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MONOTERPENOIDS (3-CARENE AND α-TERPINENE) IN ELECTROPHILIC DISULFIDE ADDITION REACTIONS

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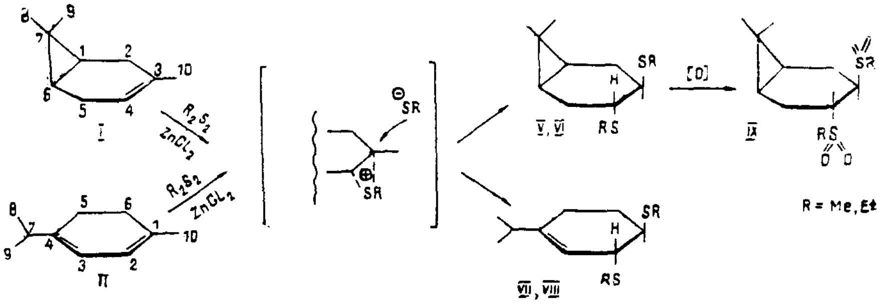
The reactions of 3-carene and α-terpinene with dialkyl disulfides have been studied.

The reactions of 3-carene (I) and of α-terpinene (II) with dialkyl disulfides (III, R = CH_3; IV, R = C_2H_5) are, primarily, a convenient method for introducing sulfur-containing functions into terpene hydrocarbons. In addition, these reactions open up a route to the use of this method as an analytical procedure for determining the positions of double bonds in terpenes and their derivatives.

We have established that the methods of introducing two sulfide functions described in the literature [4, 5] for other classes of compounds cannot be used in the case of the terpenes (I) and (II), since they lead to the total isomerization of (I) and (II) into p- and m-cymene. At the same time, the interaction of 3-carene (I) and α-terpinene (II) with the disulfides (III) and (IV) in the presence of $ZnCl_2$ has led to the formation of the addition products (V-VIII) as the main products with small amounts (not more than 5%) of p- and m-cymene as impurities. The structures of compounds (V-VIII) have been confirmed by PMR spectroscopy (Table 1). The results of elementary analysis correspond to the calculated figures. The structure of the adduct (V) was confirmed by mass spectroscopy.



To establish the stereochemistry of the addition of the disulfides to 3-carene (I), 3β-4α-di(methylthio)carane (V) was oxidized to the corresponding sulfone (IX), the crystalline structure of which has been determined by x-ray structural analysis. According to these results the sulfone group at the C^3 atoms was present in the cis- position and the sulfone group at the C4 atom in the trans- position to the cyclopropane ring, which indicates the observation of Markovnikov's rule in this reaction. The crystals of compound (IX) were rhombic; at 20°C, a = 6.526(2), b = 9.691(2), c = 22.941(5); Z = 4 (calc.), 1.348 g/cm^3; space group $P2_1$-2_12_1.

A characteristic feature of the addition of the disulfides (III) and (IV) to α-terpinene (II) is the high degree of chemoselectivity — the reaction takes place exclusively at the

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TABLE 1. PMR Spectra of Compounds (V-VIII) (δ, ppm)

Compound	2H-1,6	6H-8,9	3H-10	1H-4	$(SR)_2$
V VI	0,6—0,7 0,5—0,6	0,98, 0,95 s 0,98, 0,96 s	1,27 s 1,19 s	2,42 d 2,1—2,5	2.01, 2.12 s (Me) 1.07, 1.11 t 2.50, 2,56 q (Et)
Compound	**1H-3**	**6H-8,9**	**3H-10**	**1H-2**	**$(SR)_2$**
VII VIII	5,3 d 5,3 d	1,0, 1,1 s 1,0, 1,1 s	1,3 s 1,3 s	3,1 d 3,1 d	2,15, 2.20 s (Me) 1,2, 1,3 t 2,2—2,7 q (Et)

TABLE 2. Physicochemical Constants of Compounds (V-VIII)

Compound	Empirical formula	bp, °C (mm Hg)	n_d^{20}	α_D, deg	Yield, %
V	$C_{12}H_{22}S_2$	83 (2)	1,5382	—90	75
VI	$C_{14}H_{26}S_2$	90 (2)	1,5251	—50,7	70
VII	$C_{12}H_{22}S_2$	—	1,5410	—	85
VIII	$C_{14}H_{26}S_2$	—	1,5288	—	83

sterically less screened $C^1{=}C^2$ bond, even in the case of a manyfold excess of the reagents (III) and (IV), with the formation of E-1,2-di(alkylthio)menth-3-enes (VII) and (VIII). In the PMR spectra of the adducts (VII) and (VIII), the signal of the CH_3 group at the C^1 atom is shifted upfield as compared with the initial α-terpinene (II) and there are the signals of one olefinic proton (H-3) with a spin-spin constant of 4.0 Hz and of a methine proton at the C_2 atom. In the IR spectra of compounds (VII) and (VIII) there are characteristic frequencies of the vibrations of a double bond in the 1650 and 790 cm^{-1} regions.

It is known that sulfur-containing derivatives of terpenes possess a number of interesting practical properties (capacity for complex-formation, possibility of use as components of perfume substances) [1, 2] while at the same time being difficultly accessible compounds [3].

EXPERIMENTAL

PMR spectra in CCl_4 were measured on a Bruker WM-250 spectrometer (250 MHz) with HMDS as internal standard. Values of $[\alpha]_D$ were measured on a Polamat A instrument. Refractive indices, n_D^{20} were measured on a IRF-454 BM refractometer, and IR spectra on a UR-20 spectrometer (CCl_4). The x-ray structural analysis was conducted on an ENRAF—NONIUS CAD-4 K-diffractomter. The mass spectrum was recorded at an ionization energy of 70 eV on a LKB-2091 chromato-mass spectrometer.

Synthesis of Compounds (V-VIII). A mixture of 0.14 mole of one of the disulfides (III) and (IV), 0.06 mole of (I) or (II), and 0.1 g of $ZnCl_2$ in CH_2Cl_2 was stirred at 20°C for 1 h and was then diluted with 100 ml of ice water and extracted with CH_2Cl_2, the extract was dried with $CaCl_2$ and the product was isolated by chromatography on silica gel (hexane—ether).

Mass spectrum of compound (V) (R = CH_3) (m/z, %); 232(2), 231(3), 230(20) M, 215(4), 185(6), 184(16), 183(100), 169(9), 167(10), 155(8), 147(7), 136(13), 135(83), 134(17), 133(10), 127(7), 121(20), 119(18), 115(18), 109(10), 107(29), 105(10), 101(50), 95(9), 94(8), 93(77), 92(7), 91(24), 89(30), 81(11), 79(19), 77(18), 75(21), 69(11), 67(15), 65(7), 61(25), 59(11), 55(15), 53(15), 45(10), 43(38), 41(33), 39(12), 29(8), 27(10).

Synthesis of the Sulfone (IX). To 0.0126 mole of the sulfide (V) in 30 ml of glacial acetic acid was added 9 ml of 30% H_2O_2 solution. After being heated in the steam bath for 2 h, the reaction mixture was poured into 200 ml of ice water and was neutralized with $NaHCO_3$ and extracted with ether (4 × 50 ml), after which the extract was dried with $CaCl_2$, and was concentrated in vacuum, and the product was purified by recrystallization from ethanol. mp 105°C, ν_{SO_2} = 1125, 1280 cm^{-1}. PMR spectrum (ppm, CCl_4): 0.7-0.8 (m, h-1.6), 1.04 (s, 3H-8(9)), 1.10 (s, 3H-9(8)), 1.95 (s, 3H-10), 3.8 (dd, 1H-4), 2.96 (s, $3H-SO_2Me$), 3.00 (s, $3H-SO_2Me$). Yield 97%.

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BICYCLIC MONOTERPENOIDS OF THE ESSENTIAL OIL OF Ledum palustre

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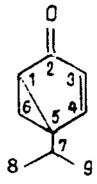
The structure of a new natural compound has been established as 5-isopropylbicyclo[3.1.0]hex-3-en-2-one, which has been called lebaikon. Two bicyclic monoterpenoids (2-formyl-5-isopropylbicyclo[3.1.0]hex-2-ene and 4-isopropyl-1-methylbicyclo[3.1.0]-hexan-2-one) have been detected in natural materials for the first time.

In an investigation of the chemical composition of the essential oil of marsh tea growing in the cis-Baikal region of the Buryat ASSR and in the environs of Tynda (Amur Province) [1], by chromatography on silica gel columns three carbonyl-containing terpenoids not previously found in nature were isolated.



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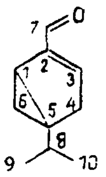

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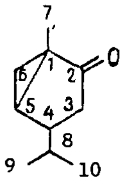

III

Ketone (I), which we have called lebaikon, was obtained from the fraction of weakly polar monoterpenoids and was identified from its spectral characteristics as 5-isopropylbicyclo[3.1.0]hex-3-en-2-one. Its amount in the essential oil of the sample studied was, according to GLC, 4-5%. According to the results of mass spectrometry, the molecular ion of this compound (M^+ 136) corresponded to the empirical formula $C_9H_{12}O$. The maximum in the UV spectrum (220 nm) and the IR spectrum (1720 cm^{-1}) indicated the presence of a double bond conjugated with a keto group. The main fragments of the molecule were readily determined from an analysis of NMR spectra. In the weak field of the ^1H NMR spectra two signals of the protons of a disubstituted double bond were observed (5.56 and 7.56 ppm, doublets of doublets, J_1 = 6 Hz, J_2 = 1 Hz). The chemical shift of the signal at 7.56 ppm showed that this proton was present in the α-position with respect to a carbonyl group. In the strong-field part of the ^1H NMR spectrum there were two doublets of methyl protons of an isopropyl group (0.97 and 1.07 ppm), while the methine proton of this group could be seen in the form of a distinct septet at 1.80 ppm.

In the ^{13}C NMR spectrum, in addition to the signals of the carbons of methyl groups at 20.59 and 20.24 ppm and also the signals of the carbon atom at a double bond (128.21 and 161.99 ppm, doublets), two other doublets could readily be seen at 29.23 and 28.93 ppm, and a triplet at 39.30 ppm. The combination of spectral characteristics corresponds to structure (I) of a bicyclic norterpenoid. The signal of the H(1) proton was observed in the form of a triplet at 1.43 ppm with J = 4 Hz. This constant was also found for two signals at 1.32

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