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FLAVONOID GALACTURONIDES AND GLUCURONIDE FROM THE AERIAL PART OF *Scutellaria schachristanica*

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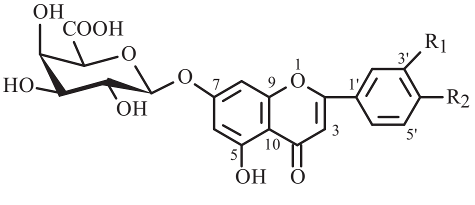
In continuation of our chemistry research on flavonoids from plants of the genus *Scutellaria* (Lamiaceae) [1–3], we isolated four compounds **1**–**4** of flavonoid nature from the EtOAc fraction of the aerial part of the indigenous species *S. schachristanica* Juz.



1 - 3

1: $R_1 = H$, $R_2 = OH$
2: $R_1 = R_2 = OH$
3: $R_1 = R_2 = H$

The structures of the isolated compounds were elucidated using UV, IR, PMR, ^{13}C NMR, DEPT, HSQC, HMBC, and COSY spectroscopy and mass spectrometry.

Compound **1** was a greenish-yellow powder. The UV spectrum of **1** (MeOH, λ_{max}, nm: 205.5, 268.5, 333.5) was characteristic of flavone derivatives. The PMR spectrum exhibited resonances characteristic of the spectrum of apigenin, a resonance for an anomeric proton, and resonances for other carbohydrate protons. Therefore, **1** was a flavonoid glycoside.

Acid hydrolysis of **1** produced apigenin with mp 347.2°C [1] and D-galacturonic acid (PC with an authentic sample). The presence of the latter was confirmed by a resonance for a COOH group at 171.75 ppm in the ^{13}C NMR spectrum and PMR spectral data (Table 1).

The sugar anomeric proton in the PMR spectrum of the glycoside of **1** resonated as a doublet at δ 5.05 ppm with SSCC J = 7.8 Hz, indicating that monosaccharide units had the pyranose form, $^4C_1$-conformation, and *β*-configuration [3].

A correlation peak between resonances of the anomeric proton and C-7 of the genin was observed in the HMBC spectrum of **1** (Table 1). This determined unambiguously the attachment site at this same position of apigenin.

Thus, **1** was apigenin 7-*O*-*β*-D-galacturonide [4]. A flavonoid with a galacturonide, nepetoside A (norwogonin-7-*O*-*β*-D-galacturonide), was isolated earlier from *S. nepetoides* [5].

Compound **2** was also a flavonoid glycoside according to PMR and ^{13}C NMR spectral data (Table 1).

Acid hydrolysis of **2** formed luteolin [6] and D-galacturonic acid.

A correlation peak between resonances of the anomeric proton and C-7 of the genin in the HMBC spectrum indicated unambiguously that the D-galacturonic acid was bonded to the C-7 position.

Thus, according to the combined analyses, physicochemical properties, and literature data, **2** was identified as luteolin-7-*O*-*β*-D-galacturonide [4].

Compound **3** was a glycoside of chrysin according to the spectral data (Table 1). The ^{13}C NMR spectrum contained a resonance for a COOH group at δ 172.00 ppm. However, the R_f values and solubilities of **3** and chrysin-7-*O*-*β*-D-glucuronide, which was isolated previously by us [2], differed. Compound **3** turned out to be much more polar than chrysin-7-*O*-*β*-D-glucuronide.

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TABLE 1. PMR and ^{13}C NMR Spectra of **1**–**3** (DMSO-d_6, δ, ppm, J/Hz)

C atom	**1**			**2**			**3**	
	δ_C	δ_H	HMBC	δ_C	δ_H	HMBC	δ_C	δ_H
2	164.28			164.81		3, 2′, 6′	163.87	
3	102.68	6.76 s	10	101.93	6.64 s	10	105.91	7.04 s
4	181.84			181.51			182.15	
5	160.89	OH, 12.95 s	6	160.96		6	161.10	
6	99.56	6.40 (d, J = 1.8)	7, 5	99.51	6.39 (d, J = 1.2)	7, 5	100.25	6.46 (d, J = 1.8)
7	162.96		1′, 6, 8	162.89		1′, 6, 8	162.85	
8	94.52	6.76 (d, J = 1.8)		94.46	6.75 (d, J = 1.2)	10	95.33	6.87 (d, J = 1.8)
9	156.85			156.83			157.2	
10	105.16			105.12			105.94	
1′	120.39			125.10			131.10	
2′	128.29	7.85 (d, J = 8.4)		112.11	7.36 br.s		126.85	8.09 (d, J = 6.6)
3′	115.92	6.88 (d, J = 8.4)	2′, 5′	146.44		2′, 5′	129.62	7.59 m
4′	161.77			149.00		2′	132.59	7.59 m
5′	115.92	6.88 (d, J = 8.4)		115.73	6.76 (d, J = 8.4)		129.72	7.59 m
6′	128.29	7.85 (d, J = 8.4)		119.50	7.39 (dd, J = 1.2; 8.4)		126.93	8.09 (d, J = 6.6)
β-D-Gal*p* unit								
1″	99.56	5.05 (d, J = 7.8)	2″, 5″	99.72	5.03 (d, J = 7.8)	2″, 5″	100.39	5.04 (d, J = 7.8)
2″	72.91	3.29 m		72.97	3.22 m	1″	73.55	3.26 m
3″	76.51	3.30 m		76.51	3.29 m	2″, 4″, 5″	77.20	3.31 m
4″	71.94	3.20 m		71.95	3.18 m	3″, 5″	72.45	3.19 m
5″	73.60	3.6 (d, J = 11.2)	3″, 4″	73.61	3.52 (d, J = 9.6)	3″, 4″	74.10	3.54 (d, J = 10.2)
6″	171.75		4″, 5″	171.68		5″	172.00	

Acid hydrolysis of **3**, as expected, formed chrysin [1]. Paper chromatography detected D-galacturonic acid in the carbohydrate part of the hydrolysate.

Based on spectral, chemical, and literature data, **3** had the structure of chrysin-7-*O*-*β*-D-galacturonide [7], which was isolated earlier from *Centaurea pseudoscabiosa* subsp. *pseudoscabiosa* Boiss. et Buhse growing in Turkey.

Compound **4** that was isolated by us was apigenin-7-*O*-*β*-D-glucuronide according to spectral, chemical, and literature data [8].

Apigenin-7-*O*-*β*-D-galacturonide (1). $C_{21}H_{18}O_{11}$, mp 236.6°C. UV spectrum (MeOH, λ_{max}, nm): 205.5, 268.5, 333.5. IR spectrum (ν, cm^{-1}): 3383.94 (OH), 2922.64 (CH), 1725 (COOH), 1658.50 (C=O), 1606.38 (C=C), 1496.13, 1413.87, 1344.19 (C=C), 1245.40, 1173.93, 1106.04, 1058.45 (C–O–C), 835.30, 763.84 (C–H), 622.26. HR-ESI-MS *m*/*z* 445.6 $[M - H]^+$, $C_{21}H_{18}O_{11}$ 446.

Apigenin-7-*O*-*β*-D-glucuronide (4) was isolated by elution of the column with MeOH:H_2O (9:1). $C_{21}H_{18}O_{11}$, mp 175.5°C. PMR spectrum (600 MHz, DMSO-d_6, δ, ppm, J/Hz): 3.14 (1H, m, H-4″), 3.23 (1H, m, H-2′), 3.27 (1H, m, H-3″), 3.51 (1H, d, J = –5.4, H-5″), 5.02 (1H, d, J = 7.2, H-1″), 6.42 (1H, br.s, H-6), 6.81 (1H, br.s, H-8), 6.83 (1H, s, H-3), 6.92 (2H, d, J = 9.0, H-3′, 5′), 7.93 (2H, d, J = 9.0, H-2′, 6′), 12.74 (1H, br.s, 5-OH).

^{13}C NMR spectrum (150 MHz, DMSO-d_6, δ, ppm): 163.61 (C-2), 103.15 (C-3), 182.12 (C-4), 161.42 (C-5), 99.86 (C-6), 163.21 (C-7), 95.07 (C-8), 157.39 (C-9), 105.69 (C-10), 120.92 (C-1′), 128.99 (C-2′), 116.43 (C-3′), 162.12 (C-4′), 116.53 (C-5′), 128.99 (C-6′), 100.24 (C-1″), 73.47 (C-2″), 77.14 (C-3″), 72.48 (C-4″), 74.09 (C-5″), 171.86 (C-6″).

Thus, compounds **1**–**3** were isolated for the first time from the genus *Scutellaria* and compound **4**, for the first time from *S. schachristanica*.

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REFERENCES

1. Z. O. Tashmatov, K. A. Eshbakova, Kh. M. Bobakulov, and N. D. Abdullaev, *Khim. Prir. Soedin.*, 737 (2009).
2. Z. O. Tashmatov, K. A. Eshbakova, and Kh. M. Bobakulov, *Khim. Prir. Soedin.*, 392 (2011).
3. Z. O. Tashmatov, K. A. Eshbakova, and Kh. M. Bobakulov, *Khim. Prir. Soedin.*, 487 (2011).
4. K. R. Markham and J. Lawrence, *Phytochemistry*, **14**, 1093 (1975).
5. M. P. Yuldashev and A. Karimov, *Khim. Prir. Soedin.*, 364 (2001).
6. K. R. Markham, B. Ternai, R. Stanly, H. Geiger, and T. J. Mabry, *Tetrahedron*, **34**, 1389 (1978).
7. G. Flamini, M. Pardini, I. Morelli, K. Ertugrul, H. Dural, Y. Bagci, and M. Kargioglu, *Phytochemistry*, **61**, 433 (2002).
8. G. Flamini, *Phytochemistry*, **57**, 559 (2001).