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ANTHRAQUINONES OF *Bergenia hissarica*

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Some species of plants of the genus *Bergenia* Moench are used in medical practice as astringent, hemostatic, and antiphlogistic agents in diseases of the gastro-intestinal tract and in obstetric-gynecological practice. They are rich sources of phenolic compounds [1].

In the present communication we give the results of a study of anthraquinones from the roots and rhizomes of *Bergenia hissarica* Boriss. (family Saxifragaceae) gathered in September, 1988 in the flood plains of the river Tupolang, Suchandar' province, Republic of Uzbekistan [2]. There is no information in the literature on any phytochemical investigation of this plant.

The comminuted air-dry roots (0.6 kg) were extracted at room temperature with chloroform 4 times, and then the raw material was dried and was exhaustively extracted with ethanol. This gave 75.0 g of alcoholic extract. Part of it (50.0 g) was chromatographed on a column of silica gel in a chloroform—methanol gradient system (97:3-95:5). This led to the isolation of five anthraquinone derivatives.

Aloe-emodin (I) — orange crystals with the composition $C_{15}H_{10}O_5$ (M^+ 270), mp 222-223°C, $\lambda_{max}^{ethanol}$ 225, 255, 289, 427 nm. The NMR spectrum showed the signals of five aromatic protons (7.15 ppm, dd, 2.0 and 8.5 Hz, H-7; 7.40 ppm, dd, $J_1{=}J_2$ = 8.5 Hz, H-6; 7.48 ppm, br.s, H-2; 7.70 ppm, dd, 2.0 and 8.5 Hz, H-5; 7.90 ppm, br.s, H-4), Ar — $\underline{CH_2}OH$ groups (4.80 ppm, s) and of chelate hydroxy groups (12.05 ppm, br.s). Consequently, substance (I) was 1,8-dihydroxy-3-hydroxymethylanthraquinone [3, 4].

Physcion (II) — orange crystals with the composition $C_{16}H_{12}O_5$ (M^+ 284), mp 200-202°, λ_{max} 225, 256, 288, 437 nm. PMR spectrum (Py-d_5): 2.09 (s, Ar$-CH_3$), 3.61 (s, OCH_3), 6.68 (d, 2 Hz, H-2), 7.03 (br.s, H-7), 7.28 (d, 2 Hz, H-4), 7.49 (br.s, H-5), 12.03 ppm (chelate OH groups). By a study of spectral characteristics and physicochemical properties, substance (II) was identified as 1,8-dihydroxy-6-methoxy-3-methylanthraquinone [5].

Aloe-emodin 8-O-β-glucoside (III) — orange-yellow crystals with the composition $C_{21}H_{20}O_{10}$ with mp 224-225°, λ_{max} 224, 256, 285, 410 nm. The acid hydrolysis of glycoside (III) yielded aloe-emodin and glucose. The acylation of glycoside (III) with acetic anhydride in pyridine gve a pentaacetyl derivative, with mp 85-86°C (M^+ 684). The ^{13}C NMR spectrum of the glycoside under consideration in DMSO-d_6 (δ, ppm) contained signals at 161.8 (C-1), 121.0 (C-2), 152.4 (C-3), 116.2 (C-4), 120.9 (C-5), 136.4 (C-6), 122.7 (C-7), 158.4 (C-8), 187.8 (C-9), 182.2 (C-10), 134.9 (C-11), 120.9 (C-12), 115.6 (C-13), 132.4 (C-14), 100.8 (C-1'), 73.5 (C-2'), 77.4 (C-3'), 69.7 (C-4'), 76.6 (C-5'), 60.8 (C-6'), 62.2 ppm ($-CH_2OH$). A comparison of the chemical shifts of the carbon atoms with literature information showed the glycosylation of the hydroxy group in position 8 of aloe-emodin [3, 6].

Chrysophanein (IV) — yellow crystals with the composition $C_{21}H_{20}O_9$, mp 234-236°, λ_{max}, 224, 260, 285, 411 nm. Acid hydrolysis of glycoside (IV) formed chrysophanol (M^+ 254, ppm 194-195°, λ_{max} 224, 289, 433 nm) and glucose. By a comparison of the physicochemical properties and spectral characteristics with the literature, compound (IV) was identified as 1-β-D-glucopyranosyloxy-8-hydroxy-3-methylanthraquinone [6, 7].

Emodin 1-O-β-D-glucopyranoside (V) — orange-yellow crystals with the composition $C_{21}H_{20}O_{10}$, mp 213-214°, λ_{max} 220, 252, 272*, 286, 425 nm [8, 9]. A comparison of PMR spectra showed that on passing from emodin to glycoside (V) the signals of H-2 and H-4 protons underwent paramagnetic shifts of 0.45 and 0.20 ppm, respectively. Consequently, the glucose residue in compound (V) was attached to the hydroxyl in the C-1 position [9].

The signal of the anomeric proton in the PMR spectrum of glycoside (V) appeared at 5.54 ppm in the form of a doublet with a SSCC of 7.0 Hz. Thus, substance (V) was 1-O-β-D-glucopyranosyloxy-6,8-dihydroxy-3-methylanthraquinone [8, 9].

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REFERENCES

1. Plant Resources of the USSR [in Russian], Nauka, Leningrad (1987), p. 8.
2. The Flora of Uzbekistan [in Russian], Izd. AN UzSSR, Vol. 3 (1955), p. 242.
3. L. Hörhammer, L. Farkas, H. Wagner, and E. Miller, Chem. Ber., **97**, 1662 (1964).
4. J. M. Conner, A. I. Gray, and P. G. Waterman, J. Nat. Prod., **53**, 1362 (1990),
5. O. A. Denisova, D. A. Fesenko, V. A. Glyzin, A. V. Patulin, and V. S. Novruzov, Khim. Prir. Soedin., 799 (1978).
6. I. Kubo, Y. Murai, I. Soediro, et al., Phytochemistry, **31**, 1063 (1992).
7. L. Hörhammer, H. Waner, and E. Miller, Chem. Ber., **98**, 2859 (1965).
8. H. Okabe, K. Matsuo, and I. Nishioka, Chem. Pharm. Bull., **21**, 1254 (1973).
9. H. J. Banks, D. W. Cameron, and M. J. Crossley, Aust. J. Chem., **29**, 2231 (1976).