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Peroxyacetylenic Derivatives of Menthol

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Abstract—Peroxyacetylenic menthol derivatives were synthesized by reaction of *l*-menthone with lithium 3-(*tert*-alkyldioxy)-3-methyl-1-butynides and were converted into the corresponding acetates by treatment with acetic anhydride. The thermal stability of the products was estimated by derivatography and quantum-chemical calculations.

Synthesis of new oxygen-containing compounds of the *p*-menthane series attracts considerable interest, for numerous known menthane derivatives possess biological activity over a wide range [1–3]. The most famous of these is 2-isopropyl-5-methylcyclohexanol (menthol) which is widely used in medicine and perfumery [4]. Despite the long time elapsed since the discovery of menthol [5], its chemical transformations have been studied relatively poorly. This is explained by the low reactivity of the hydroxy group which is sterically shielded by the neighboring alkyl groups.
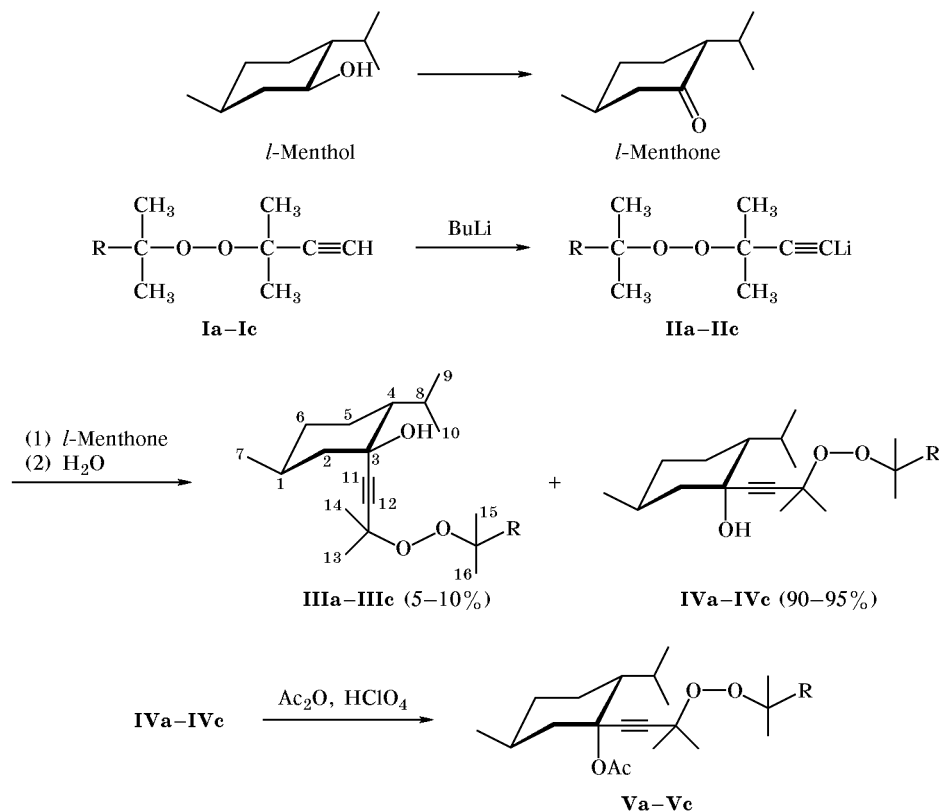
We previously demonstrated the possibility for synthesizing peroxy-containing acetylenic alcohols and their derivatives via reaction of lithium 3-(*tert*-alkyldioxy)-3-methyl-1-butynides **IIa–IIc** with cyclopentanone, cyclohexanone, camphor, and isocamphanone [6–8]. In the present study we used as starting material natural essential oil isolated from *Mentha piperita*; it was frozen to obtain *l*-menthol, and the latter was oxidized to *l*-menthone by the action of chromium trioxide in acetic acid [9]. The goal of our study was to synthesize peroxyacetylenic menthol derivatives by addition of lithium 3-(*tert*-alkyldioxy)-3-methyl-1-butynides **IIa–IIc** to *l*-menthone. It should be noted that the addition of acetylides **IIa–IIc** at the carbonyl group of *l*-menthone could give two isomeric alcohols with equatorial (compounds **IIIa–IIIc**) and axial (**IVa–IVc**) orientation of the hydroxy group (Scheme 1). Provided that the process is thermodynamically controlled, the most stable isomer (**IVa–IVc**) should be formed. Our experiments

showed that the best stereoselectivity (90–95% of isomers **IVa–IVc**) is attained when the reaction is carried out at a temperature not exceeding –5°C for 8–10 h. These conditions ensure thermodynamic control of the process. The results are also confirmed by quantum-chemical calculations.

At higher temperature (20–23°C, according to the procedures described in [6–8]) the process goes to the kinetic region, and the fraction of isomers **IIIa–IIIc** increases to 20–30%. Under the optimal conditions, we isolated peroxy alcohols **IVa–IVc** in 68–70% yield. They were additionally purified from isomers **IIIa–IIIc** by column chromatography on silica gel with hexane–diethyl ether as eluent. Treatment of peroxy alcohols **IVa–IVc** with acetic anhydride in the presence of 57% $HClO_4$ afforded 80–85% of optically active acetates **Va–Vc**.

Products **IVa–IVc** and **Va–Vc** are colorless liquids, readily soluble in common organic solvents and insoluble in water. They can be stored for a long time at 0–5°C without appreciable decomposition. Their structure and purity were confirmed by thin-layer chromatography, elemental analyses, and spectral data (Tables 1, 2). The steric structure of compounds **IIIa** and **IVa** was determined by ^{13}C NMR spectroscopy by comparing the observed carbon chemical shifts (Table 2) with those of model compounds, menthol and neomenthol [10]. Introduction of an alkynyl group into the menthol molecule only slightly affects chemical shifts of the ring carbon nuclei, so that we were able to unambiguously assign the structure with

Scheme 1.

l-Menthol   *l*-Menthone

Ia–Ic   IIa–IIc

(1) *l*-Menthone
(2) H_2O

IIIa–IIIc (5–10%)   IVa–IVc (90–95%)

IVa–IVc $\xrightarrow{Ac_2O,\ HClO_4}$

Va–Vc

I–V, R = Me (**a**), Et (**b**), Pr (**c**).

equatorial orientation of the methyl group on C^1, isopropyl group on C^4, and alkynyl group on C^3 to the major stereoisomer (**IVa**). The minor isomer (**IIIa**) has axial alkynyl group on C^3.

The IR spectra of peroxy alcohols **IVa–IVc** (films) contain broad absorption bands with their maxima at $3475 \pm 5 cm^{-1}$, which belong to stretching vibrations of associated OH groups. Esters **Va–Vc** show in the spectra strong carbonyl absorption band at 1750 cm^{-1}. Stretching vibrations of the triple C≡C bond do not appear in the IR spectra of **IVa–IVc** and **Va–Vc**. In the UV spectra we observed absorption bands with λ_{max} 208 ± 1 nm (ε = 190) for alcohols **IVa–IVc** and 236 ± 1 nm (ε = 1300) for esters **Va–Vc**. Compounds **Va–Vc** are optically active; their specific rotations are as follows, $[\alpha]_D^{20}$, deg: –11.00 (**Va**), –10.73 (**Vb**), and –9.70 (**Vc**). No optical activity was found for alcohols **IVa–IVc**.

The thermal stabilities of peroxy alcohols **IVa–IVc** and peroxy esters **Va–Vc** was estimated by derivatography [11] (Table 3). Alcohols **IVa–IVc** turned out to be relatively stable compounds. They begin to decompose at an appreciable rate and with a pronounced

exothermic effect only at 140–149°C (DTA). Acetylation of the hydroxy group in **IVa–IVc** slightly increases the thermal stability of the resulting esters **Va–Vc** which begin to decompose at 143–154°C, i.e., at a temperature higher by 3–5°C than the temperature of decomposition of the initial alcohols. On the basis of the DTA curves, using the procedure described in [12], we determined the kinetic parameters for the first stage (up to 190–215°C) of decomposition of alcohols **IVa–IVc** and esters **Va–Vc**: the order of the reaction according to Kissinger (n) and the apparent energy of activation E_a. The following values were obtained: **IVa–IVc**, n = 1.26–1.30, E_a = 120–131 kJ/mol; **Va–Vc**, n = 1.16–1.26, E_a = 131–136 kJ/mol.

Comparison of the initial decomposition temperatures and kinetic parameters shows that in the series of peroxy alcohols **IVa–IVc** and esters **Va–Vc** compounds **IVa** and **Va** having a *tert*-butyldioxy group are thermally more stable than those containing *tert*-pentyldioxy (**IVb, Vb**) and 1,1-dimethylbutyldioxy groups (**IVc, Vc**) (Table 3).

We also performed quantum-chemical calculations of compounds **IIIa**, **IVa–IVc**, and **Va–Vc** with a view

Table 1. Yields, constants, and analytical data of peroxy derivatives **IVa**–**IVc** and **Va**–**Vc**

Comp. no.	Yield, %	bp, °C (p, mm)	d_{20}^{20}	n_{D}^{20}	Found, %		Formula	Calculated, %		M	
					C	H		C	H	found	calcd.
IVa	70	89–90 (0.02)	1.0739	1.4665	73.39	11.02	$C_{19}H_{34}O_3$	73.50	11.04	302.8	310.5
IVb	69	92–93 (0.02)	1.1365	1.4650	74.40	11.30	$C_{20}H_{36}O_3$	74.03	11.18	318.0	324.5
IVc	68	101–102 (0.02)	1.1137	1.4635	74.91	11.50	$C_{21}H_{38}O_3$	74.51	11.31	330.6	338.5
Va	85	–	1.1088	1.4585	71.95	10.28	$C_{21}H_{36}O_4$	71.55	10.29	343.3	352.5
Vb	82	–	1.1150	1.4635	72.30	10.55	$C_{22}H_{38}O_4$	72.09	10.45	360.4	366.5
Vc	80	–	1.0560	1.4600	72.98	10.65	$C_{23}H_{40}O_4$	72.59	10.59	368.8	380.6

to correlate the results of calculations with the experimental DTA data (Table 3) and the assignment of their steric structure on the basis of the ^{13}C NMR spectra (Table 2). The calculations were performed by the SCF MO LCAO procedure in the MNDO valence approximation [13, 14]. All geometric parameters of compounds **IIIa**, **IVa**–**IVc**, and **Va**–**Vc** (bond lengths, bond angles, and dihedral angles) were optimized. The optimized geometric parameters, charges on atoms of the peroxide fragment COOCMe$_2$C≡C, energies of the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO), dipole moments, heats of formation (H_f) [13], and heats of hydrogenation of the O–O bond are given in Table 4. The MNDO method fairly reliably reproduces structural parameters of the compounds under study, except for some systematic underestimation of the O–O bond length (by ~0.15 Å). The heats of hydrogentation of the O–O bond (ΔH_H) were calculated on the basis of hypothetical thermochemical reaction equations:

$$\text{R—O—O—R}' + \text{H}_2 \longrightarrow \text{ROH} + \text{R}'\text{OH}$$
$$\mathbf{III\text{–}V} \qquad\qquad \mathbf{VIa\text{–}VIc} \;\; \mathbf{VIIa\text{–}VIIc}$$
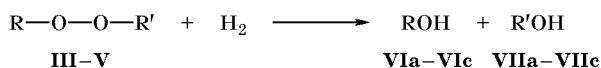
$$\Delta H_H = [H_f(\text{ROH}) + H_f(\text{R}'\text{OH})] - [H_f + H_f(\text{H}_2)].$$

VI, R = Me$_3$C (**a**), MeCH$_2$Me$_2$C (**b**), Me(CH$_2$)$_2$Me$_2$C (**c**);

VII, R′ =

(**a**), (**b**), (**c**).
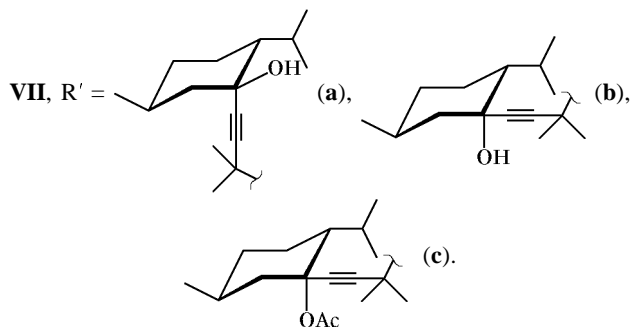
The heat of formation of hydrogen $H_f(\text{H}_2)$ was assumed to be equal to 3.021 kJ/mol [15]. The calculated heats of formation of alcohols **VI** and **VII**, which are formed by hydrogenation of compounds **III**–**V**, are given below:

Comp. no.	**VIa**	**VIb**	**VIc**
H_f, kJ/mol	−268.671	−276.588	−294.734

Comp. no.	**VIIa**	**VIIb**	**VIIc**
H_f, kJ/mol	−305.294	−305.989	−438.303

The results of quantum-chemical calculations (Table 4) are generally consistent with the experimental data obtained by thermal gravimetric analysis (Table 3). In keeping with the calculated heats of hydrogenation ΔH_H, the O–O bond in *tert*-butyldioxy derivatives **IVa** and **Va** is somewhat stronger than in compounds **IVb**, **Vb** and **IVc**, **Vb** having, respectively, *tert*-pentyldioxy and 1,1-dimethylbutyldioxy groups. Also, the O–O bond in esters **Va**–**Vc** is stronger than in the corresponding alcohols **IVa**–**IVc**. According to the calculations (H_f), the minor isomer (**IIIa**) with the axial alkynyl group is less thermodynamically favorable (by 4 kJ/mol) than equatorial isomer **IVa**. The O–O bond in **IIIa** is weaker than in **IVa** by ~3.4 kJ/mol, presumably for steric reasons.

EXPERIMENTAL

The IR spectra were recorded on a Specord 75IR instrument from samples prepared as thin films. The ^{1}H and ^{13}C NMR spectra were obtained on a Tesla BS-567A spectrometer in CDCl$_3$ using tetramethylsilane as internal reference. The UV spectra were measured on a Specord UV-Vis spectrophotometer from 1×10^{-3} M solutions in methanol. The specific rotations were determined on an SM-2 instrument in

Table 2. ^{1}H NMR spectra of compounds **IVa–IVc** and **Va–Vc** and ^{13}C NMR spectra of compounds **IIIa** and **IVa**

Comp. no.	Chemical shifts δ and δ_C, ppm
IIIa	^{13}C: 32.1 d (C^1), 52.0 t (C^2), 79.2 s (C^3), 53.5 d (C^4), 20.0 t (C^5), 32.9 t (C^6), 22.1 q (C^7), 31.1 d (C^8), 18.8 q (C^9), 21.2 q (C^{10}), 74.5 s (C^{11}), 77.7 s (C^{12}), 89.6 s (C^{13}), 27.7 q [C^{13}(CH$_3$)$_2$], 85.7 s (C^{14}), 27.3 q [C^{14}(CH$_3$)$_3$]
IVa	^{1}H: 0.80–1.05 m (9H, 3Me), 1.25 s (9H, Me$_3$COO), 1.35–2.47 m (10H, 3CH$_2$, 3CH, OH), 1.47 s (6H, Me$_2$CC≡C)
IVa	^{13}C: 24.5 d (C^1), 50.7 t (C^2), 71.8 s (C^3), 51.2 d (C^4), 21.3 t (C^5), 35.6 t (C^6), 22.1 q (C^7), 28.3 d (C^8), 19.5 q (C^9), 20.0 q (C^{10}), 74.7 s (C^{11}), 79.6 s (C^{12}), 88.0 s (C^{13}), 27.7 q [C^{13}(CH$_3$)$_2$], 86.5 s (C^{14}), 27.3 q [C^{14}(CH$_3$)$_3$]
IVb	^{1}H: 0.77–1.02 m (12H, 4Me), 1.18 s (6H, Me$_2$COO), 1.27–2.45 m (12H, 4CH$_2$, 3CH, OH), 1.47 s (6H, Me$_2$CC≡C)
IVc	^{1}H: 0.80–1.02 m (12H, 4Me), 1.20 s (6H, Me$_2$COO), 1.25–2.50 m [14H, 3CH$_2$, 3CH, (CH$_2$)$_2$, OH], 1.45 s (6H, Me$_2$CC≡C)
Va	^{1}H: 0.77–1.03 m (9H, 3Me), 1.24 s (9H, Me$_3$COO), 1.35–3.00 m (9H, 3CH$_2$, 3CH), 1.47 s (6H, Me$_2$CC≡C), 2.00 s (3H, CH$_3$CO)
Vb	^{1}H: 0.77–1.02 m (12H, 4Me), 1.18 s (6H, Me$_2$COO), 1.25–3.00 m (11H, 4CH$_2$, 3CH), 1.45 s (6H, Me$_2$CC≡C), 2.00 s (3H, CH$_3$CO)
Vc	^{1}H: 0.77–1.02 m (12H, 4Me), 1.18 s (6H, Me$_2$COO), 1.22–3.00 m [13H, 3CH$_2$, 3CH, (CH$_2$)$_2$], 1.45 s (6H, Me$_2$CC≡C), 2.00 s (3H, CH$_3$CO)

Table 3. Thermal stabilities of peroxyacetylenic alcohols **IVa–IVc** and esters **Va–Vc**

Comp. no.	Stage	Decomposition temperature, °C			Weight loss, %	Exo peak, °C		Order of reaction n^a	E_a, kJ/mol
		initial	final	maximal		initial	maximal		
IVa	1	147	215	192	37	149	194	1.30	131
	2	215	280	255	41				
	3	280	325	–	7				
IVb	1	143	202	182	35	145	182	1.28	127
	2	202	272	247	37				
	3	272	305	–	9				
IVc	1	138	205	183	41	140	184	1.26	120
	2	205	272	250	31				
	3	272	320	–	14				
Va	1	152	208	185	37	154	190	1.26	136
	2	208	248	225	23				
	3	248	295	–	14				
Vb	1	147	190	175	34	148	181	1.16	131
	2	190	230	–	25				
	3	230	290	–	13				
Vc	1	143	200	180	35	147	183	1.26	132
	2	200	230	217	25				
	3	230	295	–	15				

^{a} According to Kissinger.

Table 4. Calculated geometric parameters of the $C^1O^2O^3C^4Me_2C^5{\equiv}C^6C^7$ fragment, charges on atoms, energies of frontier orbitals, dipole moments, and heats of formation and hydrogenation of the $O-O$ bond of compounds **IIIa**, **IVa–IVc**, and **Va–Vc**

Comp. no.	Bond lengths, Å						Angles, deg			Charges on atoms, au		
	C^1-C^2	O^2-C^3	O^3-C^4	C^4-C^5	$C^5{\equiv}C^6$	C^6-C^7	$C^1O^2O^3$	$O^2O^3C^4$	$C^1O^2O^3C^4$	C^1	O^2	O^3
IIIa	1.437	1.298	1.436	1.473	1.199	1.477	114.836	114.750	169.940	0.062	–0.186	–0.188
IVa	1.437	1.298	1.441	1.475	1.198	1.480	114.845	114.426	179.273	0.065	–0.193	–0.188
IVb	1.442	1.298	1.441	1.475	1.198	1.480	115.146	114.395	179.958	0.082	–0.197	–0.188
IVc	1.442	1.298	1.441	1.475	1.198	1.480	115.184	114.392	179.116	0.081	–0.198	–0.188
Va	1.437	1.298	1.441	1.475	1.198	1.475	114.909	114.384	174.836	0.065	–0.192	–0.189
Vb	1.440	1.298	1.441	1.475	1.198	1.475	115.280	114.365	176.522	0.082	–0.196	–0.188
Vc	1.441	1.298	1.441	1.475	1.198	1.475	115.327	114.357	176.493	0.081	–0.197	–0.188

Comp. no.	Charges on atoms, au				Energy, eV		Dipole moment μ, D	ΔH_f, kJ/mol	ΔH_H, kJ/mol
	C^4	C^5	C^6	C^7	HOMO	LUMO			
IIIa	0.203	–0.134	–0.153	0.226	–10.406	1.370	1.651	–195.015	–381.971
IVa	0.206	–0.122	–0.157	0.227	–10.359	1.244	1.449	–199.084	–378.597
IVb	0.206	–0.122	–0.158	0.227	–10.347	1.245	1.485	–203.914	–381.684
IVc	0.206	–0.122	–0.158	0.227	–10.346	1.244	1.506	–221.730	–382.014
Va	0.205	–0.100	–0.160	0.276	–10.258	1.012	1.464	–331.892	–378.103
Vb	0.205	–0.098	–0.160	0.276	–10.241	1.014	1.486	–337.153	–380.759
Vc	0.205	–0.098	–0.160	0.276	–10.240	1.014	1.500	–355.081	–380.977

methanol, $c \approx 6\%$. Thermal stabilities of the products were estimated on a Paulik–Paulik–Erdey derivatograph under argon; the temperature was raised at a rate of 7 deg/min; sample amount 100 mg; DTA 1/10, DTG 1/10. The purity of the products was checked by thin-layer chromatography on Silufol plates (20 cm) using hexane–diethyl ether (3:1) as eluent and *N,N*-dimethyl-*p*-phenylenediamine as developer. Column chromatography was performed on neutral aluminum oxide (Brockman activity grade II) and on silica gel L 100/160 μm. Determination of active oxygen in the products by iodometry with the use of concentrated hydrochloric acid [16] gave too high results, presumably due to the presence of C≡C bond. The molecular weights were determined by cryoscopy in benzene.

Initial peroxy alkynes **Ia–Ic** [17] and butyllithium [18] were synthesized by known methods. *l*-Menthone had the following parameters: mp –6°C, bp 204°C, d_4^{15} 0.8946, n_D^{20} 1.4504, $[\alpha]_D^{20}$ –29.6° (ethanol); it was synthesized by oxidation of *l*-menthol [mp 42–43°C, bp 212°C (760 mm), d_4^{20} 0.890, $[\alpha]_D^{20}$ –50.1° (ethanol)] following the procedure reported in [9].

Quantum-chemical calculations were performed on an Intel Pentium II computer (300 MHz).

1-[3-(*tert*-Butyldioxy)-3-methyl-1-butynyl]-2-isopropyl-5-methylcyclohexanol (IVa), 2-isopropyl-5-methyl-1-[3-methyl-3-(*tert*-pentyldioxy)-1-butynyl]-cyclohexanol (IVb), and 1-[3-(1,1-dimethylbutyldioxy)-3-methyl-1-butynyl]-2-isopropyl-5-methylcyclohexanol (IVc) (*general procedure*). To a solution of 0.025 mol of peroxy alkyne **Ia–Ic** in 40 ml of dry diethyl ether we added at –40 to –20°C under vigorous stirring in a stream of argon 0.022 mol of butyllithium (as a solution in hexane) over a period of 0.5–1 h. The mixture was stirred for 1 h at that temperature (lithium peroxyaceylides **IIa–IIc** were thus obtained), and a solution of 0.02 mol of *l*-menthone in 10 ml of dry diethyl ether was added in one portion. The mixture was allowed to warm up to –10 to –5°C over a period of 1–2 h and was stirred for 8–10 h. It was then diluted with 100 ml of hexane, washed with water, dried over $CaCl_2$, and evaporated. Peroxy alcohols **IVa–IVc** were isolated by vacuum distillation and were additionally purified from traces

of isomers **IIIa**–**IIIc** by column chromatography on silica gel using hexane–diethyl ether as eluent.

1-[3-(*tert*-Butyldioxy)-3-methyl-1-butynyl]-2-isopropyl-5-methylcyclohexyl acetate (Va), 2-isopropyl-5-methyl-1-[3-methyl-3-(*tert*-pentyldioxy)-1-butynyl]cyclohexyl acetate (Vb), and 1-[3-(1,1-dimethylbutyldioxy)-3-methyl-1-butynyl]-2-isopropyl-5-methylcyclohexyl acetate (Vc) (*general procedure*). To a mixture of 0.005 mol of compound **IVa**–**IVc**, 2 ml of acetic anhydride, and 5 ml of dry diethyl ether we added –10 to –5°C with stirring in a dropwise manner 0.5 ml of a solution prepared from 0.01 ml of 57% $HClO_4$ and 5 ml of acetic anhydride. The mixture was stirred for 18 h at 20–23°C, diluted with 50 ml of hexane, washed in succession with water, a saturated aqueous solution of $NaHCO_3$, and water again, dried over $CaCl_2$, and evaporated. Esters **Va**–**Vc** were purified by column chromatography on Al_2O_3 using hexane as eluent.

REFERENCES

1. Carman, R.M., Greenfield, K.L., and Robinson, W.T., *Aust. J. Chem.,* 1989, vol. 39, no. 1, pp. 21–30.

2. Horning, M.G., Butler, C.M., and Stafford, M., *Adv. Mass Spectrom. Biochem. Med.,* 1976, vol. 1, no. 1, pp. 91–93.

3. Becalski, A., Cullen, N.R., and Fuyzuk, M.O., *Can. J. Chem.,* 1988, vol. 66, no. 12, pp. 3108–3115.

4. Nikitin, V.M., *Khimiya terpenov i smolyanykh kislot* (Chemistry of Terpenes and Rosin Acids), Moscow: Goslesbumizdat, 1952.

5. Pigulyavskii, G.V., *Khimiya terpenov* (Chemistry of Terpenes), Leningrad: Leningr. Gos. Univ., 1949.

6. Yuvchenko, A.P., Dikusar, E.A., and Moiseichuk, K.L., *Russ. J. Gen. Chem.,* 1994, vol. 64, no. 1, pp. 72–76.

7. Yuvchenko, A.P., Dikusar, E.A., Kozlov, N.G., Popova, L.A., and Moiseichuk, K.L., *Russ. J. Org. Chem.,* 1995, vol. 31, no. 4, pp. 498–503.

8. Yuvchenko, A.P., Dikusar, E.A., Moiseichuk, K.L., and Kozlov, N.G., *Russ. J. Org. Chem.,* 1995, vol. 31, no. 3, pp. 304–307.

9. Voisin, D. and Gastambide, B., *Bull. Soc. Chim. Fr.,* 1971, no. 7, pp. 2644–2651.

10. Pekhk, T.I., Lippmaa, E.T., Lysenkov, V.I., and Bardyshev, N.I., *Zh. Org. Khim.,* 1979, vol. 15, no. 9, pp. 1877–1887.

11. Wendlandt, W.Wm., *Thermal Methods of Analysis,* New York: Intersci., 1974, 2nd ed.

12. Gorshkov, V.S., Timashev, V.V., and Savel'ev, V.G., *Metody fiziko-khimicheskogo analiza vyazhushchikh veshchestv* (Methods of Physicochemical Analysis of Binding Substances), Moscow: Vysshaya Shkola, 1981, pp. 37–40.

13. Dewar, M.J.S. and Thiel, W., *J. Am. Chem. Soc.,* 1977, vol. 99, no. 15, pp. 4899–4917.

14. Baker, J., *J. Comput. Chem.,* 1986, vol. 7, no. 4, pp. 385–395.

15. Stewart, J.J.P., *J. Comput. Chem.,* 1989, vol. 10, no. 2, pp. 221–264.

16. Mair, R.D. and Graupner, A.J., *Anal. Chem.,* 1964, vol. 36, no. 1, pp. 194–204.

17. Yuvchenko, A.P., Moiseichuk, K.L., Dikusar, E.A., and Ol'dekop, Yu.A., *Vestsi Akad. Navuk BSSR, Ser. Khim. Navuk,* 1985, no. 2, pp. 65–70.

18. Talalaeva, T.V. and Kocheshkov, K.A., *Metody elementoorganicheskoi khimii. Litii, natrii, kalii, rubidii, tsezii* (Methods of Organometallic Chemistry. Lithium, Sodium, Potassium, Rubidium, Cesium), Moscow: Nauka, 1971, part 1, pp. 99–107, 554–555.