COMPOSITION OF THE OUTER BARK OF Betula mandschurica

T. Yu. Kochergina, G. V. Malinovskaya,
N. D. Pokhilo, V. A. Denisenko, and
N. I. Uvarova

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Birch bark — a waste of the wood processing industry — is attracting attention as a rich source of isoprenoids [1-3]. It has been shown that the composition of a lipophilic extract of the outer bark depends on a number of factors: the growth site, age, season, etc. [2].

Within a plan of comprehensive investigation of Far Eastern species of birch [4, 5], we have studied a lipophilic extract of the bark of B. mandschurica Regel (Nakai), which is the most common species in the Far East in the dynamic aspect. The complex mixture of substances called suberin [3] was not investigated. Samples of the air-dry comminuted bark of living birches collected in the Shkotovo region of Maritime Territory were extracted with chloroform (1 day × 4). After evaporation, the dry residue was chromatographed on KSK silica gel. Eight compounds were isolated and identified. The petroleum ether—acetone (40:1) system eluted lupeol (I), (25:1) oleanolic acid acetate (II), (15:1) β-sitosterol (III), and (10:1) betulin (IV) [5]. The substances obtained gave no depressions of the melting points in mixtures with authentic samples. The petroleum ether—acetone (8:1) mixture eluted a fraction containing a mixture of susbtances difficult to separate. For their more complete separation, the fraction was acetylated, after which it was rechromatographed. Betulin (IV) and oleanolic acid (V) were obtained in the form of their acetates.

From the acetylated fraction was isolated the acetate of a compound (VI) the structure of which was determined with the aid of IR and PMR spectroscopy as the acetate of the recently described betulin caffeate [6], mp 203-205°C (ethanol). The IR spectrum showed the presence of an ester bond (1706 cm^{-1}), of an ester bond in an aromatic ring (1774 cm^{-1}), and of a double carbon-carbon bond (1642 cm^{-1}). PMR spectrum ($CDCl_3$, ppm): 0.875, 0.877, 0.905, 0.98, 1.04, 1.68 (3H, s, CH_3): 2.09 (3H, s, OAc); 2.32 (6H, s, 2OAc); 3.85 (1H, d, J = 11.2 Hz), 4.25 (1H, d, J = 11.2 Hz) 2H^{28}; 4.60 (m, H^3_a); 4.59, 4.69 (1H, 2H^{30}), 7.59 (1H, d, J = 16.0 Hz, H$^{\alpha}$); 6.38 (1H, d, J = 8.1 Hz, H$^{\beta}$); 7.36 (1H, d, J = 1.9, H$^{2'}$); 7.21 (1H, d, J = 8.1 Hz, H$^{5'}$); 7.40 (1H, d-d, J = 8.1; 1.9 Hz, H$^{6'}$).

From a winter sample of bark was isolated in the petroleum ether—acetone (70:1) system a triterpene (VII) with mp 164-166°C (methanol). The IR spectrum of (VII) ($CHCl_3$) showed absorption bands at 1641 cm^{-1} (C=C) and 1698 cm^{-1} (C=O). PMR spectrum ($CDCl_3$, ppm): 0.92, 0.95, 0.98, 1.02, 1.09, 1.70 (3H, s, CH_3); 2.32-2.60 (m, 2 × H^2); 2.87 (1H, t-d, J = 5.6; 10.9 Hz); 4.63, 4.76 (2H, br.d, H^{30}); 9.66 (1H, d, J = 1.8 Hz, COH). The spectral and physicochemical characteristics of the triterpene isolated coincides with those known for betulone aldehyde [7].

From an extract of spring bark was isolated in the petroleum ether—acetone (60:1) system a compound (VIII) with mp 324-326°C (acetone), $[\alpha]_D^{20}$ +11.8 (c 0.5; chloroform). Its IR spectrum ($CHCl_3$) revealed the presence of a lactone grouping at 1754, 1715 cm^{-1} (acetate). PMR spectrum ($CDCl_3$, ppm): 0.87 (6H, s, 2 × CH_3); 0.92, 1.00, 1.05, 1.065, 1.10 (3H, s, CH_3); 2.065 (3H, s, OAc); 3012 (2H, m, H^{11}_{β} and H^{12}_{β}); 4.50-4.59 (1H, d-d, J = 10.5; 6.4 Hz, H^3_{α}). ^{13}C NMR spectrum ($CDCl_3$, ppm): 37.8 (C-1); 23.2 (C-2); 80.4 (C-3); 37.9 (C-4); 54.7 (C-5); 17.5 (C-6), 34.4 (C-7); 40.6 (C-8); 50.7 (C-9); 36.5 (C-10); 57.0, 52.5 (C-11 and C-12); 87.4 (C-13); 41.4 (C-14); 26.8 (C-15); 21.3 (C-16); 43.9 (C-17); 49.7 (C-18); 37.8 (C-19); 31.4 (C-20); 31.1 (C-21); 27.1 (C-22); 27.8 (C-23); 17.2 (C-24); 16.2 (C-25); 18.8 (C-26); 20.1 (C-27); 178.8 (C-28); 23.6 (C-29); 33.2 (C-30).

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TABLE 1.

Date of collection of bark	Total yield of extract, %	Yields of compounds, % on the air-dry bark							
		I	II	III	IV	V	VI	VII	VIII
4.V 1985	31,8	0.4	0,1	—	21,89	0,18	Tr.	—	0.043
18.VI 1984	45,4	0,4	1.6	0,045	27,2	—	0,31	—	Tr
19.IX 1985	37,7	0.15	1,17	—	22,76	0,17	Tr	—	Tr
20.XII 1984	28,3	0,2	0 09	—	9,04	—	—	0,05	—

On the basis of the results obtained, the structure of compound (VIII) was determined as 3β-acetoxy-11α, 12α-epoxylean-13,28-olide [8]. This compound has not previously been isolated from birch extracts.

In an analysis of the results obtained, a proportional change in the amount of betulin (IV) in comparison with the total yield of lipophilic substances was observed. The amount of minor components also changed. The main results of the investigation are given in Table 1.

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