Fuhsioside, a New Phenylethanoid Glucoside from *Veronica fuhsii*

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Fushioside, a new phenylethanoid glucoside, 2-(3,4-dihydroxyphenyl)ethyl 6-*O*-protocatechuoyl-β-D-glucopyranoside was isolated from the methanolic extract of the aerial parts of *Veronica fuhsii* along with a known phenylethanoid glycoside, plantamajoside, and a flavone glucoside, luteolin 7-*O*-glucoside.

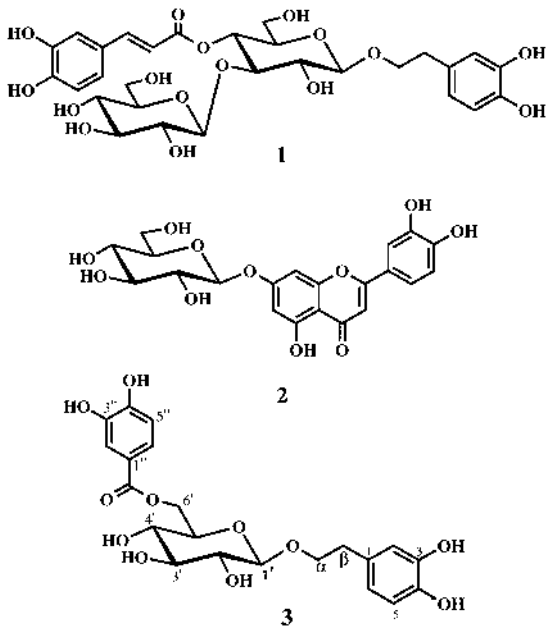
Key words *Veronica fuhsii*; Scrophulariaceae; phenylethanoid glycoside; fuhsioside

In the flora of Turkey, genus *Veronica* (Scrophulariaceae) is represented by 79 species, 26 of which are endemic.[1)] *Veronica* species contain mainly iridoid glycosides, especially catalpol esters of benzoic and cinnamic acid derivatives, and some phenylethanoid glycosides and flavonoid compounds.[2—9)] Some of the *Veronica* species are used as diuretics and for wound healing in traditional medicine.[10)]

In the previous paper, we reported the structures of iridoid glucosides isolated from *Veronica fuhsii*, which is one of the endemic species distributed in Middle Anatolia.[11)] As a continuation of our studies on the same plant, we report here the isolation and structure elucidation of a new phenylethanoid glucoside (**3**), in addition to the known phenylethanoid glycoside (**1**) and flavone glucoside (**2**).

Compound **1** was identified as plantamajoside[12)] and **2** as luteolin 7-*O*-glucoside[13)] from their UV, IR and NMR spectral data by comparison with reported data.

Compound **3** was obtained as a colourless, amorphous solid. UV spectra suggested its polyphenolic nature. The IR spectrum of **3** showed absorption bands for hydroxyl groups (3370 cm^{-1}), carbonyl (1698 cm^{-1}) and aromatic rings (1510 cm^{-1}). Compound **3** showed a $[M]^+$ peak at *m/z* 452 and a $[M+H]^+$ peak at *m/z* 453 corresponding to a molecular formula of $C_{21}H_{24}O_{11}$. The ^{1}H- and ^{13}C-NMR spectra of **3** revealed the presence of one protocatechuoyl group confirmed by the ABX-type aromatic protons (δ_H 6.77, 7.44, 7.45) and a carbonyl carbon (δ_C 168.1), and one 2,3-dihydroxyphenethyl alcohol, confirmed by ABX-type aromatic groups (δ_H 6.48, 6.63, 6.64) and two methylenes which were coupled with each other (α: δ_H 3.69, 3.93, δ_C 72.2; β: δ_H 2.76, δ_C 36.5).



The signals assigned to the sugar moiety indicated the presence of a glucose unit. In the ^{1}H- and ^{13}C-NMR spectra, the anomeric signal was observed at δ_H 4.32 (d, J=7.9 Hz) and δ_C 122.5, as a β-linked D-glucose. All protons in the glucose unit were assigned unambiguously from the correlation spectroscopy (COSY) spectrum and a heteronuclear multiple quantum coherence (HMQC) experiment correlated all proton resonances with those of the corresponding carbons in the sugar unit. The downfield signals at δ_H 4.40 (dd, J=6, 12 Hz) and δ_H 4.56 (dd, J=6, 12 Hz), belonging to H-6 of glucose suggest that the acyl moiety was attached to C-6 of glucose. The signal at δ_C 64.7, arising from C-6 of the glucose moiety showed a 3 ppm downfield shift indicating that the

Table 1. ^{1}H- and ^{13}C-NMR Spectral Data for Compound **3** in Methanol-d_4

	C	H
Aglycone		
1	131.3	
2	117.0	6.64 (d, J=2 Hz)
3	145.9	
4	144.5	
5	116.3	6.63 (d, J=8 Hz)
6	121.2	6.48 (dd, J=2, 8 Hz)
α	72.2	3.69 (m)
		3.93 (m)
β	36.5	2.76 (t, J=8 Hz)
Glucose		
1′	104.4	4.32 (d, J=8 Hz)
2′	74.9	3.22 (t, J=9 Hz)
3′	77.8	3.39[a)]
4′	71.7	3.39[a)]
5′	75.4	3.55 (m)
6′	64.7	4.40 (dd, J=6, 12 Hz)
		4.56 (dd, J=2, 12 Hz)
Protocatechuoyl		
1″	122.5	
2″	117.5	7.45 (m)
3″	146.1	
4″	151.7	
5″	115.8	6.77 (d, J=8 Hz)
6″	123.8	7.44 (dd, J=2, 8 Hz)
C=O	168.1	

a) Signal pattern unclear due to overlapping.

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acyl moiety was indeed attached to C-6. The location of glucose, the protocatechuoyl group and the 2,3-dihydroxyphenethyl alcohol were confirmed by the heteronuclear multiple bond correlation (HMBC) experiment. Correlation peaks were observed from the following pairs: H-6′/C-1″, H-1′/C-α and H-α/C-1′. Therefore, the structure of **3** was identified as 2-(3,4-dihydroxyphenyl)ethyl 6-*O*-protocatechuoyl-β-D-glucopyranoside, for which fuhsioside is proposed as the trival name.

Protocatechic acid has also been found as an acyl moiety in several iridoids isolated from different *Veronica* species.[2,11]

Experimental

General Procedures NMR spectra were recorded on a JEOL JNM-A500 spectrometer in CD_3OD with tetramethylsilane (TMS) as internal standard. FAB-MS were recorded on a JEOL JMS-DX300 spectrometer. UV spectra were recorded on a Shimadzu UV-160A spectrometer. IR spectra were recorded on a Perkin Elmer FT-IR 1720X spectrometer.

Plant Material *Veronica fuhsii* FREYN *et* SINT was collected from Kizilcahamam-Isikdagi in May 1988. The voucher specimen has been deposited in the Herbarium of the Department of Pharmacognosy, Faculty of Pharmacy, Hacettepe University, Ankara, Turkey (HUEF-88-148).

Extraction and Isolation Air dried overground parts of the plant (220 g) were extracted twice with methanol (each 2 l). The methanolic extract was evaporated *in vacuo*. The residue (48 g) was dissolved in water and then extracted with petroleum ether and the petroleum ether phase discarded. The aqueous phase was concentrated and chromatographed over a polyamide column eluting with H_2O, followed by increasing concentrations of MeOH to yield four main fractions: A—D [fr.A, 9.2 g (H_2O); fr.B, 675 mg (50% MeOH); fr.C, 400 mg (75% MeOH); fr.D, 1 g (MeOH)]. Fraction B was chromatographed over silica gel by stepwise elution with a $CHCl_3$–MeOH–H_2O (80 : 20 : 2→60 : 40 : 4) solvent system and then rechromatographed over Sephadex LH-20 with MeOH to give **1** (7 mg). Fraction C was chromatographed over silica gel by stepwise elution with the $CHCl_3$–MeOH–H_2O (80 : 20 : 2→60 : 40 : 4) solvent system and then rechromatographed over Sephadex LH-20 with MeOH to give **3** (10 mg). 250 mg of fraction D was chromatographed over silica gel by stepwise elution with the $CHCl_3$–MeOH–H_2O (80 : 20 : 1→70 : 30 : 3) solvent system and then rechromatographed over Sephadex LH-20 with MeOH to give **2** (5 mg).

Fuhsioside (3) $[\alpha]_D^{24}$ −21.1° (c=1.2, MeOH). UV λ_{max}^{MeOH} nm: 220, 242, 264, 290. IR ν_{max}^{KBr} cm^{-1}: 3370 (OH), 1698 (C=O), 1600, 1510 (arom. ring). FAB-MS *m/z*: 452 $[M]^+$, 453 $[M+H]^+$. ^1H- and ^{13}C-NMR: Table 1.

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