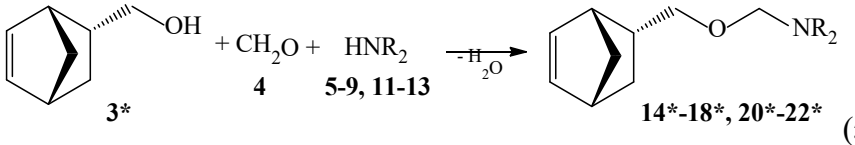
From table 2 and 4 it can be seen, that the yield in the catalytic synthesis with all the catalysts presented is higher compared to the yield of the same compounds when the reaction is carried out without a catalyst, and the highest yield of compounds was observed when using a catalyst (**23**). Also, during catalytic synthesis, the reaction time decreased.

Synthesis of chiral aminomethoxy derivatives of bicyclo[2.2.1]-hept-2-ene-5-ol[2]

Currently, it is extremely important to obtain optically active forms of new high-quality compounds used in various sectors of the economy [2]. There is a great need for the synthesis of biologically active organic compounds that have a more effective effect in medicine [4] and agriculture [3]. The synthesis of these substances using more affordable and environmentally friendly methods based on local and easy-to-use raw materials is of great scientific and practical importance [13].

On the basis of the obtained chiral alcohol (**3***), paraform and secondary amines (**5–9, 11–13**), asymmetric RM were carried out [21, 37] according to scheme 5:

[2]Mammadbayli, E.H. Synthesis and antimicrobial properties of chiral norborne-containing Mannich bases / Eldar Mammadbayli, Gulsum Hajiyeva, Samira Ismayilova [et al.] // Russian Journal of Organic Chemistry, – 2021. V. 57, № 6, – p. 860-867.



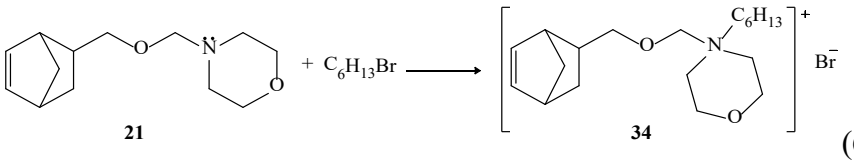
3* **4** **5-9, 11-13** **14*-18*, 20*-22*** (**5**),

where R = C_2H_5 (**5**, **14***), $[\alpha]_D^{20}$ (+)-31.94° (EtOH, *c* 1.6); C_3H_7 (**6**, **15***), $[\alpha]_D^{20}$ (+)-32.03° (EtOH, *c* 2.1); C_4H_9 (**7**, **16***), $[\alpha]_D^{20}$ (+)-30.62° (EtOH, *c* 2.1); C_5H_{11} (**8**, **17***), $[\alpha]_D^{20}$ (+)-30.11° (EtOH, *c* 1.3); C_6H_{13} (**9**, **18***), $[\alpha]_D^{20}$ (+)-30.02° (EtOH, *c* 1.8); NR_2 = piperidino (**11**, **20***), $[\alpha]_D^{20}$ (+)-32.15° (EtOH, *c* 1.3); morpholino (**12, 21***), $[\alpha]_D^{20}$ (+)-30.05° (EtOH, *c* 1.2); azepano (**13**, **22***), $[\alpha]_D^{20}$ (+)-30.82° (EtOH, *c* 1.5).

Synthesis of chiral aminomethoxy derivatives of bicyclo[2.2.1]-hept-2-ene-5-ol

Currently, it is extremely important to obtain optically active forms of new high-quality compounds used in various sectors of the economy [2]. There is a great need for the synthesis of biologically active organic compounds that have a more effective effect in medicine [4] and agriculture [3]. The synthesis of these substances using more affordable and environmentally friendly methods based on local and easy-to-use raw materials is of great scientific and practical importance [13].

On the basis of the obtained chiral alcohol (**3***), paraform and secondary amines (**5–9, 11–13**), asymmetric RM were carried out [21, 37] according to scheme 6:



21 **34** (**6**).

Were studied some of the physicochemical properties of the resulting complex: n_D^{26} – 1.4123, ρ – 906.2 kg/m^3. The resulting

complex (**34**) is a transparent liquid with a characteristic odor, unlike compound (**21**), along with organic solvents, it is well soluble in water. This phenomenon makes it possible to carry out studies of antimicrobial and other properties in an environmentally friendly solvent – water.

Mathematical description of the reaction for obtaining 5-morpholinomethoxymethylbicyclo[2.2.1]-hept-2-ene

Based on the experimental data, a regression mathematical model was developed for the catalytic production of the compound 5-morpholinomethoxymethylbicyclo[2.2.1]-hept-2-ene (**21**), reflecting the influence of the main technological factors (temperature, amount of catalyst) on its yield [32]. The statistical analysis of the obtained model is carried out, the adequacy of the developed model to the experimental data is proved. The optimal values of the input parameters are found, at which the maximum value of the target product yield is achieved.

As a result of mathematical calculations, it was found that the maximum yield of 88.2% of compound (**21**) reaches at a reaction temperature of 85°C and a catalyst (**23**) concentration of 1 mol.%. Based on the found calculated optimal values of the input variables, a control experiment was set up, the yield of the target product was 88%, which indicates the acceptability of the developed regression model. The developed model made it possible to study the influence of each input factor on the output parameter in a wide range of variation of the input variables.

Study of the antimicrobial activity of aminomethoxy derivatives of norbornenylmethanol

The synthesized compounds (**14–18, 20–22, 14*–18*, 20*–22*, 28, 30–33**) were studied as antimicrobial substances at the Azerbaijan Medical University at the Department of «Microbiology and immunology» [10, 15, 17, 18, 26, 27, 36].

Antimicrobial activity was studied by the serial dilution method. For the analysis, 1% solutions of the investigated compounds in ethyl alcohol were prepared. The following cultures

were used as test cultures: gram-positive – *Staphylococcus aureus*, *Bacillus anthracoides*, gram-negative – *Pseudomonas aeruginosa*, *Escherichia coli*, *Kelebsiella pneumoniae*, *Kelebsiella pneumoniae kind of Candida*. For comparison, the control drug (ethanol) and standards (rivanol, furacilin, carbolic acid, chloramine) were tested in the same dilutions.

The investigated compounds have high antimicrobial properties, some of them are capable of inhibiting the growth of the investigated bacteria and fungi at a concentration of 0.125% and an exposure time of 5–10 min. Comparing the antimicrobial properties of the obtained compounds, it can be noted that compounds (**14–18, 20–22, 14*–18*, 20–22***) synthesized with the participation of formaldehyde have more pronounced antimicrobial properties than compounds (**28, 30–33**), synthesized with the participation of benzaldehyde. In addition, optically active forms of compounds (**14*–18*, 20*–22***) exhibit stronger antimicrobial properties than their racemic forms (**14–18, 20–22**). Comparative studies have shown that the synthesized compounds have a higher antimicrobial activity, in contrast to the control drug, and their destructive effect on microorganisms is manifested much faster than that of antimicrobial drugs widely used in medical practice (rivanol, furacilin, carbolic acid, chloramine).

In medicine, one of the important indicators of drugs, when choosing a treatment, is the sensitivity of the causative agent of the disease to this drug. To do this, you need to know the values of the MIC and MBC of the drug. The MIC and MBC values of some of the compounds obtained (**14–18, 20–22, 14*–16*, 22*, 28, 32**) proved that the microorganisms taken are capable of exhibiting sensitivity even at very low concentrations of the compounds under study. Moreover, the sensitivity to optically active compounds turned out to be higher.

The synthesized compounds can be offered as antiseptic substances.

Study of the obtained compounds as inhibitors of sulfate-reducing bacteria.

The obtained norbornene-containing MBs were investigated as inhibitor-bactericides against SRB [22, 30, 33]. For this purpose, solutions of the studied compounds in isopropyl alcohol were prepared. *Desulfovibrio desulfuricans* strain 1143 was taken as test cultures.

The best results are presented in table 9.

Table 9. Bactericidal properties of solutions of aminomethoxy derivatives of norbornene

Solution	Concentration *c*, mg/l	Number of bacteria, number of cells/ml	Amount of H_2S, mg/l	Bactericidal effect, *Z*, %
1	2	3	4	5
5% – **21**	5	–	–	100
	50	–	–	100
	100	–	–	100
1% – **21**	5	10^4	102	60
	50	–	–	100
	100	–	–	100
1% – **34**	5	10^3	93.5	63.3
	50	–	–	100
	100	–	–	100
Nutrient medium		–	24–32	–
Nutrient medium+SRB		10^8	275	–
1% – **15**	5	10^2	38.4	82.7
	50	10^1	25.2	88.6
	100	10^1	18.4	91.7
1% – **20**	5	10^1	9.8	95.6
	50	10^1	7.0	96.8
	100	10^1	6.7	97.0
1% – **22**	5	10^1	10.3	95.4
	50	10^1	9.2	95.9
	100	10^1	7.3	96.7
Nutrient medium		–	14.0	–
Nutrient medium+SRB		10^8	222.0	–

1	2	3	4	5
10% – **30**	5	10^1	24.8	94.8
	50	10^1	18.1	96.2
	100	10^1	11.4	97.6
10% – **32**	5	10^3	131.9	72.3
	50	10^1	9.5	98.0
	100	–	–	100
10% – **33**	5	10^2	87.6	81.6
	50	10^1	46.6	90.2
	100	10^1	34.7	92.7
Nutrient medium		–	30–32	–
Nutrient medium+SRB		10^8	476	–

As you can see from the table 9, the tested compounds in all three concentrations (5, 50, 100 mg/l) exhibited bactericidal properties. Comparing the bactericidal properties of the compounds considered above with the properties of АМДОР ИК-7 and АМДОР ИК-10 standards, it can be noted that the studied compounds, in contrast to the standards, showed high bactericidal activity even at very low concentrations. Moreover, compounds (**15, 20–22, 34**) obtained on the basis of formaldehyde have higher bactericidal properties than compounds (**30, 32, 33**) obtained on the basis of benzaldehyde. This is revealed by the fact that the former exhibit a bactericidal effect even at a 1% solution concentration, while the latter exhibit a bactericidal effect starting from a solution concentration of 10%. But, despite this, they turned out to be more effective than the considered standards.

Taking into account the above, norbornene containing MBs can be proposed as inhibitor-bactericides against SRB.

Study of aminomethoxy derivatives of norbornene as antimicrobial additives to oils and fuels

The synthesized new norbornene-containing MBs were investigated as antimicrobial additives [23, 31] in synthetic oil – alkenylsuccinic acid diester, in T-22 base oil and fuel – AI-95 gasoline. The study was carried out at the Institute of Chemistry of Additives named after academician A.M. Kuliyev of the National

Academy of Sciences of Azerbaijan. Antimicrobial properties were determined by the zonal diffusion method based on ГОСТ 9.052-88 and ГОСТ 9.082-77. Bacteria – *Pseudomonas aeruginosa, Mycobakterium phle*i, fungi (in oil) – *Aspergillus niger, Penicillium chrysogenum*, fungi (in gasoline) – *Cladosporium resinae* were taken as test cultures. The results of the study were compared with the data of the standard – sodium pentachlorophenolate.

The results of the study are presented in table 10.

Table 10. Biocidal activity of norbornene-containing MBs

№	Concent-ration, %	Zone of inhibition of the growth of microorganisms, cm				
		Synthetic oil	Oil T-22		Fuel (AI-95)	
		Bacteria	Bacteria	Fungi	Bacteria	Fungi
1	2	3	4	5	6	7
16	1.0	1.5–1.5	1.4–1.6	+++	–	–
	0.5	1.0–1.2	1.0–1.0	+++	**1.6–1.8**	+++
	0.25	+++	+++	+++	1.2–1.2	+++
17	1.0	1.2–1.3	1.2–1.4	+++	–	–
	0.5	1.0–1.0	+++	+++	**1.5–1.6**	+++
	0.25	+++	+++	+++	1.1–1.2	+++
20	1.0	**3.0–2.8**	**2.5–3.0**	1.4–1.6	–	–
	0.5	**2.5–2.5**	**2.0–2.0**	1.0–1.0	1.3–1.4	+++
	0.25	**1.4–1.4**	**1.2–1.3**	+++	1.1–1.1	+++
21	1.0	**3.0–3.0**	**2.2–2.5**	1.4–1.2	–	–
	0.5	**1.8–2.0**	**2.0–1.8**	1.0–1.0	**1.8–2.0**	1.0–1.2
	0.25	1.0–1.0	1.1–1.0	+++	**1.4–1.4**	+++
28	1.0	–	1.2–1.2	1.4–1.6	–	–
	0.5	–	+++	+++	+++	**2.5–2.8**
	0.25	–	+++	+++	+++	+++
29	1.0	–	+++	1.2–1.2	–	–
	0.5	–	+++	+++	+++	**2.3–2.6**
	0.25	–	+++	+++	+++	+++
30	1.0	–	+++	1.1–1.2	–	–
	0.5	–	+++	+++	+++	**2.5–3.0**
	0.25	–	+++	+++	+++	**1.6–1.6**

1	2	3	4	5	6	7
31	1.0	–	1.4–1.6	1.6–1.6	–	–
	0.5	–	1.2–1.2	1.0–1.0	+++	**2.4–2.7**
	0.25	–	+++	+++	+++	**1.2–1.4**
32	1.0	–	1.4–1.4	1.1–1.2	–	–
	0.5	–	1.2–1.2	+++	+++	**1.6–1.8**
	0.25	–	+++	+++	+++	+++
*	1.0	1.3–1.4	1.3–1.4	1.3–1.4	–	–
**	0	+++	+++	+++	+++	+++

Note: (+++) – development of microorganisms,
(–) – not investigated,
* – standard (sodium pentachlorophenolate),
** – control.

From table 10 seen, that compounds (**16, 17**) obtained on the basis of norbornenylmethanol, formaldehyde, and secondary aliphatic amines exhibited high bactericidal properties in the composition of the fuel. Compounds (**20, 21**) obtained from norbornenylmethanol, formaldehyde, and secondary alicyclic amines showed high bactericidal properties in the composition of oils, almost two times more than the reference. Compound (**21**) also exhibited high bactericidal properties in the composition of the fuel. Compounds (**28–32**) obtained with the participation of benzaldehyde exhibited high fungicidal properties in the composition of the fuel.

As a result of the studies (Table 10), compounds (**16, 17, 20, 21**) can be proposed as antimicrobial additives to oils and fuels against bacteria, and compounds (**28–31**) can be proposed as antifungal additives to fuels.

CONCLUSIONS

1. An efficient thermal method has been developed for the synthesis of new racemic and optically active aminomethoxy derivatives of bicyclo[2.2.1]-hept-2-ene by the reaction of secondary amines, aldehyde (formaldehyde, benzaldehyde) and norbornenylmethanol. The yields of the obtained compounds were 43–71% (with formaldehyde), 42–75% (with benzaldehyde). 26 new

compounds have been synthesized. The physicochemical properties of the obtained compounds were determined, their structure and composition were confirmed by IR, ^{1}H, ^{13}C NMR spectroscopy and mass spectrometry. The optical activity of the synthesized chiral compounds was investigated by the polarimetric method.

2. Found the optimal condition for catalytic aminomethylation reactions based on norbornenylmethanol, aldehyde (formaldehyde, benzaldehyde) and secondary amines in the presence of CuCl, $Sm(NO_3)_3 \cdot 6H_2O$, *N*-methylpyrrolidonium hydrogen sulfate, 1,4-dimethylpiperazine dihydrosulfate as catalysts. It was found that when the reaction is carried out for 0.5–1.0 h at a temperature of 80°C, in the presence of 1 mol.% of the catalyst, the yield reaches 69–94% (with formaldehyde) and 71–94% (with benzaldehyde). The highest yield of 78–94% (with formaldehyde), 81–94% (with benzaldehyde) is achieved when the reaction is carried out with *N*-methylpyrrolidonium hydrogen sulfate.

3. The antimicrobial properties of the synthesized racemic and optically active aminomethoxy derivatives of bicyclo[2.2.1]-hept-2-ene against bacteria – *E.coli, P.aeruginosa*, *K.pneumoniae, S.aureus, B.anthracoide*s and fungi – *C.albicans*. It was found that all the considered compounds have the same destructive effect on microorganisms (the exception is *B.anthracoides*), and faster (in some cases in 5–10 minutes at a reagent concentration of 0.125%) than the standards (rivanol, furacilin, carbolic acid, chloramine). Comparative studies have shown that the optical forms of aminomethoxy derivatives of bicyclo[2.2.1]-hept-2-ene showed better results than their racemic form.

4. According to the data of the minimum inhibitory concentration and the minimum bactericidal concentration, the sensitivity of *S.aureus, E.coli, C.albicans* against some of the obtained MBs was studied. It was found that microorganisms react to very low concentrations of analyzed compounds; in some experiments, 0.000625% of the reagent was sufficient.

5. The bactericidal-inhibiting properties of the obtained aminomethoxy derivatives of bicyclo[2.2.1]-hept-2-ene and the complex obtained from 5-morpholinomethoxymethyl-bicyclo[2.2.1]-

hept-2-ene with hexyl bromide in relation to SRB were studied. It was found that the compounds under study slow down the growth of bacteria, and some of them completely destroy SRB. It was found that compounds based on formaldehyde exhibit a bactericidal-inhibiting effect even at a concentration of 0.005%, and compounds based on benzaldehyde – starting from 0.05%, in contrast to the standards (АМДОР ИК-7 and АМДОР ИК-10), which at these concentrations showed biostatic properties. It was also noted that the compounds synthesized with the participation of cyclic amines have stronger bactericidal-inhibiting properties in comparison with the compounds synthesized on the basis of aliphatic amines.

6. Aminomethoxy derivatives of bicyclo[2.2.1]-hept-2-ene have been studied as antimicrobial additives to oils and fuels. The results of the study showed that the analyzed compounds based on formaldehyde in oils and in AI-95 gasoline exhibited effective bactericidal properties. Moreover, the compounds containing fragments of morpholine and piperidine in synthetic oil and in T-22 oil exhibited two times greater bactericidal properties (2.5–3.0 cm) than the reference (sodium pentachlorophenolate). Compounds based on benzaldehyde had a high antifungal effect in AI-95 gasoline: 0.5% of the reagent destroys fungi in a zone with a diameter of 2.3–3.0 cm. Compounds containing fragments of dihexylamine and piperidine at a concentration of 0.25% showed a result of 1.6–1.8 cm.

The main content of the thesis is published in the following articles and abstracts:

1. Mammadbayli, E.H. Synthesis and investigation of racemic and optically active forms of functional substituted derivatives of norbornene / Eldar Mammadbayli, Ogtay Abdiyev, Tamela Kazimova, Gulsum Hajiyeva // Scientific works. Fundamental sciences, – 2013. № 2, – p. 268-281.

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