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Synthesis and Properties of Methyleneoxyamine Derivatives of 1-(Propylthio)octane

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Abstract—Synthesis of new methyleneoxyamine derivatives of 1-(propylthio)octane by condensation of 1-(propylthio)octane with secondary amines and formaldehyde was carried out. Structure of the synthesized compounds was proved by elemental analysis, IR, ^{1}H NMR, and mass spectra. Compounds were tested as antimicrobial additives to lubricating oils. They were found to suppress effectively the activity of microorganisms.

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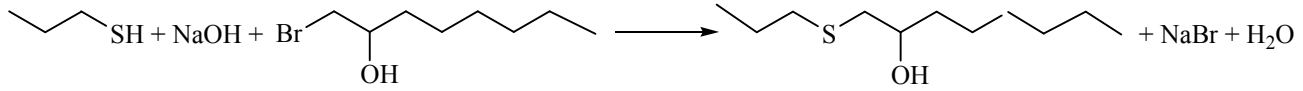
Organic compounds containing sulfur and nitrogen are widely used as antioxidative, anticorrosive and antimicrobial additives to fuels and oils [1]. Modern technology development is connected with enhanced requirements for machines operation and lubricating oils respectively. Therefore synthesis of additives of new type and study of functional properties of new organic compounds are important [2]. Substituted sulfur-containing compounds are biologically active compounds and are constituents of some pharmaceuticals used currently in medicine [3–5]. Pyrimidine S,N- or N,S-disubstituted bases show high therapeutic effect. In particular, they exhibit antiviral and antitumour action [6]. Synthesis of new representatives of the aforementioned compounds from available raw material and improvement of their preparation methods are very actual [7–9]. The Mannich reaction is one of the suitable and effective approaches to methyleneoxyamine derivatives of various kinds [10–12].

As extension of our investigations on the nitrogen- and sulfur-containing organic compounds [13–15] in this work concerns the synthesis and study of the properties of new methyleneoxyamine derivatives of 1-(propylthio)octane.

We synthesized the earlier unknown 1-(propylthio)-octan-2-ol **III** on the basis of reaction of 1-propylthiol **I** with 1-bromooctan-2-ol **II** by the following scheme:

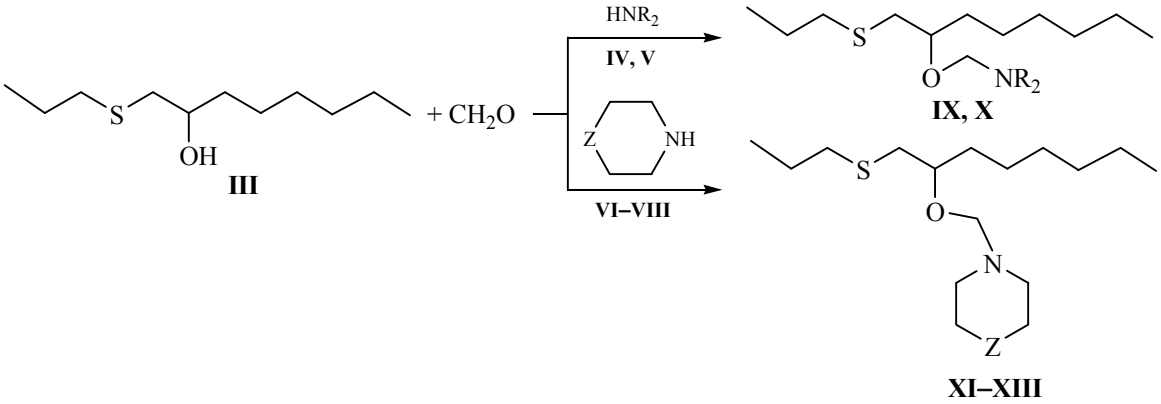


I **II** **III**

The reaction was performed at the equimolar ratio of initial components **I** and **II** in alkaline medium (40% aqueous NaOH) at 45–50°C over 3–4 h. Yield of alcohol **III** was 74%.

Further Mannich condensation of 1-(propylthio)-octan-2-ol **III** with formaldehyde and secondary amines **IV–VIII** gave new representatives of 1-(propylthio)-2-methyleneoxyaminooctanes **IX–XIII** (see scheme below).

Prepared 1-(propylthio)octan-2-ol **III** and its aminoderivatives **IX-XIII** are transparent liquids with specific odor. They are insoluble in water, but readily



R = C_2H_5 (**IV, IX**), C_4H_9 (**V, X**); Z = CH_2 (**VI, XI**), O (**VII, XII**), CH_2–CH_2 (**VIII, XIII**).

soluble in organic solvents (ethanol, acetone, benzene, CCl_4, $CHCl_3$ etc.). Synthesis of methyleneoxyaminoderivatives **IX-XIII** starting from alcohol **III** was carried out at 45–55°C over 4–5 h and at equimolar ratio of initial components. The yield of target products was 76–78%.

The structure of the obtained compounds **III** and **IX–XIII** was confirmed by elemental analysis data, IR, ^{1}H NMR spectroscopy and mass spectrometry. Purity of starting and prepared compounds and composition of the reaction mixtures were monitored with GLC.

The IR spectrum of **III** contains a wide absorption band at 3500 cm^{-1} belonging to hydroxy group [16] that is absent in the corresponding spectra of compounds **IX-XIII**. Absorption bands at 725 cm^{-1} characteristic for C−S bonds were observed in the spectra of the all obtained compounds. In the IR spectra of **IX-XIII** there are absorption bands in the range of 1220–1060 cm^{-1} originating from C−N bond vibrations, and also at 2950–2910 and 2880–2845 cm^{-1} belonging to vibrations of C−H bond and CH_3 and CH_2 groups respectively.

The ^{1}H NMR spectra of the obtained compounds prove this structure. Proton signals of CH_3 groups appear as triplets in the range of 0.90–1.0 ppm. Triplet signals of CH_2 group protons (OCH_2, NCH_2, SCH_2) were found at 2.60–2.95 ppm. Signals of OCH_2N group protons were observed as doublets of doublets at 4.20–4.25 ppm.

The mass spectra (electron impact) of compounds **III**, **IX-XIII** contain signals of corresponding molecular ions and their fragmentation products.

Compounds **IX–XIII** were tested as antimicrobial additives in Institute of Additives of National Academy of Sciences of Azerbaijan. Experiments were performed using oil "M-11" (GOST-9-052-75) as an example. Mushroom (*Aspergillus niger*, *Candida tropicalis*) and bacterial (*Pseudomonas aeruginosa*) cultures were used as test-cultures. The results of these tests are given in the table.

It was established that these compounds in certain concentrations (0.5–1 wt %) suppress effectively microorganism growth; in so doing, compounds **IX** and **X** are more effective. Antimicrobial activity of these compounds is higher that of commercial additive "8-Oxyquinoline" taken as reference. The rest of compounds display results close to the reference. It was found that at concentrations 0.5–1% negative changes in the oil working properties did not occur. Antiseptic action of these compounds remained when the moisture and temperature increased. Substances **IX–XIII** do not negatively affect the physicochemical properties of oils. They may be recommended for use as antimicrobial additives for lubricating oils.

Hence, new representatives of 2-aminomethylene oxyderivatives of 1-(propylthio)octane, effective antimicrobial oils additives, were synthesized.

EXPERIMENTAL

IR spectra were recorded on a UR-20 spectrophotometer in the range of 4000–400 cm^{-1}. The ^{1}H NMR spectra were registered on a Bruker WP-400 instrument (400 MHz) using $CDCl_3$ as solvent and TMS as reference. The mass spectra were taken on a mass spectrometer G-7070E (70 eV). Chromatographic

Test results of compounds **IX–XIII** as antimicrobial additive to "M-11" oils

Compounds	Concentration, %	Diameter of oppression zone of microorganism growth, mm		
		mushrooms	mushrooms	
		Aspergillus niger	*Candida tropicalis*	*Psendomonas aeruginosa*
Oil M-11+ **IX**	0.5	20	18	16
	1	40	35	30
Oil M-11+ **X**	0.5	20	16	18
	1	40	30	36
Oil M-11+ **XI**	0.5	14	15	15
	1	28	30	30
Oil M-11+ **XII**	0.5	14	16	16
	1	28	32	32
Oil M-11+ **XIII**	0.5	16	16	18
	1	32	32	36
Oil M-11 + "8-Oxyquinoline"	0.5	14	14	16
	1	28	28	35
Oil M-11 without additive[a]	0	+	+	+

[a] (+) abundant microorganisms growth around hole in Petri dish.

analysis of the reaction mixtures and determination of the obtained compounds purity were performed on a LKhM-8 MD chromatograph, steel column (300× 3 mm) with 5% PEGS [poly(ethylene glycol) succinate] on a dinochrom П, gas-carrier helium (40 cm^3 min^{-1}), detector katharometer, temperature of column 150°C, of evaporator, 240°C. Influence of compounds **IX-XIII** on antimicrobial properties of oil "M-11" was studied using their 0.5–1% solutions in the mentioned oil. Antimicrobial properties were determined in a thermal moisture camera by hole method. Experiments were carried out at 28–30°C for 2–3 days. Mushrooms and bacteria cultures were used as test-micro-organisms.

1-(Propylthio)octan-2-ol (III). To a mixture of 38 g (0.5 mol) of 1-propanthiol **I** and 50 g of 40% NaOH aqueous solution [20 g (0.5 mol) of NaOH in 30 ml of water] was dropwise added 104.5 g (0.5 mol) of 1-bromooctan-2-ol **II** at 50–60°C. Stirring was continued for 3–4 h at the same temperature. After cooling, to this mixture was added benzene. Organic layer was separated, washed with 5% NaOH solution and water to neutral reaction and dried over $MgSO_4$. then the solvent was removed and the residue was distilled in a vacuum. Yield 75.6 g (74%), bp 137–138°C (5 mm Hg), n_D^{20} 1.4714, d_4^{20} 1.9128, MR_D 62.6, calc. 62.61. IR spectrum, ν, cm^{-1}: 3500 (OH), 2920 (CH_3), 2880 (CH_2). ^{1}H NMR spectrum, δ, ppm: 0.95 m (6H, CH_3), 1.50–1.70 m (10H, $5CH_2$); 2.5 t (2H, SCH_2), 2.70 m (OH), 2.75 d. d (2H, $SCH_2CH)^-$, 3.70 m (OCH). Mass spectrum (EI), *m/z* (I_{rel}, %): 205 $[M]^+$ (49), 187/*M* − OH (100), 163/*M* − $OHCH_2$ (8), 96 (72), 89 (15), *M* 204.37. Found, %: C 64.53; H 11.75; S 15.61. $C_{12}H_{24}OS$. Calculated, %: C 64.64; H 11.84; S 15.69.

2-Methyleneoxyamino derivatives of 1-(propylthio)octane (IX–XIII) *(general procedure*). To a mixture of 0.04 mol of 1-(propylthio)octan-2-ol **III** and 0.04 mol of formaldehyde in 30 ml of benzene was dropwise added under stirring 0.04 mol of secondary amine **IV–VIII** at 20–22°C. The mixture was stirred for 4–5 h at 45–55°C. When benzene was removed, the residue was distilled in a vacuum.

1-(Propylthio)-2-(*N,N*-diethylaminomethyleneoxy)octane (IX) was prepared similarly from 8.16 g (0.04 mol) of 1-(propylthio)octan-2-ol **III**, 1.2 g (0.04 mol) of formaldehyde and 2.92 g (0.04 mol) of diethylamine **IV**. Yield 8.8 g (76%), bp 134–136°C (1 mm Hg), n_D^{20} 1.4636, d_4^{20} 0.8924, MR_D 89.46, calc. 89.86. IR spectrum, ν, cm^{-1}: 2940 (CH_3), 2870 (CH_2), 1215 (CN), 730 (CS). ^{1}H NMR spectrum, δ, ppm: 0.95 m (12H, $4CH_3$), 1.35–1.65 m (10H, $5CH_2$), 2.45–2.70 m (8H, $2NCH_2$, $2SCH_2$), 3.40 m (OCH); 4.20 d. d (2H, OCH_2N). Mass spectrum (EI), *m/z* (I_{rel}, %): 200/M^+ − C_4H_9S (9), 218/$C_{12}H_{25}OS$ (13), 103/*M* − $C_5H_{12}NO$ (15), 82 (100). *M* 289.2157, calc. 289.53. Found, %: C 66.22; H 12.09; N 4.81; S 10.97. $C_{16}H_{35}NOS$. Calculated, %: C 66.38; H 12.18; N 4.87; S 11.07.

1-(Propylthio)-2-(*N*,*N*-dibutylaminomethyleneoxy)octane (X) was prepared similarly from 8.16 g (0.04 mol) 1-(propylthio)octan-2-ol **III**, 1.2 g (0.04 mol) of formaldehyde, and 5.6 g (0.04 mol) of dibutylamine **V**. Yield 10.78 g (78%), bp 160–161°C (1 mm Hg), n_D^{20} 1.4628, d_4^{20} 0.8803, MR_D 108.10, calc. 108.45. IR spectrum, ν, cm^{-1}: 2930 (CH_3), 2875 (CH_2), 1220 (C−N), 730 (C−S). ^1H NMR spectrum, δ, ppm: 0.95 m (12H, $4CH_3$), 1.35–1.65 m (18H, $9CH_2$), 2.45–2.70 m (8H, $2NCH_2$, $2SCH_2$), 3.45 m (OCH), 4.30 d. d (2H, OCH_2N). Mass spectrum (EI), *m/z* (I_{rel}, %): 270/M^+ − C_3H_7S (9), 187/M – $C_9H_{20}NO$ (15), 142/M – $C_{11}H_{25}OS$ (100), 82 (33). $[M]^+$ 345.612; calc. 345.65. Found, %: C 69.36; H 12.45; N 3.98; S 9.20. $C_{20}H_{43}NOS$. Calculated, %: C 69.50; H 12.54; N 4.05; S 9.28.

1-(Propylthio)-2-(piperidinomethyleneoxy)octane (XI) was prepared similarly from 6.12 g (0.03 mol) of 1-(propylthio)octan-2-ol **III**, 0.9 g (0.03 mol) of formaldehyde and 2.55 g (0.03 mol) of piperidine **VI**. Yield 6.87 g (76%), bp 161–162°C (2 mm Hg), n_D^{20} 1.4782, d_4^{20} 0.9234, MR_D 92.47, calc. 92.45. IR spectrum, ν, cm^{-1}: 2940 (CH_3), 2880 (CH_2), 1220 (C–N), 720 (C–S). ^1H NMR spectrum, δ, ppm: 0.95 (6H, $2CH_3$), 1.35–1.65 m (6H, $8CH_2$), 2.55–2.60 m (8H, $2NCH_2$, $2SCH_2$), 3.45 m (OCH), 4.3 d.d (2H, OCH_2N). Mass spectrum (EI), *m/z* (I_{rel}, %): 218/M^+ − $C_5H_{10}N$ (100), 226/M^+ − C_3H_7S (9), 203/$C_{11}H_{22}SO$ (14), 82 (33). $[M]^+$ 304.234, calc. 304.51. Found, %: C 67.58; H 11.61; N 4.58; S 10.54. $C_{17}H_{35}NOS$. Calculated, %: C 67.72; H 11.70; N 4.64; S 10.63.

1-(Propylthio)-2-(morpholinomethyleneoxy)octane (XII) was prepared similarly from 8.16 g (0.04 mol) of 1-(propylthio)octan-2-ol **III**, 1.2 g (0.04 mol) of formaldehyde and 3.48 g (0.04 mol) of morpholine **VII**. Yield 9.35 g (77%), bp 161–163°C (1 m Hg), n_D^{20} 1.4780, d_4^{20} 0.9624, MR_D 89.27, calc.57. IR spectrum, cm^{-1}: 2910 (CH_3), 2840 (CH_2), 1220 (CN), 730 (C–N). ^1H NMR spectrum, δ, ppm: 0.95 m (6H, $2CH_3$), 1.35–1.60 m (10H, $5CH_2$), 2.55–2.65 m (8H, $2NCH_2$, $2SCH_2$), 3.45 m (OCH), 4.30 d.d (2H, OCH_2N). Mass spectrum (EI), *m/z* (I_{rel}, %): 228/M^+ − C_3H_7S (9), $C_{11}H_{23}SO$ (13), 188/M – $C_5H_{10}NO_2$ (15), 82 (100). $[M]^+$ 303.310, calc. 303.51. Found, %: C 63.20; H 10.87; N 4.53; S 10.48. $C_{16}H_{33}NO_2S$. Calculated, %: C 63.32; H 10.96; N 4.61; S 10.56.

1-(Propylthio)-2-(hexamethyleniminomethyleneoxy)octane (XIII) was prepared similarly from 6.12 g (0.03 mol) of 1-(propylthio)-2-ol **III**, 0.92 g (0.03 mol) of formaldehyde and 2.97 g (0.03 mol) of hexamethylenimine **VIII**. Yield 7.38 g (78%), bp 159–160°C (1 mm Hg), n_D^{20} 1.4816, d_4^{20} 0.9280, MR_D 9.87, calc. 97.10. IR spectrum, ν, cm^{-1}: 2920 (CH_3), 2840 (CH_2), 1060 (C–N), 730 (C–S). ^1H NMR spectrum, δ, ppm: 0.95 m (6H, $2CH_3$), 1.35–1.65 (16H, $8CH_2$), 2.55–2.65 m (8H, $2NCH_2$, $2SCH_2$), 3.45 m (OCH), 4.30 d. d (2H, OCH_2N). Mass spectrum (EI), *m/z* (I_{rel}, %): 241 $[M]^+$ − C_3H_7S (9), 203/$C_{11}H_{23}SO$ (14), 186/M − $C_7H_{15}NO$ (15), 112/$C_7H_{15}N$ (100), 82 (33). $[M]^+$ 315.542, calc. 315.561. Found, %: C 68.40; H 11.74; N 4.38; S 10.08. $C_{18}H_{17}NOS$. Calculated, %: C 68.51; H 11.82; N 4.44; S 10.16.

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