NEW FLAVANONES FROM *Scutellaria phyllostachya* ROOTS

G. U. Siddikov,[1] M. P. Yuldashev,[2] S. F. Aripova,[2]
A. D. Vdovin,[2] N. D. Abdullaev,[2] and E. Kh. Botirov[3]

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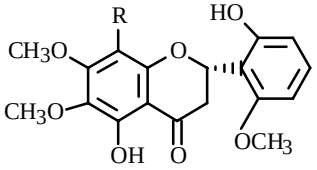
The new natural flavanones (+)-5,2′-dihydroxy-6,6′,7-trimethoxyflavanone and (+)-5,2′-dihydroxy-6,6′,7,8-tetramethoxyflavanone in addition to the known flavones chrysin, norwogonin, and wogonin were isolated from Scutellaria phyllostachya *roots. The structures of the isolated compounds were established using IR, UV and PMR spectra.*

Key words: *Scutellaria phyllostachya,* new flavanones (+)-5,2′-dihydroxy-6,6′,7-trimethoxyflavanone, (+)-5,2′-dihydroxy-6,6′,7,8-tetramethoxyflavanone, chrysin, norwogonin, wogonin.

In continuation of research on plants of the *Scutellaria* genus (Lamiaceae) growing in Central Asia, we studied flavonoids from *S. phyllostachya* Juz. roots.

We isolated previously from this plant the 7-*O*-β-D-glucuronides of wogonin, oroxylin, apigenin, and luteolin; the 7-*O*-β-D-glucopyranosides of baicalein, scutellarein, and norwogonin; and chrysin-7-*O*-β-D-methylglucuronide [1].

Herein we report results from a study of flavonoids from roots collected in March 2007 near the village Mamai of Yangikurgan Region, Namangan District, Republic of Uzbekistan. The EtOH extract of roots was dried in vacuo. The solid was diluted with water and extracted successively by shaking with hydrocarbons, $CHCl_3$, EtOAc, and *n*-BuOH. Chromatography of the $CHCl_3$ fraction over a column of silica gel using a gradient of $CHCl_3$:hydrocarbons isolated the known flavonoids chrysin (5,7-dihydroxyflavone) [2, 3], wogonin (5,7-dihydroxy-8-methoxyflavone) [3, 4], and norwogonin (5,7,8-trihydroxyflavone) [3, 5] and flavonoids **1** and **2**.



1, 2

1: R = H; **2:** R = OCH_3

The UV spectrum of optically active **1**, $C_{18}H_{18}O_7$, $[M]^+$ 346, $[\alpha]_D^{16}$ +57.16° (*c* 0.1, $CHCl_3$:CH_3OH, 1:2), was typical of flavanone derivatives and contained absorption maxima at 290 and 346 nm [6]. The IR spectrum of **1** contained absorption bands for hydroxyl (3300 cm^{-1}), methoxyl (2955, 2923), γ-pyrone carbonyl (1641), and aromatic C=C bonds (1598). PMR spectra, which exhibited characteristic resonances for protons (H-2, H-3_{ax}, H-3_{eq}) of heterocyclic ring C [5, 7], confirmed that **1** was a flavanone. The spectrum also contained resonances for four aromatic protons of rings A and B, three methoxyls, and two hydroxyls (Table 1).

The UV spectrum of **2**, $C_{19}H_{20}O_8$, $[M]^+$ 376, $[\alpha]_D^{16}$ +58.18° (*c* 0.1, MeOH) exhibited absorption maxima typical of flavanone derivatives at 282 and 321 nm [2, 7]. The PMR spectrum of **2** showed resonances for protons H-2 and 2H-3 of heterocyclic ring C of flavanones and resonances for three aromatic protons of ring B, four methoxyls, and two hydroxyls (Table 1).

1) Namangan State University, 716001, Namangan, ul. Uichi, 316, e-mail: ximiya@list.ru; 2) S. Yu. Yunusov Institute of the Chemistry of Plant Substances, Academy of Sciences of the Republic of Uzbekistan, Tashkent; 3) Surgut State University, 628412, Russia, Surgut, ul. Energetikov, 14, e-mail: botirov-nepi@mail.ru. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 24-25, January-February, 2008. Original article submitted December 24, 2007.

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TABLE 1. PMR Spectra of **1** and **2** in $CCl_4 + C_6D_6$ (100 MHz)

Flavanon **1**		Flavanon **2**	
H	δ_H, ppm (J/Hz)	H	δ_H, ppm (J/Hz)
2	5.89 dd (3.2; 13.2)	2	5.88 dd (2.9; 13.7)
3_{ax}	3.76 dd (17.3; 13.2)	3_{ax}	3.77 dd (17.3; 13.7)
3_{eq}	2.41 dd (17.3; 3.2)	3_{eq}	2.45 dd (17.3; 2.9)
8	5.93 s	8	-
3′	6.45 br. d (8.0)	3′	6.46 br. d (7.5)
4′	7.00 t (8.0)	4′	7.01 t (8.4)
5′	6.32 br. d (7.4)	5′	6.33 br. d (8.0)
$-OCH_3$	3.54 s	$-OCH_3$	3.61 s
	3.73 s		3.70 s
	3.79 s		3.73 s
2′-OH	9.29 br. s		3.91 s
5′-OH	11.97 br. s	2′-OH	9.27 br. s
		5′-OH	11.80 br. s

We previously isolated from *S. comosa* Juz. (±)-5,2′-dihydroxy-6,6′,7-trimethoxyflavanone and (-)-5,2′-dihydroxy-6,6′,7,8-tetramethoxyflavanone [2]. These same flavonoids were also isolated from other *Scutellaria* L. species [6].

The spectral data and chromatographic mobility of **1** and **2** agree with those of (±)-5,2′-dihydroxy-6,6′,7-trimethoxyflavanone and (-)-5,2′-dihydroxy-6,6′,7,8-tetramethoxyflavanone, respectively. However, **1** and **2** isolated by us were optically active and rotated the plane of planar polarized light to the right. The SSCC between H-2 and one of the C-3 protons (H-3_{ax}) in PMR spectra of **1** and **2** were 13.2-13.7 Hz, which indicated that ring B had the equatorial orientation in both compounds [8].

Therefore, **1** and **2** had the structures (+)-5,2′-dihydroxy-6,6′,7-trimethoxyflavanone and (+)-5,2′-dihydroxy-6,6′,7,8-tetramethoxyflavanone, respectively.

It is noteworthy that the dextrorotary enantiomers of flavanones are found rather rarely in nature [8, 9].

EXPERIMENTAL

General Comments. We used $CHCl_3$:hydrocarbons solvents (2:3, 1; 1:1, 2; 3:2, 3; 7:3, 4; 4:1, 5; 9:1, 6).

We used Silufol UV-254 plates for TLC. Column chromatography was performed over KSK silica gel (100/160 μm). Spots of flavonoids on TLC were developed by ammonia vapor. PMR spectra were recorded on a Tesla BS-567 A instrument (100 MHz, δ, ppm); IR spectra in mineral oil, on a Perkin—Elmer System 2000 FT—IR Fourier spectrometer; UV spectra, on a Perkin—Elmer Lambda 16 spectrometer. Melting points were measured on a Boetius instrument with an PHMK 0.5 optical device; optical rotation, on a Zeiss polarimeter.

Extraction and Isolation of Total Flavonoids. Dried and ground roots (0.9 kg) of *S. phyllostachya* were extracted at room temperature 12 times with ethanol (90%). The combined extracts were concentrated in vacuo to 0.45 L and diluted with water in a 1:1 ratio. The aqueous alcohol extract was shaken successively with hydrocarbons (5 × 340 mL), $CHCl_3$ (6 × 350 mL), EtOAc (9 × 350 mL), and *n*-BuOH (11 × 300 mL). Solvents were distilled to afford hydrocarbons (6.0 g), $CHCl_3$ (9.1), EtOAc (7.5), and *n*-BuOH (12.0) fractions.

The $CHCl_3$ fraction (9.1 g) was chromatographed over a column (1.8 × 140 cm) of silica gel (135.0 g) with elution successively by systems 1-6. Fractions of 250 mL were collected. Elution by system 1 isolated from the separate fractions **1** (0.15 g) and **2** (0.12 g). Elution by system 2 afforded wogonin (0.1 g, 5,7-dihydroxy-8-methoxyflavone); by system 5, chrysin (0.18 g, 5,7-dihydroxyflavone); by system 6, norwogonin (0.16 g, 5,7,8-trihydroxyflavone).

Wogonin, $C_{16}H_{12}O_6$, $[M]^+$ 284, mp 203-204°C, UV spectrum (EtOH, λ_{max}, nm): 248, 277, 320.

IR spectrum (cm^{-1}): 3450 (OH), 2954 (OCH_3), 1656 (γ-pyrone C=O), 1612, 1579 (aromatic C=C).

PMR spectrum (100 MHz, $CCl_4 + C_6D_6$, δ, ppm): 3.82 (3H, s, OCH_3), 6.19 (1H, s, H-3), 6.59 (1H, s, H-6), 7.40 (3H, m, H-3′,4′,5′), 7.84 (2H, m, H-2′,6′), 12.18 (1H, s, 5-OH).

Chrysin, $C_{15}H_{10}O_4$, $[M]^+$ 254, mp 265-266°C; UV spectrum (EtOH, λ_{max}, nm): 212, 269, 313.

IR spectrum (cm^{-1}): 3500, 3200 (OH), 1651 (γ-pyrone C=O), 1611, 1577, 1556 (aromatic C=C).

PMR spectrum (100 MHz, CCl_4 + DMSO-d_6, δ, ppm, J/Hz): 6.1 (1H, d, J = 1.9, H-6), 6.28 (1H, d, J = 1.8, H-8), 6.55 (1H, s, H-3), 7.45 (3H, m, H-3′,4′,5′), 7.8 (2H, m, H-2′,6′), 12.18 (1H, s, 5-OH).

Norwogonin, $C_{15}H_{10}O_5$, $[M]^+$ 270, mp 250-252°C; UV spectrum (EtOH, λ_{max}, nm): 246, 285, 357.

IR spectrum (cm^{-1}): 3300, 3250 (OH), 1640 (γ-pyrone C=O), 1600 (aromatic C=C).

PMR spectrum (100 MHz, CCl_4 + DMSO-d_6, δ, ppm): 6.55 (1H, s, H-3), 6.42 (1H, s, H-6), 7.42 (3H, m, H-3′,4′,5′), 7.81 (2H, m, H-2′,6′), 12.54 (1H, s, 5-OH).

(+)-5,2′-Dihydroxy-6,6′,7-trimethoxyflavanone (1), $C_{18}H_{18}O_7$, $[M]^+$ 346, mp 213-214°C, $[\alpha]_D^{16}$ +57.16° (*c* 0.1, $CHCl_3$:CH_3OH, 1:2).

(+)-5,2′-Dihydroxy-6,6′,7,8-tetramethoxyflavanone (2), $C_{19}H_{20}O_8$, $[M]^+$ 376, mp 153-154°C, $[\alpha]_D^{16}$ +58.18° (*c* 0.1, MeOH).

IR spectrum (cm^{-1}): 3170 (OH), 2922, 2911 (OCH_3), 1637 (γ-pyrone C=O), 1599, 1543 (aromatic C=C).

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