

BRIEF COMMUNICATIONS

FLAVONOIDS OF THE EPIGEAL

PART OF *Scutellaria comosa*

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Continuing an investigation of the flavonoids of plants of the *Scutellaria* L. genus [1], we have studied the phenolic components of the epigeal part of *S. comosa* Juz.

Norwogonin, baicalein, baicalin, wogonoside, chrysin 7-O-glucuronide, and 2'-hydroxychrysin-7-O-glucuronide [2], and also chrysin, apigenin, wogonin, (\pm)-2',5-dihydroxy-6,6',7-trimethoxyflavone, and (-)-2',5-dihydroxy-6,6',7,8-tetramethoxyflavone [1] have been isolated from this plant previously.

The comminuted air-dry raw material (2.0 kg) gathered in the flowering period (May 9, 1995) in the environs of Turakurgan (Namanganskaya oblast', Republic of Uzbekistan) was exhaustively extracted with ethanol at room temperature. The combined extract was evaporated in vacuum, and the concentrated residue was diluted with water and treated successively with chloroform, ethyl acetate, and butanol. After the solvents had been distilled off, 22 g of ethyl acetate fraction and 62 g of butanol fraction were obtained.

The ethyl acetate fraction was chromatographed on a column of silica gel in a chloroform—methanol gradient system. Apigenin, norwogonin, and compounds (1—3 and 6) were obtained.

Chromatography of the butanol fraction on a silica gel column in systems of chloroform and methanol in various ratios led to the isolation of flavonoids (4—6). The substances isolated were identified with the aid of UV, PMR, and mass spectra and also by chemical transformations and by direct comparison with authentic specimens of some of the substances.

Oroxylin A (1) (5,7-dihydroxy-6-methoxyflavone) — $C_{16}H_{12}O_5$ (M^+ 284), mp 218—219°C, λ_{max} 249, 272, 321 nm. The PMR spectrum (Py- d_5) revealed signals of protons at 3.85 (3H, s, OCH₃), 6.78 (s, H-3), 6.85 (s, H-8), 7.36 (3H, m, H-3',4',5'), 7.83 (2H, m, H-2',6') and 13.56 ppm (br. s, 5-OH) [3, 4].

Hispidulin (2) (4',5,7-trihydroxy-6-methoxyflavone) — $C_{16}H_{12}O_6$, mp 288—290°C (ethanol), λ_{max} 217, 277, 339 nm. The mass spectrum showed peaks of ions with m/z 300 (M^+), 282 ($M - H_2O$), 271, 254, 167, 153, 139, 128, 119, and others [5].

Luteolin (3) 3',4',5,7-tetrahydroxyflavone — $C_{15}H_{10}O_6$ (M^+ 286), mp 328—331°C (decomp.) λ_{max} 260, 274, 356 nm.

In the PMR spectrum (Py- d_5) proton signals appeared at 6.58 (1H, d, 2.0 Hz, H-6), 6.67 (1H, d, 2.0 Hz, H-8), 6.79 (s, H-3), 7.08 (1H, d, 8.0 Hz, H-5'), 7.51 (br.s, H-2'), and 7.56 ppm (1H, dd, 2.0 and 8.0 Hz, H-6'). Acetylation of the luteolin with acetic anhydride in the presence of pyridine led to the tetraacetate with mp 225—226°C, M^+ 454 [6, 7].

Scutellarein (4) (4',5,6,7-tetrahydroxyflavone) — $C_{15}H_{10}O_6$, mp >340°C, λ_{max} 286, 339 nm. The mass spectrum showed the peaks of ions with m/z 286 (M^+), 254, 226, 185, 169, 168, 152, 135, 101, 91, 83, 73, 69 [8].

Quercetin (5) (3,3',4',5,7-pentahydroxyflavone) — $C_{15}H_{10}O_7$ (M^+ 302), mp 313—315°C, λ_{max} 257, 268, 371 nm [7, 9].

Scutellarin (6) (scutellarein 7-O- β -D-glucuronide) — $C_{21}H_{18}O_{12}$, mp 218—220°C, λ_{max} 289, 329 nm. The IR spectrum contained the absorption bands of hydroxy groups (3450 cm^{-1}), of the carbonyl of glucuronic acid (1734 cm^{-1}), of the

carbonyl of a γ -pyrone (1654 cm^{-1}), of aromatic C=C bonds ($1608, 1542, 1508\text{ cm}^{-1}$) and of the C—O vibrations of glycosides (1099 and 1076 cm^{-1}).

In the PMR spectrum (Py- d_5) there were signals of protons at 3.75—4.45 (3H, m, H-2",3", and 4"), 4.62 (1H, d, 8.5 Hz, H-5"), 5.65 (1H, d, 7.0 Hz, H-1"), 6.88 (s, H-3), 7.09 (2H, d, 9.0 Hz, H-3',5'), 7.23 (s, H-8), 8.31 (2H, d, 9 Hz, H-2',6'), and 12.98 ppm (br.s, 5-OH).

Acid hydrolysis gave scutellarein (4) and *D*-glucuronic acid.

In the PMR spectrum of glycoside (6), the signal of the anomeric proton of *D*-glucuronic acid appeared at 5.65 ppm in the form of a doublet with the SSCC 7.0 Hz, which showed a β -glycosidic bond of the carbohydrate residue with the aglycon [3, 10].

This is the first time that flavonoids (1—6) have been isolated from *S. comosa*.

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