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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Synthesis and Examination of Antimicrobial Properties of Aminomethylated Derivatives C_6–C_7 of Alicyclic Diols

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Abstract—Synthesis of C_6–C_7 alicyclic diols was studied by a catalytic oxidation of cyclohexene, norbornene and their methyl derivatives in the presence of heterogenized molybdenum-containing catalysts. By a triple condensation of the diols with formaldehyde and secondary amines a synthesis of their aminomethylated derivatives with various substituents at nitrogen atom was examined. Antimicrobial properties of the synthesized amino alcohols in M-10 oil as additives with fungicidal and bactericidal activities were studied.

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Alicyclic amino alcohols containing alkyl-, aryl-, and heterocyclic substituents at nitrogen atom are promising intermediates of organic and petroleum synthesis whose structural features determine their rich functional capacity as monomers and biologically active substances employed in pharmaceuticals of various functions [1–3]. These compounds are of interest due to the presence of similar structural moieties in composition of many natural biologically active substances [4, 5].

Unlike amino alcohols of aliphatic and aromatic series [6–8] similar derivatives of alicyclic series [9, 10] attract significantly smaller attention. Data on the synthesis of aminomethylene derivatives from cyclohexane and norbornane diols, and on the investigation of their biological properties are practically lacking.

It is known that the simultaneous presence in a molecule of amino- and hydrosubstituents imparts to them antioxidation and antimicrobial properties [11]. Nowadays when machines and mechanisms are improved a protection of applied oils, fuels, and composed polymeric and other materials from biodamages is actual [12].

Our paper is aimed at a synthesis of N-substituentd amino alcohols of cyclohexane and norbornane series by induced oxidation of the corresponding cycloolefins with hydrogen peroxide in the presence of acetic acid and heterogenic catalysts obtained on the basis of bentonite, kaolin, and halides or oxyhalides of metalls of VI–VIII groups of the periodic system, followed by aminomethylation of the reaction products without previous separation of oxidate, and also at a research of the antimicrobial properties of the synthesized compounds.

EXPERIMENTAL

Starting cyclohexene and 1-methylcyclohexene were prepared by cyclohexanol and 3-methylcyclohexanol-1 dehydration at 220–250°C on γ-Al_2O_3. Bicyclo[2,2,1]hept-2-ene and its 5-methyl derivative we synthesized by condensation of cyclopentadiene with ethylene and propylene with the aid of a known technique [3].

Samples of catalysts we impregnated with a mixture of bentonite, kaolin, and aqueous or alcoholic solutions of $MoCl_5$, $MoOBr_3$, WCl_6, CrO_2Cl_2, $CoBr_2$, followed by their carbonization in 4-vinylcyclohexene flow at 500–550°C in the course of 4 h.

The cycloolefin oxidation was conducted in glass thermostat equipped with a magnetic stirrer at 70–80°C in the presence of the above catalysts. The reaction course was monitored by chromatography and chemical techniques (permanganate- and iodometric titration). After the reaction completion the organic and aqueous layers were separated, the latter layer was three times extracted with toluene. An extract and the organic layer were mixed, and first at 75–85°C and then at 100–105°C in a glass reactor equipped with a nozzle were subjected to aminomethylation with formaldehyde and secondary amines (under conditions of Mannich reaction). The reaction mass after toluene distillation and cooling was maintained for a day, and then aminomethylated derivatives of the corresponding diols were isolated by vacuum distillation.

IR spectra of the synthesized compounds were recorded on a UR-20 spectrometer in a range of 400–3600 cm^{-1}, ^1H NMR spectra, with Jeol-FT80A instrument (80 MHz), solvent CCl_4, internal reference HMDS. The purity of the synthesized compounds was determined by thin layer chromatography TLC on Silufol UV-254 plates in the systems of the solvents [benzene : diethyl ether = (3–5) : 1, a developer iodine].

Antimicrobial properties of the synthesized compounds were determined by GOST 9,052–88 and 9,082–77 (RF State Standard). Microoraganisms: bacterial (*Mycobacterium lacticola*, *Psendomonas aeruginosa*), fungicidal (*Aspergillus niger*, *Clodosporium resinac*), yeast (*Candida tropicalis*) were used as test-cultures. The noted microorganisms were grown at 28 ± 2°C in a special thermostat with 90–100%-moisture: fungi for 5–6 days; bacteria for 2–3 days. Beef-extract agar (BEA) and wort-agar (WA) were used as nutrient media for bacteria cultures, and fungi and yeast cultures, respectively. 8-Oxyquinoline and sodium pentachlorophenolate were used as references.

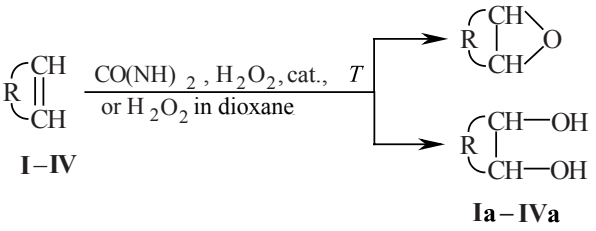
Catalytic oxidation of the cycloolefins by hydrogen peroxide was carried out in a heterophase system liquid–liquid in the presence of powdery heterogenized catalysts which react readily with hydrogen peroxide forming peroxy compounds of various compositions and stability [14]. The experimental results on catalyst selection are presented in Table 1.

The results of the experiments in the presence of both carbonized and non-carbonized samples of catalysts were listed in Table 1. As shown in these data the carbonized samples manifest higher activity in oxidation that is possibly caused by partial introduction of coal moieties in a composition of compounds of transition metals, and by a formation of more active form of a catalytic complex.

Using freshly prepared samples in the reaction course upon substrate oxidation a partial transition of salts from the catalyst composition into a liquid phase occurs. After removal of the used catalyst a rate of further oxidate oxidation is strongly decreased and consists 10–15% of the oxidation rate in the case of the presence of the catalyst.

The salt transition in the oxidate proceeds more intense use of a non-carbonized catalyst. In this case apparently salt molecules weakly attached to a contact surface pass in the solution. Due to a treatment of these samples under oxidation conditions for 3–4 h the transition of chlorides and bromides in a solution is practically stopped.

Oxidate composition obtained in the presence of the developed catalytic systems is practically identical with compositions prepared with the aid of homogeneous catalysts [15, 16]. Main products are epoxides, diols and their monoacetates. In some cases there are unsaturated alcohols and ketones in the catalysate. The molybdenum-containing samples ($MoOBr_3$, $MoCl_5$) are the most active and selective among the synthesized catalysts. The oxidation of other unsaturated hydrocarbons was performed in the presence of these samples of the catalysts according to the scheme:



where R is cyclohexene (**I**), 3-methylcyclohexene (**II**), becyclo[2,2,1]hept-2-ene (**III**), 5-methylbicyclo-[2,2,1]hept-2-ene (**IV**), the corresponding vicinal dioles (**Ia**)–(**IVa**). Experimental results are listed in Table 2.

The synthesis of the corresponding amino alcohols was carried out from the condensation of the isolated diols, and also oxidate with formaldehyde and secondary amines of various composition and structure (according to Mannich reaction).

Optimal product yields of aminomethylation of cyclohexane diol are attained at 70–80°C, of norbornane

Table 1. Activity of catalyst in the course of oxidation of cyclohexene with hydrogen peroxide. Temperature 70°C, reaction time 1 h, molar ration cyclohexene : CH_3COOH : active oxygen [O] = 1: 0.2 : 1.2

Catalyst	Conversion, %		Composition of liquid catalyst, wt %				
	H_2O_2	C_6H_{10}	epoxide	diol	monoacetate	unsaturated alcohol	ketone
$MoCl_5/nAl_2O_3{\cdot}mSiO_2$[a]	98.5	75.2	12.2	68.5	11.8	7.5	–
$MoBr_3/nAl_2O_3{\cdot}mSiO_2$[a]	100	82.5	3.8	76.3	13.7	6.2	–
$WCl_6/nAl_2O_3{\cdot}mSiO_2$[a]	95.6	78.4	29.0	49.4	9.2	12.4	–
$CoBr_2/nAl_2O_3{\cdot}mSiO_2$[a]	100	67.1	–	51.6	7.2	19.0	22.1
$CrO_2Cl_2/nAl_2O_3{\cdot}mSiO_2$[a]	97.0	77.0	7.6	43.0	11.0	3.6	34.8
$MoCl_5{\cdot}CoBr_2/nAl_2O_3{\cdot}mSiO_2$[a]	100	85.0	–	74.9	9.8	–	15.3
$MoOBr_3{\cdot}CoBr_2/nAl_2O_3{\cdot}mSiO_2$[a]	100	91.6	–	76.8	11.2	–	12.0
$MoCl_5/nAl_2O_3{\cdot}mSiO_2$[b]	97.2	81.6	17.4	65.9	14.0	2.7	–
$MoOBr_3/nAl_2O_3{\cdot}mSiO_2$[b]	98.0	83.7	10.6	71.8	11.4	6.2	–
$MoOBr_3{\cdot}CoBr_2/nAl_2O_3{\cdot}mSiO_2$[b]	98.5	83.0	3.2	68.6	10.4	8.7	9.1

[a] A support is $nAl_2O_3 \cdot mSiO_2$–bentonite : kaolin = 5 : 1. [b] Carbonized catalyst.

Table 2. Induced oxidation of cycloolefins by hydrogen peroxide in the presence of carbonized $MoCl_5/nAl_2O_3{\cdot}mSiO_2$. Temperature 80°C, reaction time 4 h, molar ratio of cycloolefin : CH_3COOH : active oxygen [O] = 1 : 0.2 : 1.2

Catalyst	Conversion, %		Composition of liquid catalyst, wt %				
	H_2O_2	C_6H_{10}	epoxide	diol	monoacetate	unsaturated alcohol	ketone
3-Methylcyclo-hexene	98.4	78.4	6.7	80.2	9.4	3.7	–
Bicyclo[2.2.1]hept-2-ene	97.0	86.0	3.4	84.6	6.2	–	2.6
5-Methylbicyclo-[2.2.1]heptene-2	95.3	84.2	6.0	81.5	5.7	–	–

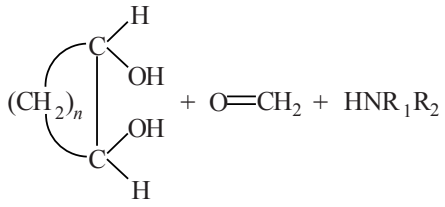
diol at 100–105°C, under an equimolar ratio of reagents and reaction time of 4–6 h (Table 3).

Structure of the synthesized diols and their amino-methylated derivatives was determined by IR and ^{1}H NMR spectroscopy [17, 18]. In ^{1}H NMR spectrum of bicyclopentadiol-2,3 (**IIIa**) in a region of strong fields appears a doublet of doublets signal with chemical shift at δ = 1.38 ppm corresponding to *endo*-protons, and triplet signal δ = 1.57 ppm corresponding to *exo*-protons at C^5 and C^6 atoms. On the basis of the coupling constants ($J_{6,6}$ = 12.2–12.5, $J_{5,6\ endo}$ = 5.0–5.3, $J_{5,6\ exo}$ = 9.5–9.7 Hz) since the high coupling constant corresponds to *exo*-protons H^5, H^6 and the low coupling constant, *endo*-protons H^5, H^6 we can conclude that the synthesized compounds have the *endo*-configuration. In a region δ 1.31 and 1.56 ppm there are H^7_{anti} protons and H^7_{sin} protons; C^2 and C^3 signals manifest themsemves as doublet at δ = 3.26 ppm with coupling constant $J_{2,3}$ = 4.5–4.7 Hz. Proton signals of two hydroxy groups reveal themselves in the region 4.81 ppm (br.s), proton signals at C^1 and C^4, in the region 1.52 ppm (d). Proton signals of methylbicyclo[2.2.1]heptane-2,3-diol (**IVa**) are identical with signals of compound **IIIa**. Protons of methyl group are manifested at δ = 1.09 ppm (s), proton signal at C^5 bearing the methyl group is shifted down field (δ = 1.61 ppm), signals of two protons at C^6 shift up field and reveal themselves at δ = 1.25 and δ = 1.50 ppm.

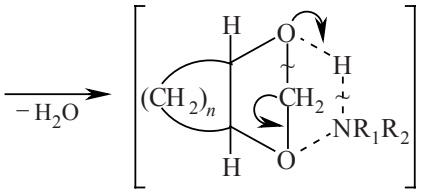
Table 3. Yield and composition of products of aminomethylation

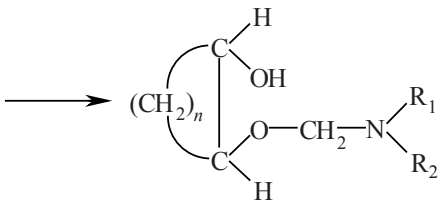
Compd.	Yield, %	bp, °C (*P*, mm Hg); mp, °C	Found, %			Formula	Calculated, %		
			C	H	N		C	H	N
Va	90.5	124–126(2.5); 34–37	62.37	11.06	8.04	$C_9H_{19}NO_2$	62.43	10.98	8.09
Vb	89.3	145–147(2.5); 58–61	65.61	11.52	6.85	$C_{11}H_{23}NO_2$	65.67	11.44	6.96
Vc	86.6	175–178	56.61	9.91	5.96	$C_{11}H_{23}NO_4$	56.65	9.87	6.01
Vd	88.4	84–87	67.57	10.87	6.61	$C_{12}H_{23}NO_2$	67.60	10.80	6.57
Ve	87.3	98–101	61.33	9.81	6.58	$C_{11}H_{21}NO_3$	61.40	9.78	6.51
Vf	85.8	126–129	70.52	8.67	6.28	$C_{13}H_{19}NO_2$	70.59	8.59	6.33
Via	89.6	121–123(3); 44–47	64.11	11.36	7.43	$C_{10}H_{21}NO_2$	64.17	11.23	7.49
VIb	88.5	65–67	69.91	11.73	6.63	$C_{12}H_{25}NO_2$	66.98	11.63	6.51
VIв	84.3	185–188	58.23	10.72	5.62	$C_{12}H_{25}NO_4$	58.3	10.12	5.67
VId	85.7	90–93	68.65	11.10	6.08	$C_{13}H_{23}NO_2$	68.72	11.01	6.17
Vie	86.4	83–86	67.55	10.84	6.62	$C_{12}H_{23}NO_2$	67.61	10.79	6.57
VIf	87.5	130–133	71.43	8.58	5.92	$C_{14}H_{21}NO_2$	71.49	8.94	5.96
VIIa	93.5	63–66	64.88	10.41	7.61	$C_{10}H_{19}NO_2$	64.82	10.27	7.56
VIIb	88.6	89–92	67.68	11.12	6.73	$C_{12}H_{23}NO_2$	67.61	10.8	6.57
VIIc	82.5	208–211	58.72	9.45	6.71	$C_{12}H_{23}NO_4$	58.78	10.71	6.51
VIId	83.6	113–116	69.47	10.42	6.34	$C_{13}H_{23}NO_2$	69.33	10.22	6.22
VIIe	85.2	128–131	63.40	9.31	6.15	$C_{12}H_{21}NO_3$	63.44	9.25	6.17
VIIf	81.4	155–158	72.02	8.23	5.96	$C_{14}H_{19}NO_2$	72.10	8.15	6.02

We established that the reaction direction and the product composition depend mainly on the reaction temperature. Reaction proceeds with equimolar ratios of the reagents, in a temperature range of 65–70°C in the course of 4–5 h in general with the formation of amino alcohols [14]. More stringent conditions (an increase in temperature up to 100–110°C and in reaction time up to 5–6 h) result in enhancement of aminomethylation of alicyclic diols. This reaction route, possibly, occurs through a stage of formation of intermediate with dioxolane moiety then attacked by the molecule of the secondary amine with formation of the corresponding six-membered complex. Decomposition of latter yields aminomethylated derivatives C_6–C_7 of alicyclic diols according to Mannich reaction.



Ia–**IVa**





Va–Vf–VIIIa–VIIIf

R_1=R_2=CH_3 **Va–VIIIa**; R_1=R_2=C_2H_5 **Vb–IIIb**; R_1=R_2=CH_2CH_2OH **Vc–VIIIc**; $R_1 + R_2 = -(CH_2)_5$ **Vd–VIIId**; $R_1 + R_2 = [-(CH_2)_2]_2O$ **Ve–VIIIe**; R_1 = H, $R_2 = -C_6H_5$ (**Vf**)–(**VIIIf**).

In the IR spectra of mono and bicyclic amino alcohols the absorption bands in a region 3615 and 1150 cm^{-1} are attributed to OH-group at tertiary carbon atom. For amino alcohols **Vc–VIIc** absorption bands were found at frequencies 3630 and 1250 cm^{-1}, attributed to primary CH_2–OH-group of alkyl radical. In the IR spectra of compounds **Vf–VIIf** there exist the vibration in a region 1570, 1590 and 770–730, 690 $см^{-1}$ typical of aminophenyl radical.

In ^1H NMR spectra of amino alcohols **Va–Vf–VIIa–VIIf** there is a wide singlet at 4.81 ppm attributed to OH-group. In spectra of products **Vc–VIIc** appeared also a wide singlet 4.78 ppm typical of hydroxy groups of oxyethylene moieties at nitrogen atom. Proton of CHOH-group at cyclohexyl radical of compounds **Va–Vf, VIa–VIf** is characterized by a triplet at 3.40–3.48 ppm in compounds **VIIa–VIIf**, and by doublet of doublets at 3.99–3.40 ppm. Spectra of amino alcohol **Va–VIIIa** possess singlet at 2.28 ppm, of compounds **Vc–VIIIc**, a singlet at 1.06–1.10 ppm attributed to protons of CH_3-groups. Protons $-NCH_2CH_2$-group of amino alcohols **Ib–IVb** are characterized by a doublet at 2.42 ppm, **Vc–VIIIc,** by a doublet of doublets at 2.56–2.64 ppm. Spectra of compounds **Id–IVd** contain doublets at 1.42 and 2.26 ppm characterizing the protons of CH_2-group of piperidine and morpholine moieties, respectively.

Spectra of amino alcohols **Vf–VIIIf** possess a doublet at 5.16 ppm and multiplets in a region of 6.43–7.08 ppm attributed to protons of $-OCH_2N=$ and of aromatic moieties, respectively.

Synthesized compounds with concentrations 1 and 2 wt% were examined as antimicrobial additives to an engine oil M-10. Experimental results are listed in Table 4.

As shown in the presented data all studied amino methylated derivatives of alicyclic diols possess fungicidal activity. A value of an inhibition area of a fungus growth in dependence on the compound structure and its concentration is on the average 0.7–1.1 cm (at 1 wt % concentration) and 1.3–2.1 cm (at 2 wt % concentration).

Phenylaminomethoxy- and morpholinemethoxy-substituentd cyclohexane-, methylcyclohexane-, and norbornane diols are characterized by fungicidal properties and are not worse than 8-oxyquinoline (reference) according to their values. As shown in Table 4, 8-oxy-quinoline does not possess fungicidal activity at 1 wt% concentration, but the fungi growth is inhibited on 2 wt% concentration. These data manifest that the examined compounds are not worse than sodium pentachlorophenolate (reference) in their fungicidal properties. As regards the used oil M-10 it is unstable for fungi and bacteria. Results of comparative researches show that iminomethylene derivatives of alicyclic diols are of practical interest, and can be applied as antimicrobial additives to lubricating oils

Table 4. Experimental results of antimicrobial properties of aminomethylated derivatives of alicyclic diols in an engine oil M-10

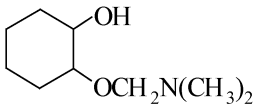
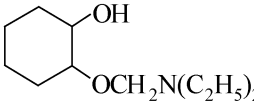
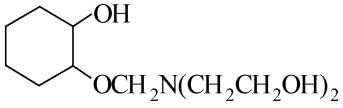
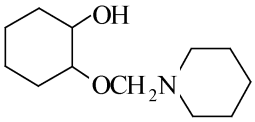
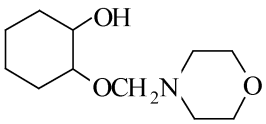
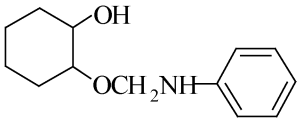
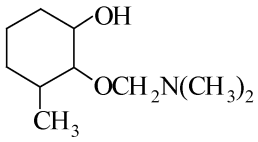
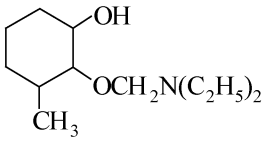
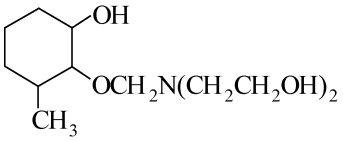
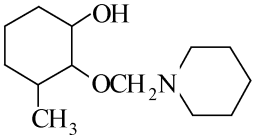
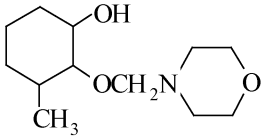
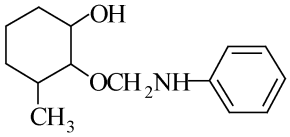
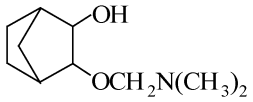
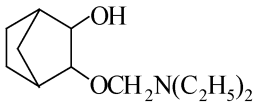
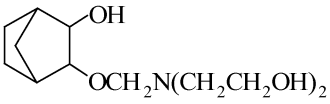
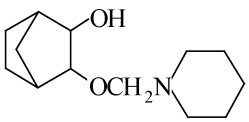
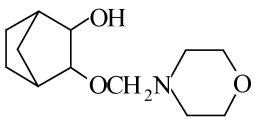
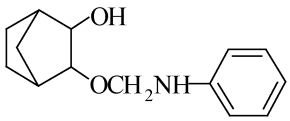
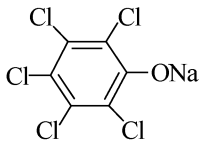
Compound	Formula	Comcemtration on oil	Inhibition area, cm	
			of bacrteria	micelial fungi
2-(*N,N′*-Dimethylamino-methylenoxy)cyclohexanol (**Va**)		1.0 2.0	+ + + +	0.9–1.0 1.6–2.0
2-(*N,N′*-Diethylamino-methylenoxy)cyclohexanol (**Vb**)		1.0 2.0	+ + + +	0.9–1.1 1.8–2.1
2-(*N,N′*-Dioxyethylenamino-methylenoxy)cyclohexanol (**Vc**)		1.0 2.0	+ + + +	+ + 1.0–1.2
2-(Piperidinomethylenoxy)-cyclohexanol (**Vd**)		1.0 2.0	+ + + +	+ + 1.0–1.2
2-(Morpholinemethylenoxy)-cyclohexanol (**Ve**)		1.0 2.0	+ + 1.2–1.4	0.8–1.1 1.2–1.8
2-(Phenylaminomethylenoxy)-cyclohexanol (**Vf**)		1.0 2.0	0.8–1.1 2.0–2.2	0.9–1.1 1.7–1.9
3-Methyl-2-[*N,N′*-(dimethyl-aminomethylenoxy)]cyclohexanol (**VIa**)		1.0 2.0	+ + + +	+ + 1.6–2.1
3-Methyl-2-(*N,N′*-diethyl-aminomethylenoxy)cyclo-hexanol (**VIb**)		1.0 2.0	+ + + +	0.8–1.1 1.5–2.0
3-Methyl-2-(*N,N′*-dioxyethyl-enaminomethylenoxy)cyclo-hexanol (**VIc**)		1.0 2.0	+ + 1.0–1.1	+ + 1.6–1.8
3-Methyl-2-(piperidino-methylenoxy)cyclohexanol (**VId**)		1.0 2.0	+ + 0.9–1.1	0.9–1.0 1.5–2.0
3-Methyl-2-(morpholinemethylenoxy)cyclo hexanol (**VIe**)		1.0 2.0	+ + 1.0–1.2	0.7–1.1 1.5–2.0

Table 4. (Contd.)

Compound	Formula	Comcemtration on oil	Inhibition area, cm	
			of bacrteria	micelial fungi
3-Methyl-2-(phenylamino-methylenoxy)cyclohexanol (**VIf**)		1.0 2.0	0.8–1.0 1.7–1.8	0.8–1.0 1.8–2.0
3-(*N,N* '-Dimethylamino-methylenoxy)bicyclo[2.2.1]-heptan-2-ol (**VIIa**)		1.0 2.0	+ + + +	0.8–1.0 1.5–2.1
3-(*N,N* '-Diethylamino-methylenoxy)bicyclo[2.2.1]-heptan-2-ol (**VIIb**)		1.0 2.0	+ + + +	0.9–1.0 1.5–1.8
3-(*N,N*'-Dioxyethylenamino-methylenoxy)bicyclo[2.2.1]-heptan-2-ol (**VIIc**)		1.0 2.0	+ + 1.1–1.4	0.8–1.1 1.0–1.3
3-(Piperidinomethylenoxy)-bicyclo[2.2.1]heptan-2-ol (**VIId**)		1.0 2.0	+ + 1.0–1.2	0.8–1.1 1.5–2.0
3-(Morpholinomethylenoxy)-bicyclo[2.2.1]heptan-2-ol (**VIIe**)		1.0 2.0	+ + 1.6–1.8	0.8–1.0 1.5–1.7
3-(Phenylminomethylenoxy)-bicyclo[2.2.1]heptan-2-ol (**VIIf**)		1.0 2.0	0.9–1.1 1.8–2.0	0.8–1.1 1.8–1.9
8-Oxyquinoline (reference) (**VIII**)		1.0 2.0	0.8–1.0 1.6–2.1	+ + + +
Engine oil M-10 (without additive) (**IX**)		–	+ +	+ +
Sodium pentachlorophenolate (reference) (**X**)		1.0	1.1–1.3	+ +

Antimicrobial action of the synthesized compounds essentially depends on the nature of substituents at nitrogen atom and increases in series.

CONCLUSIONS

By triple condensation of alicyclic diols with formaldehyde and secondary amines (according to Mannich reaction) were synthesized aminomethylene derivatives of cyclohexane- and norbornane diols, and it was stated that these compounds of 1–2 wt % concentration in the engine oil possessed high fungicidal and bactericidal activity relative to mycelial fungi.

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