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PREPARATION OF HYDROXYAMINO DERIVATIVES OF POLYCYCLIC BRIDGING HYDROCARBONS AND THEIR ANTIMICROBIAL PROPERTIES

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Abstract: The paper presents results of studies of the two-stage preparation of C_{10} - C_{12} tricyclic vicinal amino alcohols from partially hydrogenated condensation products of cyclopentadiene and cyclohexa-1,3-diene, by epoxidizing them with hydrogen peroxide in the presence of cobalt-containing polyoxomolybdate, followed by aminolysis of the oxidate with diethylamine, morpholine, or piperidine. The structure of the synthesized compounds was confirmed by IR and 1H NMR and spectroscopy. The research into the antimicrobial properties of *N*-substituted amino alcohols showed their effectiveness as antimicrobial additives to M-8 engine oil.

Keywords: tricyclodecene, tricycloundecene, tricyclododecene, hydrogen peroxide, cobalt-substituted polyoxomolybdate, epoxide, diol, morpholine, piperidine, amino alcohols.

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Introduction

Aminoalcohols with the cyclic structure, and especially with mono-, bi-, and tricyclic fragments are of considerable practical interest, due to their high biological activity and use in the production of drugs for various purposes [1].

Interest in amino alcohols containing alkyl, aryl, and heterocyclic substituents in the N, O, and C atoms of the molecule is due to the fact that some natural biologically active substances are characterized by the presence of these fragments [2].

According to the literature data, most of the studies carried out in this direction are related to the synthesis of amino alcohols of the aliphatic and aromatic series [5-8]. Amino alcohols with a cyclic structure, especially compounds with polycyclic bridging fragments, draw insufficient attention [5].

This paper presents the results of studies into the synthesis of C_{10} - C_{12} tricyclic amino alcohols with a bridged structure.

Experimental part

Partially hydrogenated products of [4+2] condensation and cocondensation of cyclopentadiene and cyclohexa-1,3-diene, as follows from the previously developed procedure [9], were used as non-reactive compounds.

Oxidation of cycloolefins was carried out in a thermostated glass reactor with the participation of an aqueous solution of H_2O_2 (29–36%, GOST 10292–76) or hydroperite (an

adduct of H_2O_2 and urea).

The initial catalyst, polyoxomolybdate, promoted with cobalt (II) carbonate and hydrobromic acid, was prepared by the method [10] of monitoring the reaction progress by chromatographic methanol on a Tsvet-500 M instrument with a flame ionization detector: column size 2000x3 mm, phase polyethylene glycol succinate (PEGS) on Chromosorb W (5

wt%), carrier gas nitrogen, column temperature 60°C, evaporator temperature -220°C.

The structure of the synthesized compounds was determined by IK, NMR ^1H and chromatography-mass spectroscopic methods.

Their antimicrobial properties were studied by the well method on agar medium in

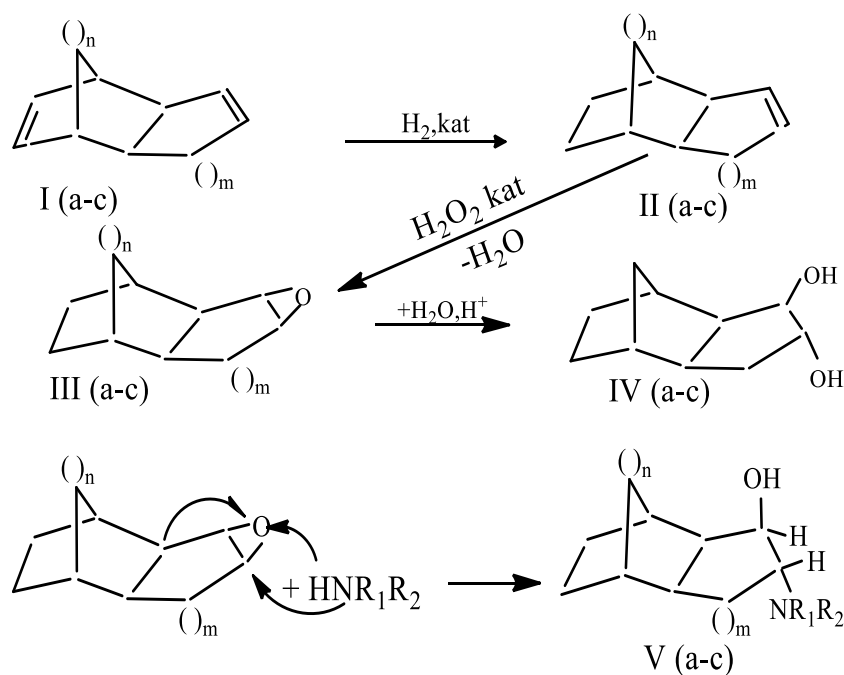
line with GOST 9.052-78 and GOST 9.082-77. For tests, pure cultures of the following types of microorganisms were used: *fungi-Aspergillus niger*, *Cladosporium resinae*, *Penicillium chrosegnum*, *Chaetium qolabosrum*. Bacteria - *Mycobacterium lacticolium*, *Pseudomanas aeruginosa*.

Results and discussion

The results of epoxidation of $\text{C}_{10}\text{-C}_{12}$ tricyclic unsaturated hydrocarbons are given by us in our earlier work [11]. The aminolysis of the oxidate at various temperatures and molar ratios of the reagents was carried out without separation of the oxyproducts in a liquid-liquid heterophase system using toluene as a solvent

and a mixture of isopropyl alcohol with water.

Amines were used in the form of hydrochlorides, which were converted into amines under the action of con "in situ" and at a temperature of 40-50°C for 6-8 hours react with epoxides (or diols) according to the scheme:



Where $n=1,2$ $m=1,2$; Ia $n=m=1$, $\text{C}_{10}\text{H}_{12}$; Ib $n=2$, $m=1$ $\text{C}_{11}\text{H}_{14}$; Ic $n=m=2$, $\text{C}_{12}\text{H}_{16}$

Aminolysis of both epoxides and vicinal diols significantly depends on the nature of the solvent used and the molar ratio of the reagents (Table 1). In the absence of a solvent or when nonpolar solvents (benzene, CCl_4) are used, aminolysis practically does not occur. Better results were obtained when using aqueous solutions of ethyl and isopropyl alcohols.

The synthesized compounds are a difficult-to-separate mixture of isomers that differ both in the position of the hydroxyl and

amine groups in the molecule and in their exo-endo orientation relative to the endo-methylene (or ethylene) group. The IR, ^1H NMR, and chromato-mass spectroscopic characteristics of some of the synthesized compounds are given below.

Depending on the molar ratio of epoxide: amine in the range of 1:2-4, the yield of amino alcohol varies over a wide range. The maximum yields are achieved with a fourfold excess of the taken amine (73.6-80.4%): A

further increase in the amount of amine has product.
practically no effect on the yield of the end

Table 1. Influence of the solvent nature on the yield of products of aminolysis of 4-oxatetracyclo [6.2.1.0^{2,7}.0^{3,5}]undecane with diethylamine (I) and morpholine (II). T=50°C, τ=8g, mol. Rat. Epoxide:amine 1:4, cat. K₂CO₃

Solvent	Solvent dielectric constant ε	Amount of solvent, mol	Exit, %	
			I	II
Carbon tetrachloride	2.3	1.0	-	-
Benzene	2.27	1.0	2.5	1.8
Toluene	2.38	1.0	3.8	4.0
tert-butanol	12.3	2.0	32.4	27.8
Propanol-2	18.3	2.0	49.6	45.4
ethanol	25.2	2.0	62.3	55.8
methanol	32.65	2.0	67.8	60.4
Propanol-2+H ₂ O	-	3.0	79.3	76.4
Ethanol + H ₂ O	-	3.0	80.5	82.3

Table 2. Yields of 4-oxatetracyclo [7.2.2.0^{2,8}.0^{3,5}] tridecane aminolysis reaction products as a function of the molar ratio of reagents (Solvent: propan-(2)-ol+H₂O)

Amine	Synthesized amino alcohol	Taken in gr.		Mol.rat. I:II	Yield of amino alcohols, %
		Epoxyd I	Amine II		
diethylamine	3(4)-N,N-diethylaminotricyclo [6.2.2.0 ^{2,7}] dodecan-4(3)-ol	8.9	7.3	1:2	58.3
		8.9	11.0	1:3	64.0
		8.9	14.6	1:4	73.6
morpholine	3(4)-N,N-morpholinotricyclo [6.2.2.0 ^{2,7}] dodekan-4(3)-ol	8.9	8.7	1:2	54.0
		8.9	13.05	1:3	63.0
		8.9	17.4	1:4	80.4
piperidine	3(4)-N,N-piperidinotricyclo [6.2.2.0 ^{2,7}] dodekan-4(3)-ol	8.9	8.5	1:2	52.7
		8.9	12.75	1:3	59.4
		8.9	17.0	1:4	74.5
		8.9	21.25	1:5	74.0

4 (3)-diethylaminotricyclo [5.2.1.0^{2,6}] decan-3 (4)-ol: IR spectrum, ν, cm⁻¹: 3496 (ν, OH), 3321 (ν, CHN), 3256 (ν, CN), 2862, 2856 (ν, CH₂), 1658 (ν, CN), 1380, 1340 (δ, CH), 1128, 1110 (δ, OH); ¹H NMR spectrum, δ, ppm: 1.05 t (6H, 2CH₃, γ, 8.1 Hz), 1.31-1.63 m (12H, H^{1,2,5,6,7,8,9,10}), 2.44 d [4H, N(CH₂)₂, γ 8.2, 7.0 Hz), 2.68t (1H, HCN, γ, 9.8 Hz), 3.42 d (1H, HSON, γ 8.2, 7.1 Hz), 3.73 u.s. (1H, OH); mass spectra (rel.int., %): 177[C₁₂H₁₉N]⁺(1.8); 132[C₁₀H₁₂]⁺(6.2); 118[C₉H₁₀]⁺(4.3);

104[C₈H₈]⁺(10.2); 92 [C₇H₈]⁺(12.4); 81[C₆H₉]⁺(36.3); 80 [C₆H₈]⁺(100); 79 [C₆H₇]⁺(21.4); 68 [C₅H₈]⁺(18.5); 66 [C₅H₆]⁺(23.7).

4 (3)-morpholinotricyclo [5.2.2.0^{2,6}] undecan-3 (4)-ol (mixture of isomers) - IR spectrum, ν, cm⁻¹: 3495 (ν, OH), 3256 (CN), 1526 (ν, CN), 1462 (δ, CH₂), 1240, 1123 (C-O-C), 1110, 1082 (δ, OH); ¹H NMR spectrum, δ, ppm: 1.28-1.62 m (14H, H^{1,2,5,6,7,8,9,10,11}), 2.70 d [1H, HCN(CH₂)₂, γ 9.8, 7.2 Hz), 2.73t (4H, N(CH₂)₂, γ 7.2 Hz), 3.42 d (1H, HCO, γ 9.8, 7.2

Hz), 3.58 a.s. (1H, OH), 3.63 m (4H, O(CH₂)₂, γ
7.2 Hz): mass spectra (rel.int., %): 233 [C₁₅H₂₁N]⁺ (2.4); 203 [C₁₄H₂₁N]⁺ (2.6); 201 [C₁₄H₁₉N]⁺ (2.7); 189 [C₁₄H₁₉N]⁺ (2.7); 188 [C₁₃H₁₈N]⁺ (3.1); 187 [C₁₃H₁₇N]⁺ (1.6); 175 [C₁₂H₁₇N]⁺ (2.1); 173 [C₁₂H₁₅N]⁺ (2.8); 147 [C₁₁H₁₅N]⁺ (5.2); 146 [C₁₁H₁₄N]⁺ (5.6); 132 [C₁₀H₁₂N]⁺ (6.8); 120 [C₉H₁₂N]⁺ (10.6); 106 [C₈H₁₀N]⁺ (7.6); 105 [C₈H₉N]⁺ (8.7); 93 [C₇H₉N]⁺ (9.2); 92 [C₇H₈N]⁺ (23.4); 81 [C₆H₉N]⁺ (37.4); 80 [C₆H₈N]⁺ (100); 79 [C₆H₇N]⁺ (21.4); 78 [C₆H₆N]⁺ (18.4); 66 [C₅H₆N]⁺ (23.1); 65 [C₅H₅N]⁺ (12.4).

The antimicrobial properties of the synthesized compounds were tested in M-8 engine oil. The results of the tests are given in table 3.

Table 3. The antimicrobial properties of the synthesized compounds

No	Connections	Consistency , mass. %	Diameter of restriction zone of microorganisms, cm	
			Bacterial mix	Mushroom mix
I	3(4)- diethylamyltricyclo [5.2.1.0 ^{2,6}] decan-4(3)ol	1.0	++	1.3-1.5
		0.5	++	1.2-1.3
		0.25	++	++
II	3(4)- morpholintritecyclo [5.2.1.0 ^{2,6}] decan-4(3)ol	1.0	1.3-1.4	1.7-1.9
		0.5	0.9-1.0	1.2-1.3
		0.25	++	0.8-1.0
III	3(4)- piperidinetricyclo [5.2.1.0 ^{2,6}] decan-4(3)ol	1.0	1.1-1.2	1.4-1.6
		0.5	0.8-1.0	1.2-1.4
		0.25	++	0.8-1.0
IV	3(4)- diethylaminetritcyclo [5.2.2.0 ^{2,6}] undecan-4(3)ol	1.0	++	1.3-1.5
		0.5	++	1.2-1.3
		0.25	++	0.7-0.9
V	3(4)- morpholintritecyclo [5.2.2.0 ^{2,6}] undecan-4(3)ol	1.0	1.4-1.5	1.7-1.9
		0.5	1.0-1.1	1.3-1.4
		0.25	0.8-0.9	0.9-1.1
VI	3(4)-morpholynotricyclo [6.2.2.0 ^{2,6}] dodekan-4(3)ol	1.0	1.3-1.4	1.5-1.6
		0.5	0.9-1.0	1.2-1.4
		0.25	++	++
	Sodium pentachlorophenolate	1.0	1.1-1.3	1.4
		0.5	0.7-1.0	0.8-1.2
	M-8 oil (no additives)	-	++	++

The results obtained indicate that, depending on the amine fragment, antimicrobial and especially fungicidal properties are declined in the series: morpholyn>piperidiny>diethylamine.

As can be seen from the data presented, morpholine-containing amino alcohols are more effective and can be used as antimicrobial additives.

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POLİTSİKLİK KÖPRÜLÜ KARBOHİDROGENLƏRİN HİDROKSİAMİN BİRLƏŞMƏLƏRİNİN ALINMASI VƏ ONLARIN ANTİMİKROB XÜSUSİYYƏTLƏRİ

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Xülasə: Məqalədə tsiklopentadien və tsikloheksa-1,3-dienin qismən hidrogenləşdirilmiş kondensasiya məhsullarının kobalt tərkibli polioksomolibdatın iştirakı ilə hidrogen peroksidlə epoksidləşməsi, daha sonra oksidatın dietilamin, morfolin və ya piperidin ilə aminolizi yolu ilə C₁₀-C₁₂ tritsiklik visinal amin spirtlərinin iki mərhələli alınması üzrə tədqiqatların nəticələri təqdim olunmuşdur. Sintez edilmiş birləşmələrin strukturu İQ, ¹H NMR və mass-spektroskopiya analiz metodları ilə təsdiq edilmişdir. N-əvəzilmiş amin spirtlərinin antimikrob xüsusiyyətlərinin tədqiqi onların M-8 mühərrik yağına antimikrob əlavələr kimi effektivliyini göstərdi.

Açar sözlər: tritsiklodesen, tritsikloundesen, tritsiklododesen, hidrogen peroksid, kobaltla əvəz edilmiş polioksomolibdat, epoksid, diol, morfolin, piperidin, amin spirtləri.

ПОЛУЧЕНИЕ ГИДРОКСАМИНОПРОИЗВОДНЫХ ПОЛИЦИКЛИЧЕСКИХ МОСТИКОВЫХ УГЛЕВОДОРОДОВ И ИХ АНТИМИКРОБНЫЕ СВОЙСТВА

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Аннотация: В работе представлены результаты исследований двухстадийного получения трициклических вицинальных аминоспиртов C_{10} - C_{12} из частично гидрированных продуктов конденсации цикlopentadiена и циклогекса-1,3-диена путем их эпоксидирования пероксидом водорода в присутствии кобальтсодержащего полиоксомолибдата с последующим аминоллизом оксидата диэтиламино, морфолином или пиперидином. Строение синтезированных соединений подтверждено данными ИК, ЯМР 1H и масс-спектрологии. Изучение антимикробных свойств N-замещенных аминоспиртов показало их эффективность в качестве антимикробных присадок к моторному маслу М-8.

Ключевые слова: трициклодецен, трициклоундецен, трициклододецен, пероксид водорода, кобальтзамещенный полиоксомолибдат, эпоксид, диол, морфолин, пиперидин, аминоспирты.