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DIOLS FROM THE OLEORESIN OF *Picea ajanensis*

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Oplodiol, 3β-hydroxyepimanool, and epitorulosol have been isolated for the first time from the oleoresin of Picea ajanensis. *On the basis of the results obtained, it may be assumed that the species studied is possibly a hybrid of Yeddo spruce and Siberian spruce.*

Earlier, in a study of the oleoresin of *Picea ajanensis* Fisch from various areas, we observed that the chemical composition of the oleoresin of a spruce growing at the boundary of Khabarovsk territory with Maritime Territory differed from that growing in the Ul'ya region of Khabarovsk territory and on Kamchatka [1, 2]. In this oleoresin we did not detect the tetracyclic alcohol phyllocladanol, the presence of which is characteristic of *Picea ajanensis*, but we found a considerable amount of *cis*-abienol, which is characteristic of the oleoresin of the Siberian spruce.

Continuing the study of composition of the most polar fraction of the neutral part of the spruce oleoresin, we have established that it contains four components (according to GLC). By adsorption chromatography of the polar fraction, we isolated compound (**1a**), which was identified by comparison with an authentic sample as epitorulosol; this diol has not previously been found in oleoresins of conifers of the *Picea* genus. We also isolated 3β-hydroxyepimanool (**1b**), which has been found in the oleoresin of the Japanese larch [3], and the sesquiterpene ketoalcohol oplopanone (**2**), previously isolated from the oleoresin of *P. ajanensis* [4], and identified them from their melting points and spectral characteristics. We may note that oplopanone was not found in the oleoresin of a spruce growing on Kamchatka [2, 5].

For the complete separation of the mixture and the isolation of the fourth component, we acetylated the initial polar fraction. The reaction mixture was chromatographed, and we then isolated an alcohol monoacetate (**3b**), the acetate of 3β-hydroxyepimanool (**1c**), and oplopanone (**2**). According to its ^{13}C NMR spectrum, the first component (**3b**) contained 17 carbon atoms, while its molecular ion corresponded to *m/z* 280 and its IR spectrum showed the absorption band of a hydroxy group (3500 cm^{-1}). From these spectral characteristics, we assumed that the product isolated was a monoacetate of a sesquiterpene diol with a selinane skeleton in which one hydroxy group was tertiary. Attempts to crystallize the diol (**3a**) and its acetate (**3b**) proved unsuccessful. To establish the structure of the diol isolated we subjected it to epoxidation and obtained the epoxide (**3c**), which crystallized. The structure and relative configuration of the epoxydiol were determined by x-ray structural analysis, and are shown in Fig. 1.

Thus, it has been established that the compound (**3a**) isolated was selin-7(8)-ene-1,4-diol; this substance (oplodiol) was first found in *Oplopanax japonicus* [6], and later in *Pulicaria paludosa*; the epoxide (**3c**) had not been described. Ajanol [8] and a germacrane alcohol [5] have been isolated from the oleoresin of *P. ajanensis* previously, but oplodiol has not been found in conifer oleoresins.

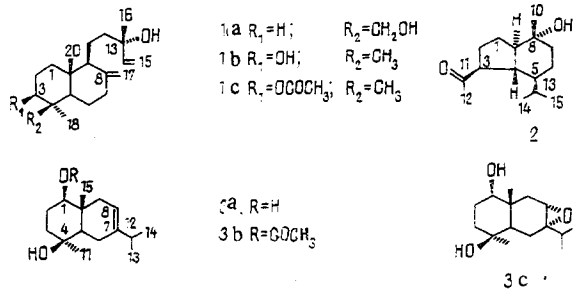

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TABLE 1. Coordinates ($\times 10^4$) and Equivalent Temperature Factors ($Å^2$, $\times 10^3$) of the Nonhydrogen Atoms of the Epoxide **(3b)**

Atom	x/a	y/b	z/c	U	Atom	x/a	y/b	z/c	U
C1	4339(6)	11327(6)	7358(3)	44	C10	3106(6)	10722(5)	6798(3)	37
C2	4299(6)	10551(6)	8078(3)	47	C11	—443(6)	10333(6)	8241(3)	50
C3	2586(7)	10667(6)	8410(3)	51	C12	—747(7)	9930(6)	5235(3)	55
C4	1226(6)	10042(5)	7914(3)	39	C13	—2528(8)	9919(10)	5383(4)	79
C5	1351(5)	10704(5)	7142(2)	32	C14	—72(8)	8442(6)	5101(3)	64
C6	105(6)	10070(6)	6610(2)	41	C15	3644(6)	9271(5)	6530(3)	43
C7	226(7)	10673(5)	5845(2)	43	O1	5946(4)	11297(5)	7039(2)	63
C8	1635(6)	11516(5)	5641(3)	45	O2	1469(4)	8528(4)	7863(2)	44
C9	3048(7)	11755(5)	6150(3)	47	O3	62(5)	12186(3)	5828(2)	53

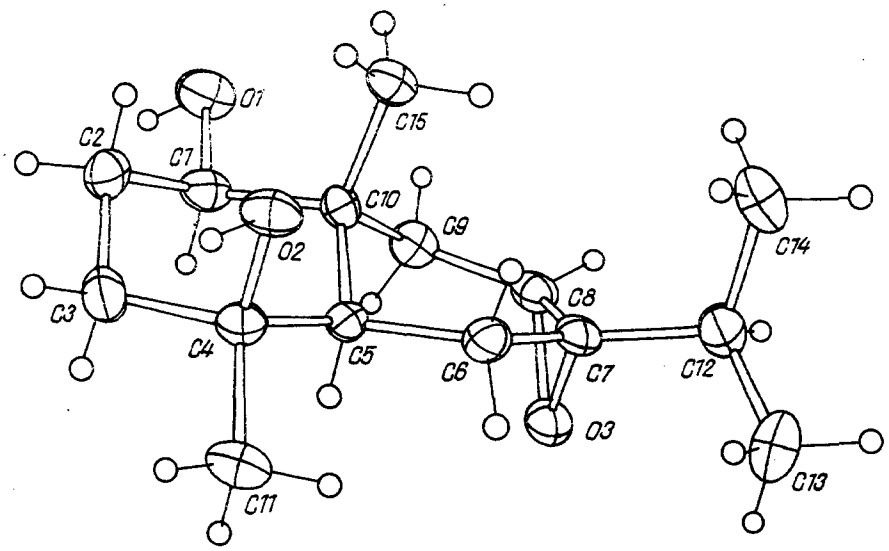

Fig. 1. Crystal structure and relative configuration of the epoxydiol (**3c**).

From the chemical composition of the oleoresin studied, it may be assumed that the tree from which it was obtained was probably not the pure species *P. ajanensis*, but was possibly a hybrid of it with *P. obovata* (Siberian spruce), which is penetrating into this part of the territory [9].

EXPERIMENTAL

The oleoresin of *P. ajanensis* was collected at the boundary of Kharabovsk territory with Maritine Territory.

IR spectra were recorded on a UR-20 instrument in CCl_4, PMR spectra on Bruker AC-200 (200.13 MHz) and WP-200 SY (200.13 MHz) instruments in $CDCl_3$ solutions (δ scale; internal standard chloroform, the signal of which was taken as 7.24 ppm), and ^{13}C NMR spectra on Bruker AC-200 (50.32 MHz) and AM-400 (100.62 MHz) instruments. Mass spectra were taken on a Finnigan MAT 8200, pW, instrument. The GLC of the substances was conducted on a Chrom-4 instrument, SE-30/Chromaton-Super (0.16-0.20 mm), column temperature 260°C, carrier gas nitrogen (30 ml/min). For chromatography we used type KSK silica gel with a grain size of 0.063-0.16 mm, and redistilled solvents: petroleum ether (PE) with bp 40-60°C, and diethyl ether (DE). The melting points of the substances were determined on a Kofler stage. Angles of optical rotation were obtained on a Polamat A polarimenter for solutions in chloroform.

Isolation of the Polar Fraction of the Oleoresin. When the neutral high-boiling part of the *Picea ajanensis* oleoresin (25 g) was subjected to chromatography, DE eluted a fraction (4.6 g) that, according to GLC, consisted of four components — oplopanone, oplodiol, hydroxyepimanool, and epitorulosol — in a ratio of 5:1:1:1, respectively.

Chromatography of the polar fraction (substrate:sorbent ratio 1:15) gave enriched fractions, eluted by DE:PE (2:3) – epitorulosol (0.6 g) – and by DE:PE (3:2) – a mixture of three components acording to GLC (1.67 g).

Epitorulosol (1a). The epitorulosol isolated (0.6 g) had mp 110-112°C (benzene). Its IR and PMR spectra and its melting point were identical with those of an authentic sample.

Rechromatography of the main fraction with DE:PE (2:3) led to the isolation of a fraction (0.2 g) containing 3β-hydroxyepimanool (**1b**) and oplopanone (**2**) in a ratio of 1:4 (GLC).

3β-Hydroxyepimanool (1b). Subsequent purification of the fraction on silica gel (ratio 1:30) with DE:PE (1:2) led to the isolation of 0.01 g of 3β-hydroxyepimanool as an oil, the IR and PMR spectra of which were identical with those given in the literature [3].

Oplopanone (2). DE:PE (1:1) eluted 0.06 g of oplopanone. mp 90-92°C (hexane + DE), having spectral characteristics corresponding to those given in the literature [4]. A 0.25-g portion of the total fraction was acetylated by the usual method (acetic anhydride, pyridine, 20°C). After working up, the reaction mixture (0.2 g) was chromatographed.

Oplodiol Acetate (3b). DE:PE (1:7) eluted 0.035 g of oplodiol acetate. Its PMR and ^{13}C NMR spectra were identical with those given in the literature [7].

Oplodiol (3a). A solution of 0.035 g of compound (**3b**) in abs. DE was treated with a solution of $LiAlH_4$ in abs. DE, and the mixture was boiled on the water bath for 1.5 h. After working up, 0.025 g of compound (**3a**) was isolated, $[\alpha]_{580}^{22}$ −44° (c 0.183), lit. [6]: $[\alpha]_D^{24}$ −51.9° (±4°) (c 0.540). The PMR spectrum was identical with that described in [7].

3β-Acetoxyepimanool (1c). DE:PE (1:6) eluted 0.03 g of 3β-acetoxyepimanool, mp 109-110°C (hexane); lit. [3]: 97-98°C. The PMR spectrum was identical with that given in [3]. ^{13}C NMR spectrum (ppm): 36.73 (t, C-1), 23.7[a], (t, C-2), 80.74 (d, C-3), 39.40[b] (s, C-4), 54.80 (t, C-5), 24.26[a] (t, C-6), 38.00 (t, C-7), 147.77 (s, C-8), 56.99 (d, C-9), 38.00[b] (s, C-10), 17.87 (t, C-11), 41.29 (t, C-12), 73.39 (s, C-13), 145.20 (s, C-14), 111.52 (t, C-15), 27.79 (q, C-16), 106.99 (t, C-17), 28.18 (q, C-18), 16.42 (q, C-19), 14.42 (q, C-20), 170.76 (s, $\underline{C}OCH_3$), 21.13 (q, $CO\underline{C}H_3$) (a, b − may be interchanged).

7,8-Epoxyoplodiol (3c). To a solution of 78 mg of the total fraction containing oplopanone, oplodiol, and hydroxyepimanool (7:4.5:1) in methylene chloride was added, dropwise, a solution of peracetic acid in chloroform. The reaction mixture was kept at room temperature for 1.5 h, and, after the usual working up, it was chromatographed: DE:PE (1:1) eluted 15 mg of compound (**3b**), mp 163-166°C (hexane). PMR spectrum: 0.96 (d, J = 1 Hz, 3H, Me-15), 0.99 (d, J = 7 Hz, 3H, Me-12), 1.02 (d, J = 7 Hz, 3H, Me-13), 1.14 (s, 3H, Me-14), 2.95 (d, J = 6 Hz, H-8), 3.19 (dd, J = 3.5 and 11.5 Hz, H-1) ppm ^{13}C NMR spectrum (ppm): 79.37 (d, C-1), 39.63[a] (t, C-2), 39.46[a] (t, C-3), 70.89 (s, C-4), 41.89 (d, C-5), 26.43[b] (t, C-6), 63.97 (s, C-7), 56.31 (d, C-8), 19.89[b] (t C-9), 36.76 (s, C-10) 29.59 (q, C-11), 34.94 (d C-12), 18.16 (q, C-13), 17.59 (q, C-14), 12.44 (q, C-15) (a, b − may be interchanged). IR spectrum ($\nu_{max}^{CCl_4}$, cm^{-1}): 1040 (C−O), 3610 (OH). Empirical formula $C_{15}H_{26}O_3$ (found, 254.1880; calculated 254.1882).

X-Ray Structural Analysis of Epoxyoplodiol (3c). The x-ray structural investigation was conducted on a SYNTEX $P2_1$ diffractometer (CuK_α radiation, ω-scanning, $2\theta < 120°C$). The crystals were rhombic: a = 8.1173(9), b = 9.454(1), c = 18.346(2), Å, V = 1407.9(3), $Å^3$, space group $P2_12_12_1$, $C_{15}H_{26}O_3$, Z = 4, d_{calc} = 1.20 g/cm^3. The measured intensities were corrected for absorption with allowance for the actual form of the crystal. The structure was interpreted by the direct method and was refined in the full-matrix anisotropic approximation to R = 0.054, R_w = 0.063, S = 0.9 for 965 observed reflections (SHELX 86 and SHELX 76 programs). The positions of the hydroxylic hydrogen atoms were found from a difference synthesis, and the coordinates of the others geometrically (the parameters of the hydrogen atoms were not refined). The atomic coordinates obtained are given in Table 1. The structure of the epoxide (**3c**) molecule is shown in Fig. 1. The bond lengths and the conformations of the rings were the usual ones. In the crystal, the molecules formed layers along the *ab* plane through O1−H...O2 (2.981 Å) and O2−H...O3 (2.987 Å) hydrogen bonds.

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