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BICYCLIC MONOTERPENOIDS OF THE ESSENTIAL OIL OF *Ledum palustre*

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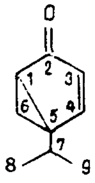
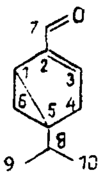
UDC 547.597:547.913:582.912

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.

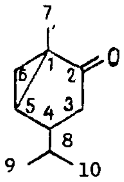
In an investigation of the chemical composition of the essential oil of marsh tea growing in the cis-Baikal region of the Buryat ASSR and in the environs of Tynda (Amur Province) [1], by chromatography on silica gel columns three carbonyl-containing terpenoids not previously found in nature were isolated.



I



II



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

Tomsk State Medical Institute. Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Novosibirsk. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 627-629, September-October, 1990. Original article submitted December 12, 1989; revision submitted April 10, 1990.

0009-3130/90/2605- 0532$12.50

and 1.98 ppm, which indicated the adjacency of methylene and methine groups. The second spin-spin coupling constant of these signals, J = 9 Hz, corresponded to the vicinal interaction of the H(6) protons. The downfield shift of the signals of the protons of the cyclopropane ring is explained by the influence of the carbonyl group.

Among the macrocomponents a monoterpene aldehyde was detected (about 17% in the essential oil), and its structure was determined from its spectral characteristics.

The molecular ion (M^+ 150) corresponded to the empirical formula ($C_{10}H_{14}O$). The UV spectrum (λ_{max} 248 nm) confirmed the existence of a conjugated system in the molecule. The IR spectrum showed the presence of a cyclopropane group (3050 cm^{-1}), and this was confirmed by the signal of two protons in the 0.04 ppm region in the ^1H NMR. From this spectrum we also determined the presence of an aldehyde group (signal at 9.63 ppm, s), of a trisubstituted double bond conjugated with it (6.49 ppm, t) and of an isopropyl group (two 3 × H doublets at 0.90 and 0.93 ppm and a septet at 1.47 ppm). The other signals in the ^1H NMR spectrum and also the ^{13}C NMR results corresponded to the structure of 2-formyl-5-isopropylbicyclo[3.1.0]hex-2-ene (II). Such a compound had been previously obtained only synthetically [2, 3] and its spectral characteristics had not been discussed in detail.

The essential oil under investigation also yielded a small amount of a ketone, the spectral characteristics of which corresponded to the structure of 4-isopropyl-1-methylbicyclo[3.1.0]hexan-2-one (III). The preparation of this compound by the hydrogenation of 4-isopropenyl-1-methylbicyclo[3.1.0]hexan-2-one and its stereochemistry are known [4, 5].

EXPERIMENTAL

The instruments and methods and also the general principle of the work, the physicochemical characteristics of the essential oils investigated, and the amounts of components from GLC results have been given in a separate communication [1].

From the fractions of oxygen-containing monoterpenoids (the weight of each fraction was 1.0 g), in addition to known substances, we isolated: from a sample of the essential oil of marsh tea gathered in the environs of Tynda, 0.08 g (20% of the weight of the essential oil) of ketone (I) and 0.05 g (1.3%) of the crystalline substance (III); from a sample of the essential oil of L. palustre from the cis-Baikal region of the Buryat ASSR we obtained 0.13 g (3.2% of the weight of the essential oil) of ketone (I) and 0.46 g (11.5%) of substance (II), a yellow liquid with a pleasant odor.

5-Isopropylbicyclo[3.1.0]hex-3-en-2-one (Lebaikon) (I). UV spectrum: λ_{max} (C_2H_5OH), nm: 220 (log ε 2.06). IR spectrum: ν_{max} (CCl_4), cm^{-1}: 1720, 2880, 2940, 2970. Mass spectrum, m/z (%): 136 (M^+, 61), 121 (71), 94 (36), 93 (100), 91 (40), 77 (40). PMR (200 MHz, $CDCl_3$): 0.70-1.05 (3H, m), 0.97 (3H, d, J = 7 Hz, H-8), 1.07 (3H, d, J = 7 Hz, H-9), 1.32 (2H, dd, J_1 = 9 Hz, J_2 = 4 Hz, H-6), 1.43 (1H, t, J = 4 Hz, H-1), 1.80 (1H, septet, J = 7 Hz, H-7), 1.98 (2H, dt, J = 6 Hz, J_2 = 4 Hz, H-6), 5.56 (1H, dd, J_1 = 6 Hz, J_2 = 1 Hz, H-4), 7.56 (1H, dd, J_1 = 6 Hz, J_2 = 1 Hz, H-3), ^{13}C NMR (50.32 MHz, $CDCl_3$): 20.24 (q, C-8), 20.59 (q, C-9) 39.30 (t, C-6), 28.93 (d, C-7), 29.23 (d, C-4), 128.21 (d, C-4), 161.99 (d, C-3); two singlets (C-5 and C-2) could not be identified.

2-Formyl-5-isopropylbicyclo[3.1.0]hex-2-ene (II). UV spectrum: λ_{max} (C_2H_5OH), nm: 248 (log ε 3.66). IR spectrum: ν_{max} (CCl_4), cm^{-1}, 1175, 1370, 1390, 1465, 1611 (C=C), 1685 (C=O), 3050. Mass spectrum, m/z (%): 150 (M^+, 7), 108(30), 107(52), 106(28), 105(31), 75 (100), 77(33). PMR spectrum (200 MHz, $CDCl_3$): 0.04 (1H, dd, J_1 = 4 Hz, J_2 = 3 Hz, H-6), 0.90 (3H, d, J = 7 Hz, H-9), 0.93 (3H, d, J = 7 Hz, H-10), 1.01 (1H, dd, superposition of signals), 1.47 (1H, septet, J = 7 Hz, H-8), 1.94 (1H, dt, J_1 = 8 Hz, J_2 = 3 Hz, H-3), 2.49 (1H, dt, J_1 = 21 Hz, J_2 = 3 Hz, H-6), 2.67 (1H, dd, J_1 = 21 Hz, J_2 = 3 Hz, H-6), 6.49 (1H, t, J = 3 Hz, H-1), 9.63 (1H, s, H-2). ^{13}C NMR (50.32 MHz, $CDCl_3$); 19.52 (q, C-9), 197.74 (q, C-10), 20.98 (t, C-6), 37.62 (t, C-4), 23.87 and 32.12 (d, C-1 and C-8), 33.47 (s, C-5), 149.20 (d, C-2), 151.86 (s, C-3), 188.64 (d, C-7).

4-Isopropyl-1-methylbicyclo[3.1.0]hexan-2-one (III). PMR (200 MHz, $CDCl_3$); 0.95 (3H, d, J = 7 Hz, H-9), 0.87 (3H, d, J = 7 Hz, H-10), 1.28 (3H, s, H-7), 0.20 (1H, dd, J_1 = 5 Hz, J_2 = 4 Hz, H-1), 0.38 (1H, dd, J_1 = 9 Hz, J_2 = 5 Hz, H-2), 1.03 (1H, dd, J_1 = 9 Hz, J_2 = 4 Hz, H-3).

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GAS-CHROMATOGRAPHIC DETERMINATION OF THE COMPOSITION OF THE VOLATILE COMPONENTS OF THE OLEORESINS OF SOME SPECIES OF CONIFERS

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UDC 547.913.2

Using the method of analytical GLC in a glass capillary column, the compositions have been studied of the volatile fractions of the oleoresins of five species of conifers: *Larix decidua*, *Pinus strobus*, *Pinus mugo*, *Picea excelsa*, and *Pinus abies*. In the oleoresins 21 monoterpene and 22 sesquiterpene compounds were identified from their relative retention times and with the aid of additives. The main components of the volatile fractions of the oleoresins were α- and β-pinenes and 3-carene among the monoterpenes, and longifolene caryophyllene, δ- and γ-cadinenes and α-murolene among the sesquiterpene compounds. The quantitative analysis of the fractions was carried out by the method of internal normalization from averaged correlation coefficients.

Continuing an investigation of the chemical compositions of the oleoresins of conifers growing in the USSR, we have determined the compositions of the volatile components of the oleoresins of the European larch (*Larix decidua* Mill.), the Swiss mountain pine (*Pinus mugo* Turra); the easterm white pine (*Pinus strobus* L.), and the Norway [Evropeiskaya] spruce (*Picea abies* Karst.), the areas of which are located in Transcarpathia, and also the Norway [Obyknovennaya] spruce (*Picea excelsa* Link.) growing in the cis-Urals region. The group compositions and also the compositions of the acid fractions of the oleoresins of these species have been published previously [1].

According to the results obtained, the percentage amounts of the volatile components in the oleoresins studied were approximately the same (14.8-17.4%):

Conifer species	Monoterpenes	High-boiling fraction
Larix decidua	13.4	1.4
Pinus strobus	15.9	0.3
Pinus mugo	16.2	1.2
Picea abies	12.6	3.0
Picea exelsa	15.8	0.6

The high relative content of monoterpene hydrocarbons did not permit the calculation of the quantitative amounts of the other components of the volatile fraction, since the capillary columns used for the analysis possessed a relatively small dynamic range and were very sensitive to overloading. The volatile substances of the oleoresins were therefore first separated into two fractions — monoterpene hydrocarbons, the compositions of which are given below, and high-boiling compounds (Table 1). The quantitative compositions of the fractions of monoterpene hydrocarbons were determined by the method of simple normalization in light of the approximately equal sensitivity of the flame-ionization detector (FID) to the compounds listed below, except for p-cymene (%):

Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Novosibirsk. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 629-632, September-October, 1990. Original article submitted December 18, 1989.

0009-3130/90/2605-0534$12.50