(C=O). PMR spectrum (ppm): 0.87 and 0.88 (3 H each, doublets with J = 7 Hz each, $-CH(C\underline{H}_3)_2$); 1.57 and 1.65 (3 H each, broadened singlets, Me-8 and Me-12); 5.01 (1 H, broadened d, J ~ 12 Hz, H-7 or H-11); 5.18 (1 H, broadened t, J = 7 Hz, H-11 or H-7); 5.28 (1 H, dd, J = 11 and 9.5 Hz, H-2); 5.47-5.54 (2 H, m, H-3 and H-4); 7.58-7.88 (4 H, protons of the aromatic ring). ORD: −52.6° (589 nm), −108° (410 nm), −60° (375 nm), −595° (315 nm) (s 0.33).

LITERATURE CITED

1. J. F. Springer, J. Clardy, R. H. Cox, H. A. Cutler, and R. J. Cole, Tetrahedron Lett., 2737 (1975).
2. V. A. Raldugin, V. E. Kozlov, V. M. Chekurov, N. I. Yaroshenko, and V. A. Pentegova, Khim. Prir. Soedin., 733 (1981).
3. A. V. Vorob'ev, S. A. Shevtsov, and V. A. Raldugin, Khim. Prir. Soedin., 180 (1988).
4. U. Nagai and H. Iga, Tetrahedron, 26, 725 (1970).
5. V. I. Kefeli, R. Kh. Turetskaya, E. M. Kof, and P. V. Vlasov, Methods of Determining Phytohormones, Growth Inhibitors, Defoliants, and Herbicides [in Russian], Nauka, Moscow (1973), p. 7.

STRUCTURE OF A NEW TRITERPENOID FROM THE BARK OF THE SIBERIAN LARCH

G. F. Chernenko, I. Yu. Bagryanskaya,
and É. N. Shmidt

UDC 634.866+547.926+548.737

A petroleum ether extract of the bark of the Siberian larch has yielded a new triterpenoid − the methyl ester of 3α-hydroxy-24S,25R-epoxylanost-9(11)-en-27-oic acid, the structure of which has been established on the basis of spectral characteristics, chemical transformations, and x-ray structural analysis.

In the study of the chemical composition of a petroleum ether extract of the bark of the Siberian larch, substance (I) with the composition $C_{31}H_{50}O_4$ (high-resolution mass spectrometry) of unknown structure was detected in the fraction containing sterols.

According to its PMR spectrum, compound (I) with mp 184.5-186°C, contained a trisubstituted double bond (multiplet at 5.23 ppm), a free hydroxyl (multiplet at 3.4 ppm), a methoxycarbonyl group (singlet at 3.7 ppm), an oxide ring (multiplet at 3.12 ppm), and seven methyl groups one of which was secondary doublet at 0.88 ppm, J = 6 Hz). The acetylation of the substance confirmed the presence of a secondary hydroxy group. A comparison of the spectra (^1H and ^{13}C NMR spectra) of compound (I) with the spectra of abieslactone and its derivatives showed that they were related [1]. From these facts it was possible to assume that the compound (I) that had been isolated was a triterpenoid of the lanostane type. To determine the structure of the new substance more accurately we performed an x-ray structural analysis (XSA). The structure, the relative configuration, the spatial arrangement, the length of the bonds are shown in Fig. 1.

The geometry of the molecule is characteristic for structures of this type [2]. The six-membered rings in the molecule have the chair-chair and half-chair form, and the five-membered ring the twist form. The long side chain can be divided into three planar fragments: the ester group, with a maximum departure from the plane of 0.01 Å (A); the epoxide ring (B); and the C_{17}, C_{20}, C_{22}, and C_{23} atoms (C) which lie in one plane with a maximum departure of 0.02 Å. The dihedral angle between A and B amounts to 101.2° and that between B and C to 110.7°. The geometry of the oxide ring is as follows: the mean bond length is 1.45 Å and the mean value of the angles 60° [4]. In the crystal a strong intermolecular hydrogen bond is observed. According to the XSA results, compound (I) has the structure of the methyl ester of 3α-hydroxy-24S,25R-epoxylanost-9(11)-en-27-oic acid.

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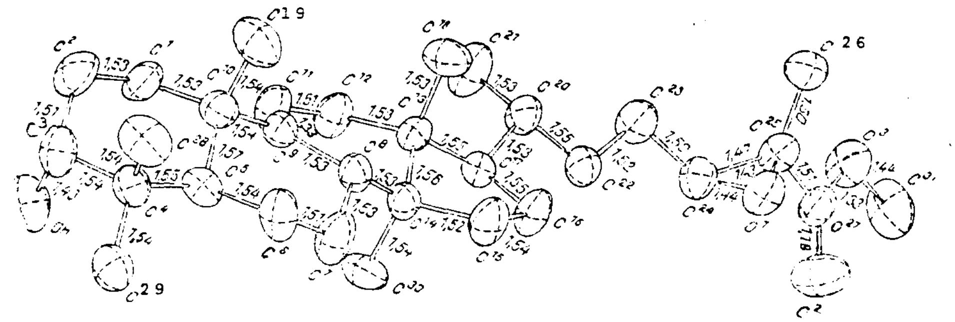
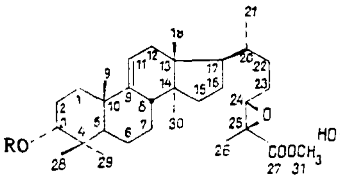


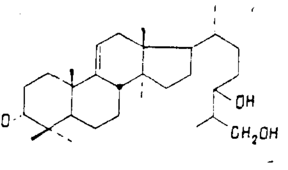
Fig. 1. Crystal structure and relative configuration of the methyl ester of 3α-hydroxy-24S,25R-epoxylanost-9(11)-en-27-oic acid (I).

The reduction of (I) with lithium tetrahydroaluminate in tetrahydrofuran gave the triol (III) with mp 155-157°C but in this process a large part of the initial substance remained unchanged.



I. R=H

II R=Ac



III

Thus, a triterpenoid of the lanostane type has been isolated from the extractive substances of the larch for the first time and its structure has been established.

EXPERIMENTAL

The PMR spectra were recorded on Bruker AC-200 (200.13 MHz) and Bruker AM-400 (400.13 MHz) instruments for solutions in $CDCl_3$ (δ scale, internal standard: chloroform, the signal of which is at 7.24 ppm). ^{13}C NMR spectra were recorded on Bruker AC-200 (50.32 MHz) and Bruker AM-400 (100.62 MHz) instruments. Conventional symbols for the description of the NMR spectra: s) singlet; d) doublet; t) triplet; q) quartet; m) multiplet. High-resolution mass spectra were obtained on a Finnigan MAT 8200, pW instrument. IR spectra were recorded on a UR-20 instrument. Specific rotations were determined on a Polamat A instrument in $CHCl_3$ solution. Melting points were determined on a Kofler stage. Petroleum ether (40-70°C) (PE) with the addition of diethyl ether (DE) was used for chromatography.

Methyl Ester of 3α-Hydroxy-24S,25R-epoxylanost-9(11)-en-27-oic Acid (I). The sterol fraction (640 mg) obtained on the separation of the neutral part of the extract from Siberian larch bark [1] was chromatographed on silica gel (71 μm) at a sorbent ratio of 1:50. The fraction (28 mg) eluted by DE–PE (15:85) contained (according to TLC) a small amount of β-sitosterol as well as compound (I). Repeated recrystallization from DE yielded 14 mg of compound (I) with mp 184.5-186°C, $[\alpha]_{594}^{23}$ + 59.52° (c 0.252). IR spectrum: $\nu_{max}^{CCl_4}$, cm^{-1}: 880 (C=C), 990, 1100, 1120 (C–O–C), 1170, 1740 (CO–O), 3620 (C–OH). PMR spectrum (200 MHz): 0.63, 0.73, 0.86, 0.94, 1.04, 1.50 (3 H each , s, tertiary methyl groups), 0.88, (3 H, d, J = 6 Hz, CH_3-21), 3.12 (1 H, m, H-24), 3.40 (1 H, m, H-3), 3.73 (3 H, s, OCH_3), 5.23 (1 H, m, H-11). For the ^{13}C NMR spectrum, see Table 1. Empirical formula $C_{31}H_{50}O_4$ (found, m/z 486.3704; calculated, 486.3709). Mass spectrum, m/z (%): 486(45) – M^+, 471(50) – $(M - 15)^+$, 453(100), 383(10), 313(37), 175(15), 121(15), 95(22), 81(27), 69(45).

X-Ray Structural Analysis of Compound (I). The x-ray structural experiment was conducted on a SYNTEX $P2_1$ [sic] diffractometer, using Mo radiation with a graphite monochromator. Crystallographic characteristics of (I): crystals of the rhombic system, a = 11.217(2), b = 14.254 (3), c = 17.269(2) Å, space group $P2_12_12_1$, Z = 4, d_{calc} = 1.09 g/cm³. The intensities of

TABLE 1. Chemical Shifts (ppm) and Multiplicities of the Signals in the ^{13}C NMR Spectra of Compounds (I), (II), and (III)

Atom C	I	II	III	Atom C	I	II	III
1	30,46 t	31,55 t	30,44 t	18	18,43[c] q	18,51[c] q	18,42[b] q
2	21,18 t	21,06 t	21,17 t	19	21,97 q	21,95 q	21,96 q
3	76,15 d	78,22 d	76,16 d	20	35,83 d	35,84 d	35,90 d
4	37,05[a] s	36,91[a] s	37,03[a] s	21	14,35 q	14,36 q	14,33 q
5	41,78 d	41,80 d	41,76 d	22	39,27 t	39,24 t	39,25 t
6	25,09 t	23 14 t	25,18 t	23	27,90[b] t	27,60[b] t	29,60 t
7	25,61 t	25,11 t	25,58 t	24	62,71 d	62,72 d	60,45 d
8	46,61 d	47,67 d	46,59 d	25	57,33 s	57,35 s	22,83 d
9	148,46 s	148,52 s	148,43 s	26	13,37 q	13,39 q	14,09 q
10	37,78[a] s	37,03[a] s	37,76[a] s	27	172,03 s	170,70 s	65,29 t
11	114,46 d	114,42 d	114,49 d	28	22,24 q	22,09 q	22,43 q
12	32,53 t	32,53 t	32,73 t	29	18 07[c] q	18,09[c] q	18,13[b] q
13	44,23 s	44,24 s	44,19 s	30	28,24 q	27,79 q	28,25 q
14	47,07 s	47,05 s	47,05 s	OCH_3	50,79 q	50,82 q	
15	33,77 t	33,79 t	33,77 t	COO		172,04 s	
16	27,93[b] t	27,89[b] t	27,93 t	|			
17	52,43 d	52,45 d	50,79 d	CH_3		21,24 q	

[a,b,c]The positions may be interchanged.

TABLE 2. Coordinates of the Nonhydrogen Atoms (in fractions of the cell × 10^4)

Atom	x	y	z	Atom	x	y	z
C^{1}	1019 (5)	6727 (3)	7171 (2)	C^{19}	—0720 (5)	6861 (4)	6287 (4)
C^{2}	0957 (5)	7683 (4)	7556 (3)	C^{20}	0659 (5)	2232 (3)	4749 (3)
C^{3}	1729 (5)	8403 (3)	7161 (3)	C^{21}	0822 (7)	1838 (4)	5547 (3)
C^{4}	1419 (4)	8522 (3)	6318 (3)	C^{22}	1221 (5)	1571 (3)	4153 (3)
C^{5}	1371 (4)	7552 (3)	5926 (3)	C^{23}	0725 (5)	0577 (3)	4134 (3)
C^{6}	0998 (6)	7600 (4)	5089 (3)	C^{24}	1227 (4)	0063 (3)	3464 (3)
C^{7}	1337 (6)	6694 (4)	4708 (3)	C^{25}	0589 (5)	—0676 (3)	3051 (3)
C^{8}	0807 (4)	5808 (3)	5763 (2)	C^{26}	—0646 (5)	—0988 (4)	3268 (3)
C^{9}	0942 (4)	5823 (3)	5924 (2)	C^{27}	1355 (5)	—1356 (3)	2619 (3)
C^{10}	0647 (4)	6754 (3)	6334 (3)	C^{28}	0276 (5)	9112 (4)	6249 (4)
C^{11}	1211 (5)	5043 (3)	6314 (3)	C^{29}	2399 (5)	9125 (4)	5954 (3)
C^{12}	1342 (5)	4078 (3)	5964 (2)	C^{30}	2668 (5)	4928 (4)	4743 (3)
C^{13}	0814 (4)	4030 (3)	5165 (2)	C^{31}	1714 (6)	—2937 (4)	2355 (4)
C^{14}	1299 (4)	4898 (3)	4726 (2)	O^{1}	0663 (3)	0252 (2)	2749 (2)
C^{15}	0892 (5)	4684 (3)	3920 (3)	O^{2}	2147 (4)	—1142 (3)	2213 (3)
C^{16}	1014 (5)	3612 (3)	3844 (2)	O^{3}	1042 (3)	—2240 (2)	2763 (2)
C^{17}	1204 (4)	3207 (3)	4649 (2)	O	2928 (3)	8079 (2)	7255 (2)
C^{18}	—0544 (5)	4051 (3)	5238 (3)				

reflections were measure by the 2θ/θ scanning method in the range 2θ < 45°. The structure was interpreted by the direct method and was refined by the method of least squares in the anisotropic approximation to R = 0.051 and R_w = 0.049 for 2110 independent reflections, of which 1819 (I > 2σ) were used in the calculations. The positions of the hydrogen atoms were found from a difference synthesis. All the calculations were made by means of the Shelx-86 program. The coordinates obtained for the nonhydrogen atoms are given in Table 2. Intermolecular hydrogen bonds were characterized by the parameters: OH—HOH 0.93(5) Å, HOH...O1 2.13 Å, OH....O1 2.98 Å, the angle OH-HOH...O1 153.9°.

Methyl Ester of 3-Acetoxy-24S,25R-epoxylanost-9(11)-en-27-oic Acid (II). The mixture of β-sitosterol and compound (I) obtained on the separation of the sterol fraction (37 mg) was dissolved in 2 ml of pyridine, and 2 ml of acetic anhydride was added, after which the reaction mixture was left at room temperature for 15 h. The usual working up and further chromatography of the reaction mixture on SiO_2 (71 μm) led to the isolation of 5 mg of β-sitosterol acetate and 15 mg of the acetate of (II), with mp 133.5-134.5° (hexane), $[\alpha]^{22}_{594}$ + 48.54° (c 0.206). IR spectrum, $\nu_{max}^{CCl_4}$, cm^{-1}: 1250, 1740 (C—O—Ac).

PMR spectrum (200 MHz): 0.64, 0.76, 0.83, 0.91, 1.05, 1.50 (3 H each, s, tertiary methyl groups), 0.89 (3 H, d, J = 7 Hz, CH_3-21), 2.04 (3 H, s, CH_3COO), 3.12 (1 H, m, H-24), 3.73 (3 H, s, OCH_3), 4.64 (1 H, m, H-3), 5.22 ppm (1 H, m, H-11). For the ^{13}C NMR spectrum (200 MHz), see Table 1. Mass spectrum, m/z (%): 528(30) – M^+, 513(30) – $(M - 15)^+$, 453(100), 395(22), 355 (40), 309(12), 295(15), 187(12), 175(20), 159(13), 135(15), 109(15), 95(22), 69(20),43(38).

Lanost-9(11)-ene-3,24,27-triol (III). The mixture obtained on the chromatography of the sterol fraction and containing β-sitosterol, compound (I) and epitorulosol acetate (90 mg) was dissolved in 3 ml of THF (dry), and 0.09 g of lithium tetrahydroaluminate and then another 3 ml of THF were added and the mixture was boiled on the water bath at 80°C for 2 h. After the usual working up, the reaction mixture was chromatographed on silica gel. PE—DE (3:1) eluted a fraction (24 mg) containing β-sitosterol and unchanged triterpene (I); PE—DE (1.5:1) eluted 10 mg of epitorulosol; and PE—DE (1:1) eluted a fraction (12 mg) the recrystallization of which from acetonitrile with the addition DE gave 6 mg of compound (III) with mp 155-157°C.

PMR spectrum (400 MHz): 0.63, 0.73, 0.86, 0.94, 1.04 (3 H each, s, tertiary methyl groups), 0.89 (3 H, d, J = 6.5 Hz, CH_3-21), 1.25 (3 H, d, J = 6.5 Hz, CH_3-26), 3.0 (1 H, m, H-24), 3.41 (1 H, m, H-3), 3.60 (2 H, dd, J = 4, 5, and 12 Hz, dd, J = 8.5 and 12 Hz 2H-27), 5.25 (1 H, m, H-11). For the ^{13}C NMR spectrum (400 MHz), see Table 1. Mass spectrum, m/z (%): 458(11) – M^+, 440 (20) – $(M - 18)^+$, 425(45), 407(32), 400(53), 385(78), 367(100), 313(90), 295(10), 246(15), 229(14), 213(15), 201(15), 187(20), 175(30), 161(25), 147(20), 135(28), 119(35), 81(27), 69(32), 55(40), 43(45).

Compound (I) (8 mg) was reduced with lithium tetrahydroaluminate, as described above. After working up, 6 mg of the initial compound (I) and traces of compound (III) (according to TLC) were obtained.

When 9 mg of compound (II) was reduced, again only traces of compound (III) (according to TLC) were detected, and the acetate (II) was isolated in unchanged form.

LITERATURE CITED

1. N. I. Yaroshenko and V. A. Raldugin, Khim. Prir. Soedin., 220 (1989).
2. A. I. Kitaigorodskii, P. M. Zorkii, and V. K. Bel'skii, The Composition of Organic Matter. Results of Structural Investigations [in Russian], Moscow (1971-1973), pp. 442, 414.
3. L. Ward, D. Templeton, and A. Zalkin, Acta, Cryst., 29, 2016 (1973).

EXTRACTIVE SUBSTANCES OF THE BARK OF Picea ajanensis

G. F. Chernenko, K. I. Demenkova,
E. E. Ivanova, and É. N. Shmidt

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A study of the chemical composition of a petroleum ether extract of the bark of Yeddo spruce growing in Khabarovsk Territory has shown that the neutral fraction of the extract contained waxes, glycerides, diterpenoids — epimanool, cis- and trans-abienols, and phyllocladenol, and triterpenoids — the epimeric 3α- and 3β-methoxy-21-hydroxy-Δ^{14}-serratenes and a ketone which has been ascribed the structure of 21-keto-3β-methoxy-Δ^{14}-serratene.

There is information in the literature on the study of the chemical composition of the terpenoid components of extracts of the bark of various species of spruce [1-3]. The phenolic substances of the bark of the Yeddo, Korean, and Siberian spruces have been investigated [4]. However, the lipid and terpene substances of extracts of domestic species have been studied inadequately.

In the present paper we give information on a study of the group and component compositions of a petroleum ether extract of the bark of the Yeddo spruce Picea ajanensis Fisch. (Picea jezoensis) growing in Khabarovsk Territory. The Yeddo spruce is the main forest-forming species of the Far East and is widely involved in forestry operations, but the bark finds

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