Chemistry of Natural Compounds, Vol. 32, No. 4, 1996

FLAVONOIDS OF THE ROOTS OF *Scutellaria comosa*

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UDC 547.972

Continuing an investigation of flavonoids of plants of the genus *Scutellaria* L. [1-3], we have studied the roots of the skullcap *Scutellaria comosa* Juz. The raw material was gathered in the environs of Turakurgan, Namangan Oblast, Republic of Uzbekistan. The epigeal part of the plant is used by the local population in cases of hypertension. Norwegian, baicalein, baicalin, and wogonoside, and also the 7-O-glucuronides of chrysin and of 2′-hydroxychrysin have been found in the roots of *S. comosa* previously [4].

From various fractions of an alcoholic extract of the roots, by chromatography on a silica gel column, we have isolated — in addition to wogonoside — five aglycons (**1—5**) and two glycosides (**6, 7**). Flavonoids (**1-7**) have been identified on the basis of the results of a study of UV, PMR, and mass spectra and some chemical transformations, and also by direct comparison with authentic specimens of substances (**1-3**).

Chrysin (1) (5,7-dihydroxyflavone) — $C_{15}H_{10}O_4$ (M^+ 254), mp 290-292°C, λ_{max} 270, 311 nm [1].

Apigenin (2) (4′,5,7-trihydroxyflavone) — $C_{15}H_{10}O_5$ (M^+ 270), mp 347-348°C, λ_{max} 270, 298, 338 nm [5].

Wogonin (3) (5,7-dihydroxy-8-methoxyflavone) — $C_{16}H_{12}O_5$ (M^+ 284), mp 201-202°C, λ_{max} 247, 277, 319 nm [1].

(±)-2′,5-Dihydroxy-6,6′,7-trimethoxyflavanone (4) — $C_{18}H_{18}O_7$, mp 217-218°C. The flavanone nature of compound (4) was confirmed by its UV spectrum (λ_{max} 288, 345 nm; + $AlCl_3$: 314, 375 nm) [5], and its PMR spectrum, which contains the characteristic signal of a H-2 proton in the form of a double doublet at 6.10 ppm with SSCCs of 3.1 and 13.5 Hz and the signals of the protons at C-3 in the form of two double doublets with SSCCs of 13.5 and 17.5 Hz for the axial proton at 3.19 ppm, and of 3.1 and 17.5 Hz for the equatorial proton at 2.75 ppm. The PMR spectrum ($CDCl_3$) also showed the signals of the protons of three CH_3O- groups (3.70, 3.73, and 3.85 ppm, singlets), H-8 (6.13 ppm, s), H-3′ (6.55 ppm, br.d, 8.0 Hz), H-4′ (7.12 ppm, 8.0 and 8.5 Hz), H-5′ (6.41 ppm, br.d, 8.5 Hz) and 5-OH (11.88 ppm, br.s).

The mass spectrum of (4) contained the peaks of ions with *m/z* 346 (M^+), 328 ($M - H_2O$), 313 ($M - H_2O - CH_3$) (100%), 285, 197, 196, 181, 168, 153, and others. Consequently, flavone (4) contained three methoxy and two hydroxy groups. The peak of ion a^+ with *m/z* in the mass spectrum showed the presence of two CH_3O groups and one OH group in ring *A*. According to the PMR spectrum, the OH group in ring *A* occupied the C-5 position. The positions of one CH_3O group and one OH group at C-5′ and C-2′, respectively, followed from the chemical shifts of the signals of the protons of ring *B* [6].

(−)-2′,5-Dihydroxy-6,6′,7,8-tetramethoxyflavone (5) — $C_{19}H_{20}O_8$, mp 148-149°C. The UV spectrum of substance (5) (λ_{max} 289, 358 nm; +$AlCl_3$: 316, 372) was characteristic for 5-hydroxyflavanones [5].

The PMR spectra of flavanones (4) and (5) differed from one another by the presence in the spectrum of the latter of an additional three-proton signal of an OCH_3 group at 4.03 ppm and by the absence of the H-8 signal. Otherwise, the spectra of (4) and (5) were very close.

The mass spectrum of flavanone (5) had the peaks of ions with *m/z* 376 (M^+), 358 ($M - H_2O$), 343 ($M - H_2O - CH_3$), 315, 226 (a^+), 211, 183, 131, 119, 83, and 69 (100%). According to the PMR and mass spectra three methoxy groups and one hydroxy group were located in ring *A*, and one OCH_3 and one OH group in ring *B*. A one-proton signal at 11.82 ppm and the chemical shifts of the signals of the protons of ring *B* (6,36 ppm, br.d, 8.2 Hz, H-5′; 6.50 ppm, br.d, 7.8 Hz, H-3′; and 7.10 ppm, dd, 7.8 and 8.2 Hz, H-4′) in the PMR spectrum, showed the presence of free hydroxy groups in positions 5 and 2′ of the flavanone nucleus. Thus, flavanone (5) differs from compound (4) by an additional 8-OCH_3 group [7].

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0009-3130/96/3204-0592$15.00 ©1997 Plenum Publishing Corporation

Chrysin 7-O-(methyl glucuronide) (6) — $C_{22}H_{20}O_{10}$, mp 184-186°C, λ_{max} 270, 305 nm. The absorption band of an ester carbonyl (ν_{max} 1728 cm^{-1}) in the IR spectrum and a three-proton singlet at 3.48 ppm ($-COOCH_3$) in the PMR spectrum gave grounds for considering that substance **(6)** contained a methoxycarbonyl group. The alkaline hydrolysis of **(6)** gave chrysin 7-O-glucuronide [1].

Oroxyloside (7) (oroxylin 7-O-glucuronide) — $C_{22}H_{20}O_{11}$, mp 199-201°C, λ_{max} 280, 315 nm. The acid hydrolysis of compound (7) gave oroxylin A and *D*-glucuronic acid [1, 5, 6].

This is the first time that flavonoids **(1-7)** have been isolated from *S. comosa*.

REFERENCES

1. M. P. Yuldashev, É. Kh. Batirov, and V. M. Malikov, Khim. Prir. Soedin., 471 (1993); 822 (1994).
2. M. P. Yuldashev, É. Kh. Batirov, A. Nigmatullaev, and V. M. Malikov, Khim. Prir. Soedin., 355 (1994).
3. M. P. Yuldashev, É. Kh. Batirov, and V. M. Malikov, Khim. Prir. Soedin., 317 (1995).
4. B. Yusupova, R. Atazhanov, I. Toshmatov, Sh. Abdullaev, and V. Litvinenko, Khim. Prir. Soedin., 172 (1995).
5. T. T. Mabry, K. R. Markham, and M. B. Thomas, The Systematic Identification of Flavonoids, Springer, New York (1970)
6. T. Tomimori, Y. Miyaichi, Y. Imoto, H. Kizu, and T. Namba, Chem. Pharm. Bull., **33**, 4457 (1985).
7. I. I. Chemesova, M. Iinuma, and A. A. Budantseva, Rastit. Resur., **29**, No. 4, 75 (1993).