TERPENOIDS AND FLAVONOIDS FROM THE LEAVES OF SIBERIAN SPECIES OF THE GENUS Betula

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Continuing a study of the genus Betula [1-4], we have investigated the leaves of four species of birch collected in the Selenginsk region of the Buryat ASSR in July, 1981. The leaves were exhaustively extracted with diethyl ether, and the extract obtained was saponified by the method of Fischer and Seiler [5]. The individual substances were isolated from the unsaponifiable fraction by repeated chromatography on a column of silica gel L (125-80 μ).

Four compounds were isolated from the leaves of B. humilis (I), $C_{30}H_{52}O_4$, mp 238-239°C (acetone); (II), $C_{30}H_{52}O_4$, mp 218-220°C (acetone); (III), $C_{30}H_{52}O_3$, mp 193-197°C (acetone); and (IV), $C_{30}H_{52}O_4$, mp 132-135°C (acetone). From the results of comparisons of IR and PMR spectra and mixed melting point tests with authentic samples, substances (I)-(IV) were identified as betulafolienetriol oxide [6], pyxinol [7], betulafolienetriol [5], and dammar-25-ene-3α,12β,20(S),24-tetraol [8], respectively.

From the leaves of B. pendula, we obtained triterpenoids: (V), $C_{30}H_{48}O_3$, mp 216-218°C (petroleum ether–acetone); (VI), $C_{30}H_{52}O_4$, mp 195-199°C (acetone); and (VII), $C_{30}H_{52}O_3$, mp 140-142°C (petroleum ether), which were identified by a direct comparison with authentic samples as 20(S),24(S)-dihydroxydammar-25-en-3-one [2], 20(S),24(R)-epoxydammarane-3α,17α,25-triol [2], and dammar-24-ene-3α,17α,20(S)-triol [1], respectively. In addition to triterpenoids, a flavonoid (VIII) was isolated – $C_{17}H_{14}O_5$, mp 174-175°C (acetone), giving no depression of the melting point in admixture with an authentic sample of 4',7-di-O-methylapigenin [9, 4].

In the leaves of B. pubescens, in addition to compound (VIII) we found two other substances of flavonoid nature: (IX), $C_{17}H_{14}O_6$, mp 177-180°C (acetone), and (X), $C_{16}H_{14}O_5$, mp 152-153°C (benzene). The results of a comparison of the physicochemical constants and IR, PMR, and ^{13}C NMR spectra with the literature permitted them to be identified as 4',7-di-O-methylkaempferol and 4',5-dihydroxy-7-methoxyflavanone (sakuranetin), which have been isolated previously from the buds of B. verrucosa [10].

The leaves of B. fusca yielded compounds (I), (II), VI), and (VIII) and a compound not previously described in the literature (XI), $C_{30}H_{52}O_5$, mp 230-231°C (petroleum ether–acetone), $[\alpha]_D^{18}$ +13.5 (c 0.5; chloroform). Its mass spectrum was characterized by the presence of peaks with m/z 456, 441, 349, 313, and 143 and was similar to that of betulafolienetetraol oxide [1]. The IR spectrum of the triterpenoid (XI) had absorption bands at 3624 and 2435 cm^{-1}. The PMR spectrum showed the signals of the protons of eight tertiary CH_3 groups in the 0.77-1.35 ppm region and, in the weak field, signals at 3.19 ppm (1 H, q, J = 5.2 Hz, J = 10.9 Hz, H_a^3) 3.76 ppm (1 H, sextet, ΣJ = 25.8 Hz, H_a^{12}), and 3.85 ppm (1 H), q, H^{24}). The ^{13}C NMR spectrum of the triterpenoid (XI) contained the signals of six carbinyl atoms: (ppm) 78.9 (C-3); 67.7 (C-12); 85.5 (C-17); 89.9 (C-20); 85.7 (C-24); 70.2 ppm. On the basis of a comparative study of the spectra of the triterpene (XI) and betulafolienetetraol oxide [1], we came to the conclusion that these substances differed only by the orientation of the substituents at C-3. Thus, triterpenoid (XI) was assigned to the structure of 20(S),24(R)-epoxydammarane-3β,12β,17α,25-tetraol.

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ALKALOIDS OF Thalictrum minus

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Continuing a study of the alkaloid composition of *Thalictrum minus*, we have investigated the roots, stems, seeds, and epigeal part of *Th. minus* L. from various growth sites. To isolate the individual bases we used column and thin-layer chromatography, and in addition to the alkaloids obtained previously [1] we isolated aromoline, thalbadenzine, corunnine, thalicsimidine, and N-methylargemonine. The results of the investigation are given below:

Site and date of collection	Plant organ	Total alkaloids, % on the weights of the dry raw material	Alkaloids
TadzhSSR, gorge of the R. Sagirdasht, July 10, 1974	Roots	0,71	Thalicsimidine
KirgSSR, Fergana range, May 29, 1975	Epigeal part	0,19	Thalicmine
TadzhSSR, gorge of the R. Sagirdasht, June 7, 1976	"	0,23	Thalmine, O-methylthalicberine
UzSSR, Tashkent province, Bol'shoi Chimgan, July 1976	Seeds	0,03	"
Ibid., May 24, 1977	Flowers	0,53	"
"	Roots	0,66	Thalicsimidine, glaucine, berberine, magnoflorine
TadshSSR, gorge of the R. Sagirdasht, June 17, 1977	"	0,39	Corunnine, thalicmidine
UzSSR, Tashkent province, valley of the R. Angren, May 31, 1979	Roots	1,00	Thalicminine, corunnine
UzSSR, Tashkent province, valley of the R. Angren, May 10, 1978	Epigeal part	0,86	Thalicmidine, thalmine, thalbadenzine, O-methylthalicberine
Ibid, May 31, 1979	Stems	0,06	O-Methylthalicberine, berberine
UzSSR, Dzhizak province, gorge of the R. Uvobsai, May 25, 1980	Epigeal part	0,74	Thalmine, thalbadenzine, O-methylthalicberine
TSSR, Kara-Kala region, June 1, 1980	Stems	0,08	Thalmethine
"	Epigeal part	0,70	Thalmethine, argemonine, base (I), base (II)

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