Chemistry of Natural Compounds, Vol. 37, No. 3, 2001

FLAVONOIDS OF *Haplophyllum foliosum* AND *H. pedicellatum*

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UDC 547.972

In continuation of the study of flavonoids from plants of the *Haplophyllum* A. Juss. genus, we studied the aerial part of *H. foliosum* Vved. [1, 2]. Previously several alkaloids were isolated from its subterranean part [2, 3].

Ground air-dried raw material (1.4 kg) collected during flowering (June 1981) in Kugart (Fergana range, Dzhalalabad District, Republic of Kyrgyzstan) was exhaustively extracted with ethanol at room temperature. The combined extracts were evaporated in vacua. The condensed residue was treated with water and then worked up with $CHCl_3$ and ethylacetate. Solvents were evaporated to yield 28.0 g ($CHCl_3$) and 20.0 g (ethylacetate) of solid.

The ethylacetate fraction was chromatographed over a silica-gel column using gradient elution by $CHCl_3$—CH_3OH (97:3-85:15). Compounds **1-3** were isolated. They were identified using UV, mass, and PMR spectra in addition to chemical transformations and comparison with authentic samples.

Isorhamnetin (1). (3,5,7,4′-tetrahydroxy-3′-methoxyflavone) $C_{16}H_{12}O_7$ (M^+ 316), mp 305-307°C, UV spectrum (EtOH, λ_{max}, nm): 256, 266, 372.

PMR spectrum (100 MHz, C_5D_5N, δ, ppm, J/Hz): 3.87 (3H, s, OCH_3), 6.09 (1H, d, J = 2.5, H-6), 6.44 (1H, d, J = 2.5, H-8), 6.85 (1H, d, J = 8.5, H-5′), 7.55 (1H, d, J = 2.5, H-2′), 7.62 (1H, dd, J = 2.5, J = 8.5, H-6′) [4, 5].

Limocitrin-7-O-*β*-D-(6″-O-acetyl)glucoside (2). $C_{25}H_{26}O_{14}$, mp 231-233°C, UV spectrum (EtOH, λ_{max}, nm): 260, 276 sh, 338 sh, 379. IR spectrum (cm^{-1}): 3360-3600 (OH), 2936 (OCH_3), 1734 (ester carbonyl), 1654 (γ-pyrone carbonyl), 1606, 1564, and 1523 (aromatic C=C), 1104-1005 (glycoside C–O).

PMR spectrum (100 MHz, C_5D_5N, δ, ppm, J/Hz): 2.05 (3H, s, $OCOCH_3$), 3.84 (3H, s, OCH_3), 4.01 (3H, s, OCH_3), 3.90-4.30 (sugar protons), 5.66 (1H, d, J = 7.5, H-1″), 7.06 (1H, s, H-6), 7.25 (1H, d, J = 8.0, H-5′), 8.20 (1H, br.s, H-2′), 8.25 (1H, dd, J = 2.0, J = 8.0, H-6′).

Acid hydrolysis of **2** afforded limocitrin (3,5,7,4′-tetrahydroxy-8,3′-dimethoxyflavone) and D-glucose.

Acetylation of **2** by acetic anhydride in pyridine gave a heptaacetyl derivative with mp 113-115°C, the mass spectrum of which gave a molecular ion with *m/z* 760 [M - 42] and strong peaks for fragments of tetraacetylhexoses with *m/z* 331, 271, 229, and 169 [6].

Haploside C (3) (7-O-[*α*-L-rhamnopyranosyl(1→2)-*β*-D-(6″-O-acetyl)-glucopyranosyl)]-3,5,4′-trihydroxy-8,3′-dimethoxyflavone): $C_{31}H_{36}O_{18}$, mp 142-144°C, UV spectrum (EtOH, λ_{max}, nm): 260, 275 sh, 384.

PMR spectrum (100 MHz, C_5D_5N, δ, ppm, J/Hz): 1.75 (3H, d, J = 6.0, CH_3), 2.03 (3H, s, $OCOCH_3$), 3.76-4.95 (sugar protons), 3.88 (3H, s, OCH_3), 4.13 (3H, s, OCH_3), 5.63 (1H, d, J = 7.0, H-1″), 6.96 (1H, s, H-6), 7.30 (1H, d, J = 8.5, H-5′), 8.22 (1H, br.s, H-2′), 8.26 (1H, dd, J = 2.0, J = 8.5, H-6′).

Acid hydrolysis of **3** gave limocitrin, D-glucose, and L-rhamnose.

Acetylation of **3** by acetic anhydride in pyridine gave a nonoacetyl derivative with mp 191-194°C, the mass spectrum of which gave a molecular ion with *m/z* 990 $[M - 42]^+$ and strong peaks for fragments of acylated biose with *m/z* 561 and terminal rhamnose with *m/z* 273, 213, and 153 [7].

Flavonoids **1-3** from *H. foliosum* were isolated for the first time.

The dried and ground subterranean part (0.9 kg) of *H. pedicellatum* Bunge collected at the start of flowering (June 10, 1980) near Bairamali, Republic of Turkmenistan [1, 2], was exhaustively extracted with ethanol (95%). The alcohol was evaporated in vacua. The aqueous residue was purified of lipophilic substances by treatment with $CHCl_3$. Flavonoids were extracted with ethylacetate to yield 35.0 g of product that was separated on a silica-gel column with gradient elution by $CHCl_3$—CH_3OH (97:3-85:15). Compounds **4** and **5** and haploside C were isolated.

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Haploside A (4) [haplogenin-7-O-β-D-(6″-O-acetyl)-glucoside], $C_{24}H_{24}O_{14}$, mp 193-195°C, UV spectrum (EtOH, λ_{max}, nm): 262, 280 sh, 343, 387. IR spectrum (cm^{-1}): 3210-3540 (OH), 1725 (ester carbonyl), 1653 (γ-pyrone carbonyl), 1615, 1608, 1565, and 1514 (aromatic C=C), and 1094, 1047, 1025, and 1000 (glycoside C–O).

PMR spectrum (100 MHz, C_5D_5N, δ, ppm, J/Hz): 1.94 (3H, s, $OCOCH_3$), 3.70 (3H, s, OCH_3), 3.72-4.93 (glucose), 4.42-4.88 (m, J_{gem} = 12.0, 2H-6″), 5.53 (1H, d, J = 7.0, H-1″), 7.08 (1H, s, H-6), 7.17 (1H, d, J = 8.0, H-5′), 8.24 (1H, dd, J = 2.5, J = 8.0, H-6′), 8.25 (1H, br.s, H-2′).

Acid hydrolysis of **4** gave haplogenin (3,5,7,8,4′-pentahydroxy-3′-methoxyflavone) and D-glucose; alkaline hydrolysis, haploside B [8].

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, J = 8.5, H-6′), 8.23 (1H, br.s, H-2′).

Acid hydrolysis of **5** gave haplogenin and D-glucose [9].

Haplosides A, B, and C from *H. pedicellatum* were isolated for the first time.

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