Chemistry of Natural Compounds, Vol. 44, No. 4, 2008

FLAVONOIDS AND OLEANOLIC ACID FROM *Scabiosa caucasica*

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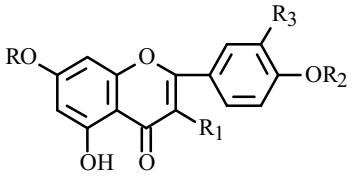
UDC 547.944/945+547.918:547.914.4

In continuation of phytochemical investigations of plants of the Dipsacaceae family growing in the Republic of Azerbaidzhan [1, 2], we studied flowers of *Scabiosa caucasica* M.B. for flavonoid and triterpenoid content. Air-dried flowers (2 kg) collected during full flowering at the end of July 2006 near the village Slavyanka of Kedabek region of the Republic of Azerbaidzhan were extracted with ethanol (95%, 2×). The combined extracts were evaporated to 250 mL and left at room temperature. The resulting white precipitate was filtered off after a day.

The filtrate was evaporated to 100 mL and diluted with water (300 mL). The resulting aqueous solution was treated successively with a mixture of ethylacetate and petroleum ether (1:1), ethylacetate, and *n*-butanol.

Recrystallization of the aforementioned white precipitate from ethanol gave oleanolic acid, $C_{30}H_{48}O_3$, mp 303-305°C, $[\alpha]_D^{20}$ -79 ± 2° (*c* 1.02, pyridine:methanol, 1:1) [2].

The extract obtained using ethylacetate:petroleum ether was evaporated and recrystallized from chloroform:ethanol to afford apigenin (**1**), $C_{15}H_{10}O_5$, mp 343-345°C. IR spectrum (KBr, ν_{max}, cm^{-1}): 3300 (OH), 1655 (C=O), 1645, 1550 (C_6H_5). UV spectrum (MeOH, λ_{max}, nm): 270, 340 [3].



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1: R = R_1 = R_2 = R_3 = H
2: R = *β*-D-Glc*p*, R_1 = R_2 = H, R_3 = OH
3: R = *β*-D-Glc*p*, R_1 = R_3 = OH, R_2 = H
4: R = *α*-L-Ara*p*(1→6)-*β*-D-Glc*p*, R_1 = H, R_2 = CH_3, R_3 = OH

The ethylacetate extract was evaporated to dryness. The solid was dissolved in water (100 mL). The aqueous solution was shaken with ethylacetate (150 mL) and left for a day. The crystals that formed between the phases were separated and recrystallized from ethanol to afford cinaroside (**2**), $C_{21}H_{20}O_{11}\cdot 2H_2O$, mp 270-272°C, $[\alpha]_D^{20}$ -48 ± 2° (*c* 0.5, formamide). UV spectrum (MeOH, λ_{max}, nm): 256, 268, 350 (no change upon adding sodium acetate) [1].

The aqueous phase was evaporated to dryness. The solid was recrystallized from ethanol to afford quercimeritrin (**3**), $C_{21}H_{20}O_{12}$, mp 245-247°C, $[\alpha]_D^{20}$ -52 ± 2° (*c* 0.5, methanol). IR spectrum (KBr, ν_{max}, cm^{-1}): 3480-3300, 2930, 1658, 1610, 1530, 1480, 1080, 1060, 1020, 892. UV spectrum (MeOH, λ_{max}, nm): 256, 268, 375 [1].

The butanol extract was evaporated to dryness. The solid was dissolved in water (50 mL), treated with an equal volume of ethylacetate, and shaken. Crystals that formed after two days on the walls of the separatory funnel were recrystallized from ethanol to afford a flavonoid glycoside of composition $C_{27}H_{30}O_{15}$, mp 188-190°C, $[\alpha]_D^{20}$ -50 ± 2° (*c* 0.5, DMF). Interpretation of one- and two-dimensional NMR spectra of this glycoside (Table 1) suggested structure **4**. Palustroside, which was isolated previously from *Galium palustre* L. (Rubiaceae), has the identical structure [4].

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 0009-3130/08/4404-0520

TABLE 1. Chemical Shifts of C and H Atoms of Palustroside (**4**), DEPT Data, and 2D NMR ^{1}H-^{1}H COSY, HMQC, HMBC, and ROESY Spectra (δ, ppm, J/Hz, C_5D_5N and DMSO-d_6, 0 = TMS)

C atom	DEPT	Data in Py-d_5				Data in DMSO-d_6			
		δ_C	δ_H, J/Hz	HMBC (C atoms)	ROESY (H atoms)	δ_C	δ_H, J/Hz	HMBC (C atoms)	ROESY (H atoms)
2	C	164.94	-			164.66	-		
3	C	104.68	6.94 s	2, 10, 11		104.23	6.84 s	2, 4, 10, 11	12, 16
4	C	182.80	-			182.44	-		
5	C	162.38	-			161.56	-	5, 7, 8, 10	G1
6	CH	100.77	6.82 d (1.91)	5, 7, 8, 10	G1	100.31	6.46 s		
7	C	164.01	-			163.40	-	6, 9, 10	G1
8	CH	95.41	7.03 d (1.98)	6, 9, 10	G1	95.24	6.84 s		
9	C	157.88	-			157.49	-		
10	C	106.63	-			105.92	-		
11	C	124.27	-			123.30	-		
12	CH	114.43	7.93 d (1.99)	2, 13, 14, 16	3, 15, 16	113.59	7.48 s	2, 14, 16	
13	C	148.39	-			147.21	-		
14	C	152.08	-			151.79	-		
15	CH	112.30	7.18 d (8.5)	11, 13, 14	16, CH_3O	112.66	7.14 d (7.9)	11, 13	16, CH_3O
16	CH	119.19	7.64 dd (8.5, 1.99)	2, 12, 14	15, CH_3O	119.52	7.62 d (8.4)	12, 14	3, 12, 15
CH_3O	CH_3	55.82	3.78 s	14	15, 16	56.25	3.94 s	14	15
				β-D-Glc*p* (G)					
1	CH	101.97	5.67 d (7.5)	7	G3, G5, 6, 8	100.14	5.10 d (6.6)	7	G3, G5, 6, 8
2	CH	74.59	4.25			73.51	3.30		
3	CH	78.16	4.25	Gl	G1	76.59	3.30		
4	CH	71.01	4.25			69.84	3.30		
5	CH	77.53	4.30			76.06	3.74		
6	CH_2	69.24	4.80* (9.16) 4.30			68.09	3.95* (10.2) 3.45		
				α-L-Ara*p* (A)					
1	CH	105.35	4.90 d (6.53)	G6	A3, A5a	103.65	4.18 d (5.9)	G6	
2	CH	72.25	4.52 t (6.18)	A1, A3		70.97	3.40		
3	CH	74.19	4.16 dd (8.44, 2)	A1	A1, A5a	72.91	3.40		
4	CH	69.00	4.25			67.66	3.60		
5	CH_2	66.35	3.69* (10.83) 4.28	A1	A1, A3	65.18	3.74 3.30		

*Doublets with broad components.

Chemical shifts of protons without multiplicities and SSCC were found from 2D spectra.

PMR spectra were obtained on a Bruker AM-300 spectrometer.

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