OLEANOLIC ACID CAFFEATE FROM THE OUTER BARK OF *Betula davurica*

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A new compound of a phenolic nature has been isolated from the outer bark of *Betula davurica* Pall. by column chromatography on silica gel in the petroleum ether–acetone (5:1) system (in a thin layer the fraction containing this compound gave a yellow coloration on treatment with 0.5% diazotized sulfanilic acid in 10% NaOH).

The compound made up 0.6% of the weight of an ethereal extract of the bark of *B. davurica* and was identified with the aid of chemical and spectroscopic methods as the ester of a monohydroxytriterpene acid and a phenolic acid (I), $C_{39}H_{54}O_6$, mp 301-304°C (MeOH). The IR spectrum of (I) contained the absorption bands of a carboxy group (1700, 3570-2500 cm^{-1}), of a hydroxy group (3546, 3600 cm^{-1}), and of double bonds (1634, 1606 cm^{-1}).

The alkaline hydrolysis of (I) with 0.5 M KOH in 90% ethanol (70°C, 3 h) gave a crystalline product, which was identified as oleanolic acid. The acid methanolysis of the ester (I) (10% H_2SO_4 in dry methanol, boiling under reflux for 2 h) gave methyl caffeate and methyl oleanolate, which were identified by GLC.

The methylation of (I) with diazomethane in diethyl ether followed by alkaline hydrolysis gave methyl oleanate and dimethylcaffeic acid, as was confirmed by the results of GLC. The acetylation of (I) with a mixture of acetic anhydride and pyridine (20°C, 12 h) led to a crystalline product (II), $C_{43}H_{58}O_8$, mp 220-223°C (EtOH). The IR spectrum of (II) contained the characteristic absorption bands of a carbonyl group (1696 cm^{-1}), of double bonds (1640 cm^{-1}), and of an ester group in the aromatic moiety of the molecule (1770 cm^{-1}). ^1H spectrum of (II) (250 MHz, $CDCl_3$, ppm, Hz): 0.76, 0.89, 0.91, 0.93, 0.97, 1.14, 1.25 (c, 3H, CH_3); 2.30, 2.31 (c, 3H + 3H; 2 × OAc); 2.83 (dd, J = 13.6, J = 4.5, 1 H, H^{18}); 4.63 (t, J = 8.0, 1 H, H^3); 5.30 (t, J = 3.6, 1 H, H^{12}); 6.39 (d, J = 15.8, 1 H, H^{β}); 7.22 (d, J = 8.3, 1 H, $H^{5'}$); 7.38 (d, J = 2.9, 1 H, $H^{2'}$); 7.41 (dd, J = 8.3, J = 2.0, 1 H, $H^{6'}$); 7.60 (d, J = 15.8, 1 H, H^{α}).

Below we give the ^{13}C chemical shifts of compound (II) (ppm, $CDCl_3$, TMS):

C-atom		C-atom		C-atom		C-atom		C-atom	
1	38,0	10	37,1	19	45,9	28	184,4	4′	143,4
2	23,7	11	22,9	20	30,7	29	33,1	5′	122,7
3	81,3	12	122,7	21	33,9	30	23,7	6′	123,9
4	38,2	13	143,7	22	32,6	C=O	166,4	O	
5	55,4	14	41,7	23	28,2	α	142,5	O–C–CH_3	168,8
6	18,3	15	27,8	24	16,9	β	120,1	O	
7	32,6	16	23,7	25	15,5	1′	133,5	O–C–CH_3	20,7
8	39,4	17	46,6	26	17,3	2′	126,3		
9	47,6	18	41,0	27	26,0	3′	142,5		

A comparison of the ^1H and ^{13}C NMR spectra of (II) with those of methyl 3-O-acetyloleanolate [1] and of caffeic acid (III) and its acetate (IV), and also literature information [2], permitted the structure of (II) to be determined unambiguously as oleanolic acid diacetylcaffeate. Compound (IV) was obtained by acetylating caffeic acid with a mixture of acetic anhydride and pyridine (90°C, 3 h).

Thus, on the basis of the results of hydrolysis, methylation, acetylation, and IR and NMR spectroscopy, compound (I) has been assigned the structure of 3β-O-(3',4'-dihydroxycinnamoyl)olean-12-en-28-oic acid (oleanolic acid caffeate). The isolation of caffeates of be-

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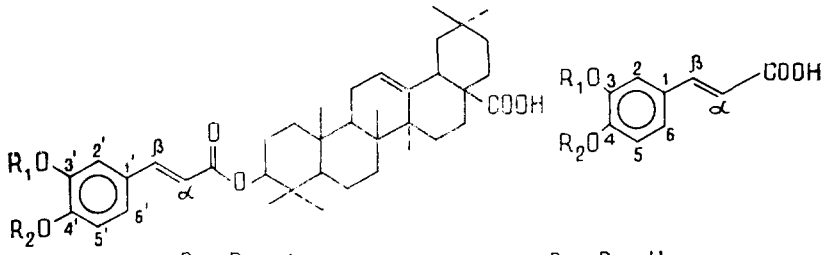
tulin [3], of betulic acid [4], and of some other triterpene alcohols [5] from natural materialshas been reported previously. In these papers, the antioxidant [5] and antiinflammatory activity [4] of these compounds were also discussed.



I. $R_1=R_2=H$ III. $R_1=R_2=H$

II. $R_1=R_2=Ac$ IV. $R_1=R_2=Ac$

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TRITERPENE ACIDS OF SOME REPRESENTATIVES OF *Eucalyptus*

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Continuing a study of the chemical composition of cultivated plants [1-4], we have investigated the leaves of some representatives of the genus *Eucalyptus* (*E. albens*, *E. camaldulensis*, *E. globulus*, *E. leucoxylon*, *E. obliqua*, *E. ovato*, *E. rostrota*, *E. polynthemos*, *E. siderocylon*, and *E. umbellatum*), family *Myrtacene*, collected in October, 1982, in the Mardakyan Arboretum of the Academy of Sciences of the Azerbaidzhan SSR.

A powder (0.1 kg) of the air-dry leaves of each plant was separately extracted succesively with hexane and with ethyl acetate in a Soxhlet apparatus. In the ethyl acetate extract the presence of two triterpene acids was established by TLC (sorbent: silica gel L5/40 μm; solvents: chloroform—ethanol (20:1); benzene—ether (1:1); revealing agent: 25% ethanolic solution of tungstophosphoric acid).

The ethyl acetate was evaporated and the residue was chromatographed on KSK silica gel. The substances were eluted with hexane—ethyl acetate (8:2) and (1:1). This gave substances (I) and (II).

Substance (I) — mp 300-302°C (ethanol), $[\alpha]_D^{20}$ + 78° (c 0.8; pyridine), $C_{30}H_{48}O_3$, mol. wt. 456 (mass spectrometry).

Substance (II) — mp 264-266°C (ethanol), $[\alpha]_D^{20}$ + 40° (c 0.9; pyridine), $C_{30}H_{48}O_4$, mol. wt. 472 (mass spectrometry).

On the basis of their physicochemical properties and chromatographic and IR- and mass-spectrometric characteristics, substance (I) was identified as oleanolic acid — 28-carboxy-3-hydroxyolean-12-ene — and substance (II) as maslinic acid — 28-carboxy-2,3-dihydroxyolean-12-ene [5, 6].

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