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FLAVONOIDS AND COUMARINS OF *Haplophyllum leptomerum* AND *H. dubium*

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In continuation of a study of flavonoids and coumarins from plants of the *Haplophyllum* A. Juss. species, we studied the epigeal part of *H. leptomerum* Lincz. et Vved. [1]. Several alkaloids were observed in the epigeal part of *H. leptomerum* [2].

Ground and air-dried raw material (1.0 kg) that was collected during budding (May 1989, Babatag, Republic of Tadzhikistan) was extracted with ethanol. The extract was evaporated in vacuum. The condensed solid was diluted with water and successively treated with petroleum ether, $CHCl_3$, and ethylacetate. The solvents were removed to give petroleum-ether (20.0 g), $CHCl_3$ (12.0 g), and ethylacetate (15.0 g) fractions.

The ethylacetate fraction was chromatographed over a silica-gel column using a $CHCl_3$—CH_3OH gradient (97:3-85:15) to isolate **1** and **2**. These were identified using PMR, UV, and mass spectra and chemical transformations compared with authentic samples.

Isorhamnetin (1) (3,5,7,4′-tetrahydroxy-3′-methoxyflavone), $C_{16}H_{12}O_7$, $[M]^+$ 316, mp 305-306°C. UV spectrum (EtOH, λ_{max}, nm): 256, 265, 371 [3, 4].

Haploside D (2) [haplogenin-7-O-β-D-glucopyranosyl-(6″-O-acetyl)-2←1-α-L-rhamnopyranoside], $C_{30}H_{32}O_{18}$, mp 225-227°C. UV spectrum (EtOH, λ_{max}, nm): 261, 275sh, 347sh, 388.

The IR spectrum contains absorption bands for hydroxyls (3560-3130 cm^{-1}), methoxyl (2930 cm^{-1}), ester carbonyl (1733 cm^{-1}), γ-pyrone carbonyl (1657 cm^{-1}), aromatic C=C (1618, 1576, 1520 cm^{-1}), and glucoside C–O (1095, 1050, 1026 cm^{-1}).

The PMR spectrum (100 MHz, C_5D_5N, δ, ppm, J/Hz) contains signals for protons at 1.63 (3H, d, J = 6.0, CH_3), 1.91 (3H, s, $OCOCH_3$), 3.66 (3H, s, OCH_3), 3.72-4.75 (sugar protons), 5.55 (1H, d, J = 6.5, H-1″), 6.96 (1H, s, H-6), 7.05 (1H, d, J = 9.0, H-5′), 8.10 (1H, dd, J = 2.5 and J = 9.0, H-6′), 8.16 (1H, br.s, H-2′), 12.42 (1H, br.s, 5-OH).

Acid hydrolysis of **2** produced haplogenin (3,5,7,8,4′-pentahydroxy-3′-methoxyflavone), D-glucose, and L-rhamnose.

Acetylation of **2** with acetic anhydride in pyridine gave the decaacetyl derivative with mp 128-130°C. The mass spectrum contains strong peaks for fragment ions from the terminal rhamnose with *m*/*z* 273 (100%), 213, and 153 and acylated biose with *m*/*z* 561 [5].

Flavonoids **1** and **2** from *H. leptomerum* are isolated for the first time.

The dried and ground epigeal part (1.2 kg) of *H. dubium* Korov. that was collected during budding (May 1989, Babatag, Republic of Tadzhikistan) [1, 6] was extracted with ethanol. The ethanol was removed in vacuum. The solid was diluted with water and treated successively with petroleum ether, $CHCl_3$, and ethylacetate. The solvents were removed to give petroleum-ether (21.0 g), $CHCl_3$ (14.0 g), and ethylacetate (17.4 g) fractions.

The ethylacetate fraction was chromatographed over a silica-gel column using a $CHCl_3$—CH_3OH gradient (97:3-85:15).

We isolated **3-5** and haploside D.

Scopoletin (3) (7-hydroxy-6-methoxycoumarin), $C_{10}H_8O_4$, $[M]^+$ 192, mp 203-204°C. UV spectrum (EtOH, λ_{max}, nm): 230, 255, 300, 355 [7].

Scopolin (4) (scopoletin-7-O-β-D-glucopyranoside), $C_{16}H_{18}O_9$, mp 207-209°C. UV spectrum (EtOH, λ_{max}, nm): 229, 280, 338. PMR spectrum (100 MHz, C_5D_5N, δ, ppm, J/Hz): 3.62 (3H, s, OCH_3), 4.00-4.42 (m, sugar protons), 5.65 (1H, m, H-1′), 6.20 (1H, d, J = 10.0, H-3), 6.92 (1H, s, H-8), 7.37 (1H, s, H-5), 7.59 (1H, d, J = 10.0, H-4). Acid hydrolysis produced

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scopoletin and D-glucose [7].

Haploside B (5) (haplogenin-7-O-β-D-glucoside), $C_{22}H_{22}O_{13}$, mp 212-213°C. UV spectrum (EtOH, λ_{max}, nm): 261, 280 sh, 392. PMR spectrum (100 MHz, C_5D_5N, δ, ppm, J/Hz): 3.72 (3H, s, OCH_3), 3.79-4.30 (glucose protons), 5.62 (1H, d, J = 7.5, H-1″), 6.95 (1H, s, H-6), 7.09 (1H, d, J = 8.5, H-5′), 8.22 (1H, dd, J = 2.5 and J = 8.5, H-6′), 8.23 (1H, br.s, H-2′).

Acid hydrolysis produced haplogenin and D-glucose [8].

Compounds **2-5** are isolated from *H. dubium* for the first time.

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