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VERBASCOSIDE FROM *Verbascum phlomoides*

L. N. Gvazava[1] and V. S. Kikoladze[2]

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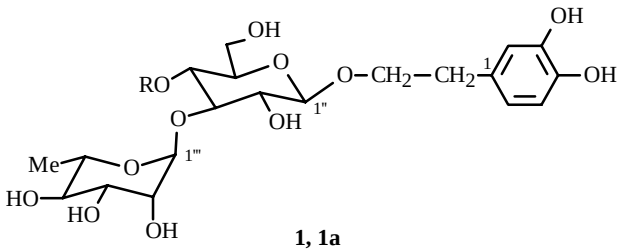
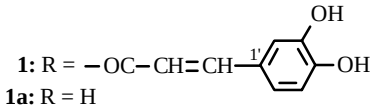
Plants of the genus *Verbascum* L. (Scrophulariaceae) are rich in biologically active compounds [1-3], are widely used in folk medicine [4, 5] and homeopathic practice [6] of many countries, and are interesting as pharmacological materials. In particular, wild *V. phlomoides* in Georgia is used for many diseases [7] so that its chemical composition was thoroughly studied.

The aerial parts of *V. phlomoides* together with the flower heads (500 g of air-dried raw material) were extracted with methanol (50%) on a water bath at 60°C. The extracts were combined, filtered, and distilled in vacuo. The aqueous residue was evaporated and treated with petroleum ether to remove ballast materials. The resulting aqueous concentrate was filtered over columns (5 × 10 cm) of nylon and Al_2O_3. The total phenolic compounds were separated and fractionated repeatedly over a column (1.2 m × 2.5 cm) of polyamide with elution by H_2O:MeOH with an increasing gradient of alcohol from 0 to 100%. This isolated phenolic compound **1**, which was not a flavonoid and was identified using chemical transformations and mass and NMR spectroscopy.



1, 1a



Alkaline hydrolysis of **1** in NaOH solution (0.05 N) produced caffeic acid and glycoside **1a**, the mass spectrum of which displayed a weak peak for a molecular ion with *m*/*z* 462, corresponding to the formula $C_{20}H_{30}O_{12}$. Therefore, **1** was an ester of caffeic acid and glycoside **1a**. Acetylation of **1a** by acetic anhydride in pyridine produced its octaacetate (*m*/*z* 798 $[M]^+$), which was hydrolyzed by H_2SO_4 (5%). GC of the carbohydrate part of the hydrolysate detected the acetates of sorbitol and rhamnol in a 1:1 ratio.

The aglycon was prepared by hydrolyzing **1** (50 mg) with H_2SO_4 (5%). After the carbohydrate part was removed, the mixture was chromatographed over a column of silica gel (1.2 m × 3.0 cm) with elution successively by $H_2O \rightarrow MeOH \rightarrow BuOH$ to afford the aglycon (18.7 mg) that was identified using mass, PMR, and ^{13}C NMR spectroscopy as (3,4-dihydroxyphenyl)ethanol.

The configuration of the glycosidic bonds of the sugars and the attachment site of the components in **1** were established using PMR spectra (double homo- and heteronuclear resonance) and ^{13}C NMR spectra (Table 1) in addition to nuclear Overhauser effect experiments. The results agreed with those in the literature [8] and enabled **1** to be assigned the structure β-(3,4-dihydroxyphenyl)ethyl-*O*-α-L-rhamnopyranosyl-(1→3)-β-D-(4-*O*-caffeoyl)glucopyranoside or verbascoside.

The isolation from *V. phlomoides* of the separate components of **1** has been reported [9]. However, verbascoside itself has not been isolated from the studied species until now. We are inclined to explain this by the climatic and geographical peculiarities of the habitat of this plant.

1) I. Kutateladze Institute of Pharmacochemistry, 0159, Tbilisi, ul. P. Sarajishvili, 36, e-mail: liligvazava@yahoo.com; 2) P. Melikishvili Institute of Physical and Organic Chemistry, 0186, Tbilisi, ul. Jikia, 5. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 589-590, November-December, 2007. Original article submitted May 23, 2007.

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TABLE 1. PMR and ^{13}C NMR Spectra of **1** (DMSO-d_6, δ, ppm, J/Hz, 0 = TMS)

H	^{1}H	C	^{13}C
		Aglycon	
2	6.60	1	129.4 (C)
5	6.51 (d, 7.8)	2	116.5 (CH)
6	6.60 (d, 7.8)	3	145.2 (C)
7	2.74 (2H, t, 7.8)	4	143.7 (C)
8	3.62 (m, 7.8; 9.1)	5	115.6 (CH)
	3.89 (m, 7.8; 9.1)	6	119.7 (CH)
		7	35.2 (CH_2)
		8	70.6 (CH_2)
		Caffeic acid	
2′	7.05	1′	125.8 (C)
5′	6.79 (d, 7.8)	2′	114.8 (CH)
6′	6.96 (d, 7.8)	3′	145.8 (C)
7′	7.47 (d, 15.8)	4′	148.7 (C)
8′	6.22 (d, 15.8)	5′	113.9 (CH)
		6′	121.7 (CH)
		7′	145.6 (CH)
		8′	115.9 (CH)
		9′	166.0 (C)
		Glucose	
1″	4.36 (d, 7.6)	1″	102.6 (CH)
2″	3.24 (dd, 7.6; 8.8)	2″	74.8 (CH)
3″	3.72 (m)	3″	79.4 (CH)
4″	4.75 (t, 9.4)	4″	69.3 (CH)
5″	3.46 (m)	5″	74.5 (CH)
6″	3.46-3.72	6″	61.0 (CH_2)
		Rhamnose	
1‴	5.10 (br.s)	1‴	101.1 (CH)
2‴	3.70 (dd, 1.2; 2.4)	2‴	70.8 (CH)
3‴	3.34 (dd, 2.4; 9.4)	3‴	70.6 (CH)
4‴	3.14 (t, 9.4)	4‴	71.9 (CH)
5‴	3.36 (m)	5‴	68.9 (CH)
6‴	1.04 (d, 6.2)	6‴	18.1 (CH_3)

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