TRITERPENOIDS OF LEAVES OF Betula pendula GROWING IN HIGH MOUNTAIN REGIONS OF THE ALTAI

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We have previously investigated the composition of the triterpene fraction of the unsaponifiable part of an ethereal extract of the leaves of the birch Betula pendula as a function of its geographical position [1]. In the present investigation we have solved the problem of determining the composition of the triterpene fraction of extracts from the leaves of B. pendula Roth, growing in different height zones of vegetation. The height profile for the investigation was selected along the Chuiskii road in the section from the village of Maima to the Seminskii pass. With a total length of the profile of about 120 km, the difference in heights amounts to almost 1500 m. The leaves for analysis were collected from the central part of the crown of a number (3-10) of trees in a common sample having a weight in the air-dry state of about 1 kg, from five experimental sections. The treatment of the leaves and the isolation and identification of the major and minor compounds in them were performed by procedures described previously [2]. The following compounds were isolated: betulafolienetriol (I), betulfolienetriol oxide (II), 12β,20 (S)-dihydroxy-dammar-24-en-3-one (III), 20(S), 24(R)-epoxydammarane-3α,17α,25-triol (IV), and dammar-24-ene-3α,17α,20(S)-triol (V). In addition, the presence of another four compounds was established by the TLC method in the benzene—ethanol (10:1), benzene—ethyl acetate (1:1), and chloroform—ethanol (10:1) systems in all the samples investigated: dammar-25-ene-3α,12β,20(S),24(R)-tetraol, dammar-24-ene-3α,12β,20(S),24(S)-tetraol, 12β,20(S),25-trihydroxydammar-23-en-3-one, and dammar-23-ene-3α,12β, 20(S), 25-tetraol.

The results of the determination of the qualitative and quantitative composition of the triterpenoids of the leaves of B. pendula from different heights are given in Table 1.

In the chemical composition of the leaves, in view of the clear predominance of betulafolienetriol (I) in them, the Altai birch is closest to populations from the Central Urals and Leningrad province [1]. Some indices of the chemical composition of the leaves of B. pendula change with height in a peculiar fashion. Thus, with an increase in absolute height above sea level the amount of extractive substances in the leaves gradually diminishes, although the total amount of triterpenoids does not fall but raches a maximum in the central part of the height series, i.e., the specific amount of triterpenoids in the extract increases

TABLE 1

Time and place of gathering the leaves (height zone of vegetation, height above sea level, m), 1986	Ethereal extract	Unsaponifiable part of ether extract	Compound	Total amount of triterpenoids
	% on the weight of the air-dry leaves			
July 4, environs of the village of Maima (deciduous forest zone with the participation of light coniferous species, 400)	9,50	1,63	I (0,088) II (tr.) III (tr.)	0,09
July 5, environs of the village of Cherga (deciduous forest zone with the participation of light coniferous species, 750)	8,58	1,52	I (0,079) II (tr.) III (tr.)	0,08
July 5, environs of the village of Shebalino (larch forest zone with the participation of deciduous species, 1100)	7,67	1,65	I (0,114) II (0,062) IV (tr.)	0,176
July 9, environs of the village of Topuchaya (larch-cedar forest zone, 1400)	6,47	0,87	I (,0.088) II (tr.) III (0,051) V (tr.)	0,139
July 7, Seminskii pass (larch-cedar forest zone, 1850).	5,81	0,71	I (0.047) II (0,013) III (0,026) V (tr.)	0,086

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with height. As canm be seen from Table 1, appreciable differences are observed in the qualitative and quantitative composition of the triterpenoids in the leaves of B. pendula with height only on passing from one height zone of vegetation to another.

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STEROID COMPOUNDS OF MARINE SPONGES.

IX. STEROL COMPOSITION OF THREE SPECIES OF FAR EASTERN SPONGES

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Continuing a study of steroidal sponges [1], we have investigated the sterols of the sponges Halichondria panicea (1 and 2, different samples), Hymeniacidon assimiles and Suberites japonicus gathered in July-August, 1986, during the second voyage of the Scientific Research ship Akademic Operin. The H. panicea (1) was collected in the sea of Okhotsk on the Kashevarova bank from a depth of 147 m by beam trawl, H. panicea (2) in Cratee Bay, Island of Ushishir (Kurile Islands) from a depth of 10-15 m, and H. assimiles and S. japonicus were collected by sigsbee trawl on the oceanic side of the island of Urup (Kurile Islands), from depths of 125 and 64 m, respectively.

Fractions of free sterols were isolated as described in [2]. Then part of the free sterols was acetylated with acetic anhydride in pyridine (1:1). The resulting acetates of the sterols from H. panicea (1), H. assimiles, and S. japonicus were separated into fractions by preparative TLC (hexane–benzene (4:1)) on silica gel impregnated with silver nitrate.

The combined free sterols and the acetate fractions obtained from the three species of sponges were analyzed in a similar manner to that described previously [2].

The steroidal components were identified from their mass spectra with consideration of their chromatographic behavior in capillary GLC. In total, 19 components were identified in H. panicea (1), nine in H. panicea (2), 14 in H. assimiles, and 12 in S. japonicus. The results of the analyses are given in Table 1.

As can be seen from Table 1, 27 known steroids were identified in the sterol fractions of the sponges studied. The total sterol fractions consisted of C_{26}–C_{30} steroid alcohols and were characterized by high levels of the C_{27} compounds. Great interest is presented by the two isomeric C_{27}-stanols detected in fractions from the sponge S. japonicus. We identified one of them by the methods of GLC, GLC-MS, and ^1H NMR as 5α-cholestanol (5). Its isomer (6) has a large RRT and does not coincide in chromatographic mobility with the sterols known previously. It is possible that this compound possesses a less branched side chain and is 27-methyl-26-nor-5α-cholestanol. No such side chain has hiterto been detected in natural sterols, although an analogous C_{26}-sterol has been found among the minor steroids of the sponge Axiella cannabina [3].

We must also mention the presence in the fractions studied of new isomers of $C_{26}\Delta^{7,22}$ (4) and $C_{27}\Delta^{7}$ (7) sterols not coinciding in their RRTs with known natural steroids.

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