NEW TRITERPENE ACIDS FROM Abies sibirica NEEDLES

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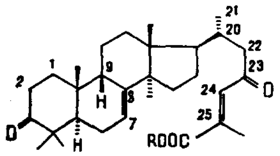
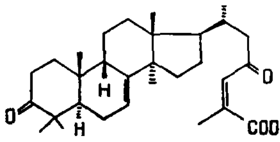
Fir bark and needles contain neutral lanostane and cycloartane triterpenoids [1]. In an investigation of the composition of the acidic fraction of an extract of the needles of Abies sibirica Ledeb. (Siberian fir) we have isolated two new triterpenoids, for which structure (I) and (II) are suggested



I. R=H
III. R=CH$_3$



II. R=H
IV. R=CH$_3$

Substance (I) formed crystals from acetonitrile with mp 210-212°C. Mass spectrum: m/z 468.3247 (M^+, $C_{30}H_{44}O_4$); 325.2525 ($C_{25}H_{33}O$), [M^+ − CH_3 − (H + side chain with cleavage at C_{20}–C_{22})]; 113.0250 ($C_5H_5O_3$, the fragment $\cdot^+COCH{=}C(CH_3)COOH$); $\lambda_{max}^{C_2H_5OH}$: 239 nm (ε 17,200); $\nu_{max}^{CHCl_3}$, cm^{-1}: 1270, 1630, 1700 (broad), 3100-3400 (Broad) (COOH, C=O, C=C–C=O). PMR spectrum ($CDCl_3$, 200 MHz, δ scale, TMS, ppm): 0.80, 0.95, 0.99 (s, 3H each, angular CH_3 groups), 0.88 (3H, d, J = 6.4 Hz, CH_3-20), 1.07 (6 H, s, two angular CH_3 groups), 2.19 (3 H, singlet, CH_3-25), 5.62 (1 H, doublet of triplets, J = 7.0, ∿2.5, and 2.5 Hz, H_7), 7.14 (1 H, s, $W_{1/2}$ = 4.5 Hz, H_{24}).

When the acid (I) was methylated with an ethereal solution of diazomethane, the corresponding methyl ester (III) was obtained with mp 98-99°C (from hexane); mass spectrum: m/z 482.3396 ($C_{31}H_{46}O_4$. PMR spectrum: 3.79 ppm (s, 3 H, $COCH_3$). The circular dichroism curve (for a solution in methanol) showed a positive maximum at ∿300 nm (Δε +0.7), as in analogous triterpenoids with a 3-keto group [2], and a negative maximum of approximately the same intensity at 238 nm (π–π* transition in an α-enone system).

Acid (II) was isolated and characterized on the form of its methyl ester (IV), mp 183-184°C (from acetonitrile). Its mass spectrum practically coincides with that for the ester (III). The molecular ion corresponded to the empirical formula $C_{31}H_{46}O_4$, m/z 482.3380). $\lambda_{max}^{C_2H_5OH}$ 239 nm (shoulder, ε 8800). PMR spectrum, ppm: 0.79, 0.96, 0.99, 1.06, 1.07 (c, 3 H each, angular methyl groups), 0.89 (3 H, d, J = 6.4 Hz, CH_3-20), 2.01 (3 H, d, J = 1.8 Hz, CH_3-25), 5.62 (1 H, doublet of triplets, J = 7, 3, and 3 Hz, H_7), 6.14 (1 H, quartet, J = 1.8 Hz, H_{24}). As in the PMR spectrum of (I), the assignment of the signals for CH_3-25 and H_{24} was confirmed by double resonance. The ester (IV) was obtained in quantitative yield when a solution of the ester (III) in pentane–diethyl ether (3:1) was irradiated with the light of a high-pressure mercury lamp (DRSh-100) for 1 h.

The configurations of the C_{24} double bond in the molecules of the substances under investigation are proposed on the basis of the chemical shifts of the CH_3-25 and H_{24} signals in the PMR spectra of compounds (I), (III), and (IV). When it has the trans configuration (compounds (I) and (III)), the H_{24} proton is descreened by the COOH or $COOCH_3$ group and its signal is found in a weaker field (7.05 ppm for (III)) than in the spectrum of the ester (IV). On the other hand, the C_{25}-methyl groups in the molecules of compounds (I) and (III) undergo a descreening similar to in nature under the action of the C_{23}-carbonyl groups, which is expressed in a greater chemical shift for its signal (2.19 ppm for (III)) as compared

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with that for the ester (IV).

The stereochemistry of the carbon skeleton of compounds (I-IV) is suggested on the basis of biogenetic consideration [1], the positive Cotton effect ($\pi-\pi^*$ transition) for the ester (III), and the values of the chemical shifts for the signal of the H_7 proton in the PMR spectra of substances (I), (III), and (IV), which is characteristic for the linkage of rings B and C in the lanost-7-ene carbon skeleton shown in the formula [1].

LITERATURE CITED

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2. C. Djerassi, J. Osiecki, and W. Closson, J. Am. Chem. Soc., 81, 4587 (1958).

TRITERPENOIDS OF THE OUTER BARK OF *Betula maximowicziana*

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Continuing a study of the triterpene composition of the outer bark of Far Eastern species of birch [1, 2], we have investigated a chloroform extract of the birch of *Betula maximowicziana* Regel (monarch birch) collected on July 5, 1984, on the island of Kunashir. This species is the only representative of the subtropical section of the *Acuminata* growing on the territory of the Soviet Union [3]. The extraction of 638 g of the comminuted air-dry bark five times with chloroform at room temprature gave 78 g (12.3%) of extract of which 12 g were taken for separation. Individual compounds were isolated by repeated chromatography on a column of silica gel L 100/160 μ with elution by the following solvent systems: 1) Petroleum ether—acetone, and 2) chloroform. Nine compounds of triterpene nature (I-IX) were obtained, the triterpenes (IV-IX) being isolated and identified in the form of their acetates after acetylation of the corresponding fraction:

	Substance	Yield, % on the weight of the air-dry bark	Literature
1.	Oleanolic acid acetate	0.16	[1]
II.	Lupeol	0,19	[1]
III.	Betulin	3.2	[1]
IV.	Betulinic acid	0 6	[4]
V.	Lupane-3β,20-diol	0,72	[5]
VI.	Lupane-3β,20,28-triol	0 33	[5]
VII.	Betulin caffeate	1,0	[6]
VIII.	Betulinic acid caffeate	0,27	[4]

Compounds (I-III) were identified by comparison with authentic samples and (IV-VIII) by comparing their physicochemical properties and spectral characteristics (IR, ^1H and ^{13}C NMR) with those given in the literature, while this is the first time that compound (IX) has been isolated.

Acetylation by the usual method of the most polar fraction of the extract followed by chromatography of the acetates obtained gave 0.5 g of substance (X) with mp 120-125°C (ethanol). The IR spectrum showed the presence of a hydroxy group (3621 cm^{-1}), of double bonds (1638 cm^{-1}), of ester groups (1726, 1705 cm^{-1}), and of ester groups in an aromatic ring (1771 cm^{-1}).

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