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# FLAVONE GLUCOSIDES FROM THE AERIAL PART OF *Scutellaria comosa*

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The phytochemistry of available species of *Scutellaria* is being systematically investigated because of the wide use of *S. baicalensis* in folk and official medicine and the limited raw-material resources. Flavonoids from plants of the genus *Scutellaria* L. were studied by us to discover new biologically active compounds and their available resources. The aerial part and roots of *S. comosa* Juz. (skullcap) contained 18 flavonoids, mainly flavone and flavanone derivatives [1–3]. In continuation of this research, flavonoids from the aerial part of *S. comosa* collected during full flowering (May 1, 2015) in the foothills town of Gov, Chustski District, Namangan Region, Republic of Uzbekistan, were studied.

Milled air-dried plant raw material was extracted (6×) at 65–70°C with EtOH (93%). The combined extracts were evacuated *in vacuo*, diluted with $H_2O$, and washed with $CHCl_3$ to remove lipophilic compounds. The precipitate that formed upon cooling the purified extract was rinsed with $H_2O$ and dried. Part (10 mL) of the mother liquor was filtered off, evaporated *in vacuo*, and analyzed by reversed-phase HPLC on a Shimadzu LC10VP using a diode-array detector at 254 and 360 nm. Flavonoids were determined using a linear gradient of AcOH–MeCN over a C18 column (4.6 × 250 mm, 5 μm). The flavonoids chrysin, wogonin, norwogonin, oroxylin, and scutellarein were detected using authentic standards [4–6].

The precipitate was chromatographed over a column of Sephadex LH-20 using EtOH (96%). Separate eluates afforded flavonoids **1** (53 mg), **2** (97 mg), **3** (186 mg), and **4** (201 mg).

Spots of flavonoids **2**–**4** on Silufol plates turned brown during storage. Their EtOH solutions gave a positive gossypetin reaction with *p*-benzoquinone, indicating the presence of C-5 and C-8 hydroxyls in their molecules.

**Flavonoid 1**, $C_{21}H_{20}O_{11}$, mp 193–195°C. UV spectrum (EtOH, $\lambda_{max}$, nm): 288, 337; +NaOAc, 290, 340. PMR spectra and production of scutellarein and D-glucose by acid hydrolysis of **1** identified it as scutellarein 7-*O*-*β*-D-glucopyranoside [5–7].

**Flavonoid 2**, $C_{21}H_{20}O_{10}$, mp >275°C (dec.). UV spectrum (MeOH, $\lambda_{max}$, nm): 279, 350 (sh). Enzymatic hydrolysis of **2** by *β*-glycosidase produced norwogonin and D-glucose. PMR spectra and direct comparison with an authentic sample identified **2** as norwogonin 7-*O*-*β*-D-glucopyranoside [5–7].

**Flavonoid 3**, $C_{21}H_{20}O_{12}$, mp 263–265°C, $[\alpha]_D$ –63.4° (*c* 0.2, $Me_2CO$). UV spectrum (MeOH, $\lambda_{max}$, nm): 257 (sh), 278, 306, 337; +NaOAc 258, 277, 337; +NaOAc+$H_3BO_3$ 267, 380; +NaOMe 267, 344, 392. IR spectrum (KBr, $\nu_{max}$, $cm^{-1}$): 3389, 3361, 3285 (OH), 1656 (*γ*-pyrone C=O), 1618 (arom. C=C), 1097, 1082, 1049 (glycoside C–O). $^1$H NMR spectrum (400 MHz, DMSO-$d_6$, δ, ppm, J/Hz): 3.09–3.47 (4H, m, H-2″–5″), 3.67 (2H, m, 2H-6″), 4.64 (1H, br.s, 6″-OH), 4.88 (1H, d, J = 7.6, H-1″), 5.09 (1H, br.s, 2″-OH), 6.68 (1H, s, H-6), 6.58 (1H, s, H-3), 6,85 (1H, d, J = 8.4, H-5′), 7.42 (1H, dd, J = 2.3, 8.4, H-6′), 7.44 (1H, d, J = 2.3, H-2′), 12.34 (1H, s, 5-OH).

Enzymatic hydrolysis of **3** by *β*-glycosidase produced hypolaetin (5,7,8,3′,4′-pentahydroxyflavone), $C_{15}H_{10}O_7$, mp 286–290°C. UV spectrum ($\lambda_{max}$, nm): 256, 284, 344 [6, 8] and D-glucose. $^{13}$C NMR spectrum (100 MHz, DMSO-$d_6$, δ, ppm): 182.32 (C-4), 164.26 (C-2), 152.35 (C-5), 151.13 (C-7), 149.88 (C-4′), 145.72 (C-9), 144.32 (C-3′), 126.95 (C-8), 121.62 (C-1′), 119.25 (C-6′), 116.04 (C-5′), 113.55 (C-2′), 105.19 (C-10), 102.69 (C-3), 101.30 (C-1″), 98.60 (C-6), 77.31 (C-5″), 75.70 (C-3″), 73.23 (C-2″), 69.70 (C-4″), 60.67 (C-6″). A comparison of $^{13}$C NMR spectra of hypolaetin glucosides [9, 10] and **3** found that the last was hypolaetin 7-*O*-β-D-glucopyranoside. This flavonoid was isolated earlier from the plants

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*Juniperus macropoda* and *Caryopteris mongolica* [8]. The $^{13}C$ NMR spectrum of **3** is published for the first time. Hypolaetin glycosides possessed anti-inflammatory, antioxidant, and antiulcer properties [11].

**Flavonoid 4**, $C_{21}H_{20}O_{11}$, mp > 300°C (dec.), $[\alpha]_D$ –19.2° (*c* 0.10, 60% EtOH). UV spectrum (MeOH, $\lambda_{max}$, nm): 279, 309, 329 (sh), 363 (sh). Enzymatic hydrolysis of **4** by β-glycosidase produced isoscutellarein (5,7,8,4′-tetrahydroxyflavone) and D-glucose. These results and a comparison with an authentic sample identified **4** as isoscutellarein 7-*O*-β-D-glucopyranoside [8, 12]. PMR and $^{13}C$ NMR spectra of **4** agreed with those published before [12].

Flavonoids **1**, **2**, and **4** were isolated for the first time from *S. comosa*. Flavonoid **3** was not previously observed in plants of the genus *Scutellaria*.

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