

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 H₇ 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].

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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 temperature 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:

<u>Substance</u>	<u>Yield, % on the weight of the air-dry bark</u>	<u>Literature</u>
I. Oleanolic acid acetate	0.16	[1]
II. Lupeol	0.19	[1]
III. Betulin	3.2	[1]
IV. Betulinic acid	0.6	[4]
V. Lupane-3 β ,20-diol	0.72	[5]
VI. Lupane-3 β ,20,28-triol	0.33	[5]
VII. Betulin caffeoate	1.0	[6]
VIII. Betulinic acid caffeoate	0.27	[4]

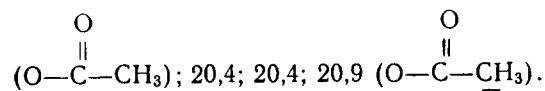
Compounds (I-III) were identified by comparison with authentic samples and (IV-VIII) by comparing their physicochemical properties and spectral characteristics (IR, ¹H and ¹³C NMR) with those given in the literature, while this is the first time that compound (IX) has been isolated.

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}).

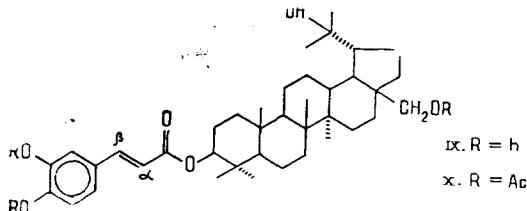
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The alkaline hydrolysis of (X) with 0.5 M KOH in methanol (65°C, 1 h) gave lupane-3 β , 20,28-triol [5].

PMR spectrum of (X) (250 MHz, CDCl_3), w, ppm, Hz): 0.886; 0.886; 0.908; 0.998; 1.081; 1.136; 1.237 (3H, s, CH_3); 2.06; 2.294; 2.300 (3H, s, 3 v OAc); 4.61 (1H, d-d, J = 6.0; 8.0; H^3); 3.84 (1H, d, J = 11.4), 4.33 (1H, d, J = 11.4, $-2\text{H}^{2\beta}$), 6.37 (1H, d, J = 16.0; H^b); 7.58 (1H, d, J = 16.0; H^a); 7.21 (1H, d, J = 8.3; $\text{H}^{5'}$); 7.35 (1H, d, J = 2.0; $\text{H}^{2'}$); 7.39 (1H, d-d, J = 2.0; 8.3; $\text{H}^{6'}$). ^{13}C NMR spectrum of (X) (CDCl_3 , TMS, w, ppm, C-atom): 38.4(1); 23.8(2); 81.1(3); 38.0(4); 55.3(5); 18.3(6); 34.0(7); 41.5(8); 50.2(9); 37.0(10); 21.4(11); 28.8(12); 36.7(13); 43.4(14); 27.3(15); 30.4(16); 47.9(17); 48.9(18); 49.7(19); 73.0(20); 28.1(21); 34.4(22); 28.0(23); 16.7(24); 16.2(25); 16.2(26); 15.2(27); 62.8(28); 24.8(29); 31.6(30); 167.5 (C=O); 142.3(α); 119.9(β); 133.2($1'$); 123.6($2'$); 142.1($3'$); 143.3($4'$); 122.4($5'$); 126.0($6'$); 170.9; 167.4; 166.0



A comparison of the ^1H and ^{13}C NMR spectra of compound (X) with the spectra of known triterpenoid caffeates [2, 4, 6] and also the results of the hydrolysis of (X) permitted the structure of (X) to be determined unambiguously as lupane-3 β , 20, 28-triol caffeate triacetate. Consequently, triterpene (IX) was lupane-3 β , 20, 28-triol caffeate (3β -(3', 4'-dihydroxycinnamoyl-oxy)lupane-20, 28-diol).



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