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FLAVONOIDS FROM *Knautia montana* FLOWERS GROWING IN AZERBAIJAN

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The family Dipsacaceae (teasel) comprises 10 genera and about 300 species that are distributed mainly in Mediterranean and Western Asian countries. The genus *Knautia* L. is one of the genera in this family. It is represented by two species in the flora of Azerbaijan, *K. montana* (M.B.) D.C. and *K. involucrate* Somm. et Lev [1]. *K. montana* is the most widely distributed species, is a biennial or perennial plant, and reaches 100–150 cm in height.

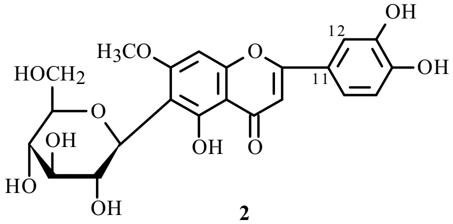
Isolation of Flavonoids from *K. montana* Flowers. Air-dried flowers (1.2 kg) were collected on July 11, 2009, below Budug village, Gubin Region, Azerbaijan Republic and were extracted with EtOH (95%, 3×, 1:8) at room temperature. The extracts were filtered, evaporated *in vacuo* to 200–250 mL, diluted with H_2O (300 mL), and evaporated to an aqueous residue. The aqueous solution was extracted with hexane, EtOAc:hexane (1:1.5), and EtOAc.

The EtOAc:hexane extract was evaporated. The solid was recrystallized from $CHCl_3$:MeOH to afford **1**.

The EtOAc extract was evaporated to dryness. The solid was dissolved in hot H_2O and left overnight. The resulting crystals were separated to afford **2**. The filtrate was evaporated. The solid was recrystallized from EtOH to afford **3**.

Compound 1, $C_{15}H_{10}O_5$, mp 345–346°C ($CHCl_3$:MeOH). UV spectrum (MeOH, λ_{max}, nm): 268, 335. Yellow crystals, soluble in alcohols and acetone, insoluble in hexane and H_2O. R_f 0.90 (*n*-BuOH:AcOH:H_2O, 4:1:5). Bryant's cyanidin test indicated that the aglycon was a flavonoid. These data and direct comparison with an authentic sample identified **1** as apigenin.

Compound 2, $C_{22}H_{22}O_{11}$, mp 260–262°C (H_2O). UV spectrum (MeOH, λ_{max}, nm): 245, 260, 344; +CH_3COONa: 268, 404; +$AlCl_3$: 274, 300, 336, 428. Yellow crystals, soluble in DMF and Py, insoluble in alcohol, poorly soluble in H_2O. Fluoresces in filtered UV light as dark spots. The compound under normal conditions (5% H_2SO_4, 10 h) is not hydrolyzed. Kiliani acid hydrolysis formed 7-*O*-methylluteolin and D-glucose [2–5], which indicated that the studied compound was a C-glucoside. This was also confirmed by NMR spectra (Table 1). PMR and ^{13}C NMR spectra of **2** were interpreted as the structure shown below. Swertiajaponin, 7-*O*-methylluteolin-6-*C*-*β*-D-glucopyranoside, had an identical structure [6].



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Compound 3, $C_{26}H_{28}O_{16}\cdot H_2O$, mp 220–222°C (EtOH). Lemon yellow crystals, soluble in H_2O and EtOH, very soluble in aqueous EtOH, insoluble in Et_2O and $CHCl_3$. $[\alpha]_D^{20}$ –45° (*c* 0.52, DMF). UV spectrum (MeOH, λ_{max}, nm): 262, 358; +CH_3COONa/H_3BO_3: 266, 384. The IR spectra of **3** and giganteoside A [7] were identical.

K. montana is the second representative of the family Dipsacaceae for which giganteoside A and quercetin-7-*O*-[*α*-L-arabinopyranosyl(1→6)]-*β*-D-glucopyranoside (**3**) [7] was found in its flowers.

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TABLE 1. Chemical Shifts of C and H Atoms of **2**, DEPT Data, and 2D NMR $^1H-^1H$ COSY and HMQC Spectral Parameters (C_5D_5N and DMSO-d_6, 0 = TMS, δ, ppm, J/Hz)

C atom	DEPT	Data in DMSO-d_6		Data in Py-d_5	
		δ_C	δ_H	δ_C	δ_H
2	C	164.37	–	164.89	–
		164.19		164.59	
3	CH	103.56	6.75 s	103.61	6.90 s
			6.77 s		6.93 s
4	C	182.63	–	183.01	–
		182.29		182.75	
5	C	160.78	–	161.59	–
		160.04		161.18	
6	C	110.10	–	110.66	–
7	C	165.41	–	165.65	–
				165.01	
8	CH	91.38	6.79 s	91.07	6.64 s
		90.53		90.36	
9	C	157.27	–	157.71	–
		157.16		157.56	
10	C	105.06	–	105.56	–
		104.55		105.40	
11	C	121.79	–	122.45	–
12	CH	113.96	7.46 s	114.52	7.98 s
13	C	146.26	–	147.67	–
14	C	150.30	–	151.76	–
15	CH	116.44	6.91 d (8.5)	116.85	7.42 d
16	CH	119.53	7.49 d (8.5)	119.59	7.60 d
CH_3O	CH_3	56.95	3.90 s	56.41	3.80 s
		56.71	3.88 s	56.09	3.75 s
		C-*β*-D-Glc*p*			
1	CH	79.53	3.17	80.84	4.42
2	CH	73.28	4.59	74.56	5.70
		73.04	4.59	74.36	5.60
3	CH	71.29	3.05	72.32	4.40
4	CH	70.72	4.16	72.14	5.40
		70.07	4.00	71.52	5.14
5	CH	82.35	3.14	83.06	4.20
		82.18	3.14		
6	CH_2	62.22	3.32, 3.69	63.43	4.40, 4.60

Chemical shifts of protons without multiplicities and SSCC were found from 2D spectra.
PMR spectra were taken on a Bruker AM-300 spectrometer.

REFERENCES

1. *Flora of Azerbaijan* [in Russian], Vol. VIII, Baku, 1961, p. 98.
2. G. N. Zemtsova and V A. Bandyukova, *Khim. Prir. Soedin.*, 705 (1977).
3. L. I. Borodin, V. I. Litvinenko, and N. V. Kurinnaya, *Khim. Prir. Soedin.*, 19 (1970).
4. R. Komatsu and T. Tomimori, *Tetrahedron Lett.*, **15**, 1611 (1966).
5. T. J. Mabry, K. R. Markham, and M. B. Thomas, *The Systematic Identification of Flavonoids*, Springer-Verlag, New York, 1970, p. 354.
6. D. Davoust, M. Massias, and D. Molho, *Org. Magn. Reson.*, **13**, 218 (1980).
7. I. S. Movsumov, E. A. Garaev, and M. I. Isaev, *Khim. Prir. Soedin.*, 552 (2006).