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A MONOTERPENE GLYCOSIDE OF CRIMEAN SPECIES OF *Paeonia*

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Two species of the genus *Paeonia* L. (fam. Paeoniaceae Rudolphi) — *Paeonia tenuifolia* L. and *Paeonia triternata* Pall. ex DC — grow in the Crimea. The roots of *P. tenuifolia* are widely used in folk and officinal medicine for diseases of the heart, pulmonary tuberculosis, anemia, fevers, and poisonings. Bactericidal, protistocidal, and phytoncidal actions have been reported. The rare species, *P. triternata*, has no practical use. Phenolic compounds and a fatty oil have been isolated from these species previously [1].

Using TLC, we have investigated extracts from the seeds, flower petals, calyces, leaves smoothly passing into the stem, and the cortex and pith of the roots and tubers. With the exception of the petals, in all the extracts we detected lipids, phenolic compounds, and, conjecturally, a glycoside of terpene nature on the basis of the specific violet coloration of the spot when a chromatogram was treated with tungstophosphoric acid. The cortex of the roots and tubers and the seeds were the richest in this substance. For the preparative isolation of the glycoside we used the hypogeal part of *P. tenuifolia* gathered in August, 1997, in the environs of Simferopol'. In order to denature enzymes, the raw material was subjected to a 15-minute treatment with boiling water, and it was then comminuted and dried. The powder so obtained (575 g) was extracted with water-saturated butanol twice (3 liters each time). After evaporation at 60°C, 71 g of residue was obtained. This was dissolved in aqueous butanol (500 ml) and, to eliminate phenolic compounds, this solution was washed three times with cold 5% ammonia (300 ml) and then with water to neutrality. The butanol layer was evaporated to dryness, the viscous mixture obtained (8.7 g) was dissolved in 80% isopropanol, and the solution was washed three times with heptane.

The total material from the alcohol layer (6.3 g) was subjected to gradient elution on silica gel (40—100 μm) in the ethyl acetate → ethyl acetate—water-saturated butanol (100:30) system. This gave 4.6 g of a fraction containing the desired glycoside. This was then chromatographed with gradient elution in the chloroform—water-saturated isopropanol (100:15 → 100:20) system and yielded 3.9 g of the individual glycoside. Final purification was achieved on alumina (20—40 μm) with elution by the isopropanol—water (100:20) system. This gave 3.762 g (0.65% on the dry weight) of a white hygroscopic substance.

After acid hydrolysis (5% H_2SO_4, 100°C, 2 h), glucose was identified by TLC as a component of the glycoside. On alkaline hydrolysis (15% KOH, 100°C, 1 h), a benzoic acid residue was split off, as was shown by TLC. The glycoside did not undergo methylation with diazomethane in methanolic ether solution, which showed the absence of a free carboxylic or phenolic group.

Japanese authors [3, 4] have isolated from *P. lactiflora* the monoterpene glycoside paeoniflorin and derivatives of it the structures of which were established on the basis of chemical transformations. We assumed that the glycoside that we had isolated could be one of these compounds, and, as a result of a detailed analysis and assignments made in the PMR and ^{13}C NMR spectra (taking into account the magnitudes of the chemical shifts, the SSCCs, and APT editing) we found that the glycoside that we had isolated was identical with paeoniflorin (**1**):

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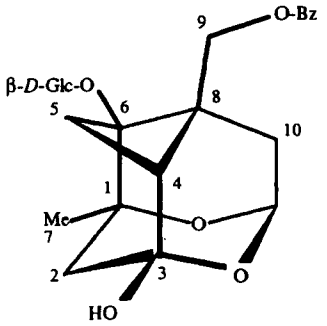

The aglycon has a pinane skeleton, and we propose to number the carbon atoms accordingly.

IR spectrum of (1) (KBr, ν, cm^{-1}): 3400 (OH), 2920 (aliphat), 1710 (C=O), 1450, 1275, 1175 (Bz), 1170 (C-O), 710 (Bz).

PMR of (1) (300 MHz, δ, ppm, 0-TMS, C_5D_5N): 8.10 (2H, d, $J_{2'',3''}$=8.0, H-2", H-6"); 7.47 (1H, t, $J_{3'',4''}$=7.0, H-4"); 7.31 (2H, t, H-3", H-5"); 5.91 (1H, s, H-10); 5.20 (1H, d, $J_{9a,9b}$=13.0, H-9a); 5.12 (1H, d, $J_{1',2'}$=8.0, H-1'); 5.09 (1H, d, H-9b); 4.32-3.81 (6H, m, H-2', H-3', H-4', H-5', H-6a', H-b'); 3.06 (1H, d, $J_{4,5a}$=7.0, H-4); 2.86 (1H, dd, $J_{5a,5b}$=11.0, H-5a); 2.50 (1H, d, $J_{2a,2b}$=12.5, H-2a); 2.32 (1H, d, H-5b); 2.29 (1H, d, H-2b); 1.65 (3H, s, H-7).

^{13}C NMR of (1) (75 MHz, δ, ppm, 0-TMS, C_5D_5N): 165.3 (C-7"); 131.9 (C-4"); 129.1 (C-1"); 128.5 (C-2", C-6"); 127.4 (C-3", C-5"); 104.5 (C-3); 100.3 (C-1'); 99.0 (C-10); 87.5 (C-1); 84.7 (C-9); 76.9 (C-3'); 76.8 (C-5'); 73.4 (C-2'); 70.3 (C-4'); 70.2 (C-6); 63.2 (C-2); 61.4 (C-6'); 60.1(C-8); 43.3 (C-5); 42.4 (C-4); 18.4 (C-7).

Compound (1) was also found, at the same quantitative level, in *Paeonia triternata*.

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