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A NEW FLAVONE GLYCOSIDE FROM THE AERIAL PART OF *Scutellaria schachristanica*

Z. O. Tashmatov, K. A. Eshbakova,* and Kh. M. Bobakulov

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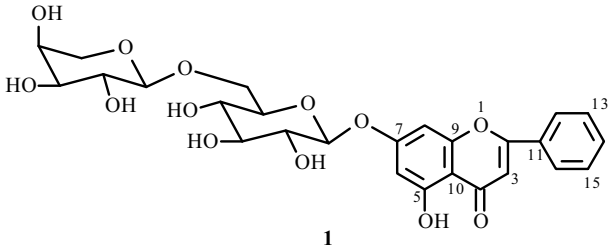
The new flavone glycoside schachristanoside was isolated from the aerial part of Scutellaria schachristanica *Zuz. (Lamiaceae). Spectral data and chemical transformations found that schachristanoside had the structure chrysin-7-*O*-[α-L-arabinopyranosyl-(1→6)]-β-D-glucopyranoside.*

Keywords: *Scutellaria schachristanica* Zuz. (Lamiaceae), flavonoid, chrysin, schachristanoside, PMR, ^{13}C, and DEPT spectra.

In continuation of chemical research on the aerial part of *Scutellaria schachristanica* Zuz. (Lamiaceae) collected during flowering in Samarkand Oblast, Republic of Uzbekistan [1, 2], we isolated a new bioside of chrysin. Herein we report the structure of **1**, which we called schachristanoside.



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The IR spectrum of **1** showed absorption bands consistent with the presence of aromatic double bonds (1613.98, 1492.53) and γ-pyrone carbonyl (1656.01). The presence of the latter was confirmed by the resonance for C-4 at 182.20 ppm in the ^{13}C NMR spectrum [3]. The UV spectrum of **1** (MeOH, λ_{max}, nm): 272, 307; +CH_3COONa, 270, 309) was characteristic of flavone derivatives [4]. This was confirmed by the PMR spectrum, which contained resonances for eight aromatic protons that were very characteristic of the chrysin spectrum, two anomeric protons, and the other protons of the carbohydrate part. Therefore, the studied compound was a bioside.

Acid hydrolysis of the new flavonoid glycoside **1** produced chrysin (5,7-dihydroxyflavone) (**2**), $C_{15}H_{10}O_4$, mp 290–292°C [1]. Paper chromatography (PC) detected L-arabinose (**3**) and D-glucose (**4**) in the carbohydrate part of the hydrolysate.

We concluded from a study of the PMR and ^{13}C NMR spectra of **1** (Table 1), which contained the same set of resonances for the H and C atoms of the monosaccharide units, that the new flavonoid glycoside was in fact a bioside of chrysin and contained D-glucose and L-arabinose in a 1:1 ratio.

The anomeric protons resonated in the PMR spectrum of **1** as doublets at δ 5.10 ppm with SSCC J = 7.32 Hz (D-glucose H-1) and δ 4.90 with SSCC J = 7.33 Hz (L-arabinose H-1). These facts indicated that the monosaccharides D-glucose and L-arabinose had the pyranose form and $^4C_1$-conformation and, therefore, the *β*- and *–α*-configurations, respectively [5].

The chemical shifts of the carbohydrate resonances in the PMR and ^{13}C NMR spectra (Table 1) showed that **1** was a monodesmoside with a pentose in the terminal position [6].

S. Yu. Yunusov Institute of the Chemistry of Plant Substances, Academy of Sciences, Republic of Uzbekistan, Tashkent, fax (99871) 120 64 75, e-mail: e_komila@yahoo.com. Translated from Khimiya Prirodnykh Soedinenii, No. 4, July–August, 2011, pp. 487–488. Original article submitted January 31, 2011.

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TABLE 1. Chemical Shifts of C and H Atoms of **1** and DEPT Data (DMSO-d_6, δ, ppm, J/Hz)

C atom	DEPT	δ_C	δ_H	C atom	DEPT	δ_C	δ_H
2	C	163.87	–	*β*-D-Glc*p*			
3	CH	105.49	6.95 s	1	CH	100.06	5.10 (d, J = 7.32)
4	C	182.20	–	2	CH	73.25	*
5	C	161.15	–	3	CH	77.20	
6	CH	98.96	6.61 br.s	4	CH	69.72	
7	C	163.26	–	5	CH	77.31	
8	CH	95.12	7.00 br.s	6	CH_2	69.84	
9	C	157.19	–	*α*-L-Ara*p*			
10	C	104.99	–	1	CH	101.33	4.90 (d, J = 7.33)
11	C	130.62	–	2	CH	73.17	*
12	CH	126.54	8.06 m	3	CH	76.46	
13	CH	129.22	7.56 m	4	CH	75.88	
14	CH	132.20	7.56 m	5	CH_2	60.75	
15	CH	129.22	7.56 m				
16	CH	126.54	8.06 m				
5-OH	–	–	12.17 s				

*Protons of carbohydrate units were observed in the range 3.25–3.85 ppm as complex multiplets.

The PMR spectrum of **1** (Table 1) exhibited a 1H resonance for the 5-OH as a singlet at 12.16 ppm. This unambiguously defined the site of attachment of the sugar to the aglycon as C-7.

Stepwise hydrolysis of **1** formed chrysin-7-*O*-*β*-D-glucoside [7].

The resonance for D-glucose C-6 in the ^{13}C NMR spectrum experienced a glycosylation effect and was found at δ 69.84, indicating that the L-arabinose was bonded to this same atom. It is noteworthy that unglycosylated D-glucose C-6 resonated at δ 62–63.

Thus, the analysis as a whole established that schachristanoside had the structure chrysin-7-*O*-[*α*-L-arabinopyranosyl-(1→6)]-*β*-D-glucopyranoside.

EXPERIMENTAL

General Comments. UV spectra were measured on a Lambda-16 spectrophotometer (Perkin–Elmer). Melting points were determined on a Boetius heating stage. IR spectra were recorded in KBr on a Perkin–Elmer Model 2000 Fourier-spectrometer. PMR and ^{13}C NMR spectra were recorded in DMSO-d_6 on a Unity-400plus spectrometer (Varian) at operating frequency 400 MHz using HMDS as an internal standard for PMR spectra and the DMSO-d_6 resonance (39.5 ppm vs. TMS) for ^{13}C NMR spectra. TLC used Silufol UV 254 plates with detection by iodine vapor, ammonia vapor, UV emission at 254 and 365 nm, and vanillin solution (1%) in conc. H_2SO_4. PC was carried out on Filtrak No. 11 paper using *n*-BuOH:HOAc:H_2O (4:1:5, 1) and *n*-BuOH:Py:H_2O (6:4:3, 2). Free monosaccharides were detected in PC by spraying with anilinium phthalate.

Extraction and Isolation of Flavonoid from the Aerial Part of *S. schachristanica*. Air-dried ground plant material (1 kg) was extracted at room temperature by EtOH (70%, 6 × 5 L). The combined extracts were vacuum distilled. The condensed residue (120 g) was diluted with H_2O (1:1) and worked up successively with petroleum ether (6 × 0.5 L), $CHCl_3$ (6 × 0.5 L), EtOAc (10 × 0.5 L), and *n*-BuOH (10 × 0.5 L). Solvents were distilled off to afford petroleum-ether (10.5 g), $CHCl_3$ (12.0), EtOAc (20), and *n*-BuOH (40) fractions.

The total EtOAc fraction (20 g) was chromatographed over a column (2.5 × 150 cm) of silica gel (450 g) using $CHCl_3$ and a $CHCl_3$:MeOH gradient (25:1→1:1).

Compound **1** was isolated upon elution by $CHCl_3$:MeOH (2:1) as yellowish crystals, $C_{26}H_{28}O_{13}$, mp >340°C (MeOH). UV spectrum (MeOH, λ_{max}, nm): 272, 307; +CH_3COONa: 270, 390. IR spectrum (ν, cm^{-1}): 3408.95 (OH), 2952.38 (CH), 2917.72 (CH), 1656.01 (C=O), 1613.98, 1581.86, 1492.53 (C=C), 1451.63, 1372.43 (CH), 1314.95, 1174.38, 1101.24, 1071.06 (C–O), 950.95, 838.96, 767.51, 688.13 (CH), 666.36, 521.77.

Table 1 presents the PMR and ^{13}C NMR spectra.

Acid Hydrolysis. Compound **1** (20 mg) was hydrolyzed in aqueous methanolic H_2SO_4 (15 mL, 5%) for 5 h on a boiling-water bath. The resulting precipitate of the aglycon was filtered off and recrystallized from $CHCl_3$ to afford chrysin (5,7-dihydroxyflavone, **2**, 6 mg), mp 290–292°C, $C_{15}H_{10}O_4$ [1].

The carbohydrate part of the hydrolysate was neutralized with $BaCO_3$ and evaporated. PC of the solid using system 2 identified D-glucose (**4**) and L-arabinose (**3**).

Stepwise Hydrolysis of 1. The glycoside (30 mg) was treated with HCl solution (20 mL, 1%), heated on a water bath for ~1 h, cooled, and extracted with EtOAc. The extract was washed with H_2O until neutral and chromatographed over a column of silica gel with elution by $CHCl_3$:MeOH (4:1) to isolate the progenin, mp 188–191°C (MeOH), which was identified as chrysin-7-*O*-β-D-glucoside.

Continued elution of the column by $CHCl_3$:MeOH (2:1) isolated starting **1**.

PC of the hydrolysate detected L-arabinose.

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