

Fushioside, a New Phenylethanoid Glucoside from *Veronica fushii*

Meltem OZİPEK,^a Iclal SARACOĞLU,^a Keisuke KOJIMA,^b Yukio OGIHARA,^{*,b} and Ihsan CALIS^a

Department of Pharmacognosy, Faculty of Pharmacy, Hacettepe University,^a TR-06100 Ankara, Turkey and Department of Pharmacognosy, Faculty of Pharmaceutical Sciences, Nagoya City University,^b Tanabe-dori, Mizuho-ku, Nagoya 467–8603, Japan. Received October 22, 1998; accepted December 28, 1998

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 fushii* along with a known phenylethanoid glucoside, plantamajoside, and a flavone glucoside, luteolin 7-O-glucoside.

Key words *Veronica fushii*; Scrophulariaceae; phenylethanoid glycoside; fushioside

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 fushii*, 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 plantamajoside¹²⁾ and **2** as luteolin 7-O-glucoside¹³⁾ 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 C₂₁H₂₄O₁₁. The ¹H- and ¹³C-NMR spectra of **3** revealed the presence of one protocatechuoyl group confirmed

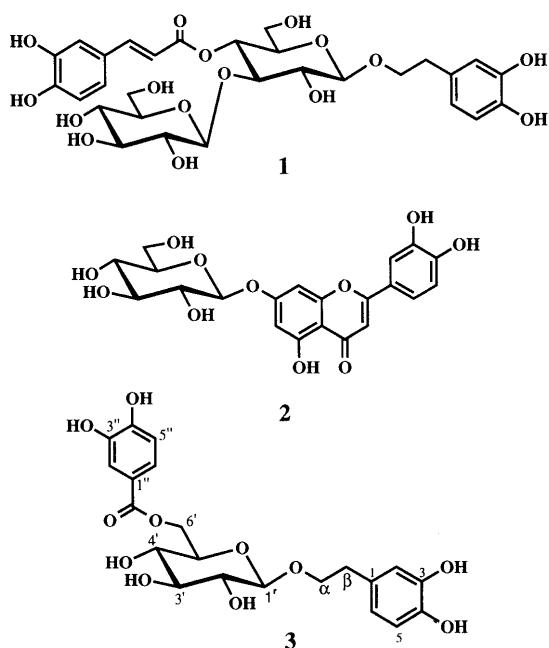
by the ABX-type aromatic protons (δ_{H} 6.77, 7.44, 7.45) and a carbonyl carbon (δ_{C} 168.1), and one 2,3-dihydroxyphenylethyl alcohol, confirmed by ABX-type aromatic groups (δ_{H} 6.48, 6.63, 6.64) and two methylenes which were coupled with each other (α : δ_{H} 3.69, 3.93, δ_{C} 72.2; β : δ_{H} 2.76, δ_{C} 36.5).

The signals assigned to the sugar moiety indicated the presence of a glucose unit. In the ¹H- and ¹³C-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. ¹H- and ¹³C-NMR Spectral Data for Compound **3** in Methanol-*d*₄

	C	H
Aglycone		
1	131.3	
2	117.0	6.64 (d, <i>J</i> =2 Hz)
3	145.9	
4	144.5	
5	116.3	6.63 (d, <i>J</i> =8 Hz)
6	121.2	6.48 (dd, <i>J</i> =2, 8 Hz)
α	72.2	3.69 (m)
		3.93 (m)
β	36.5	2.76 (t, <i>J</i> =8 Hz)
Glucose		
1'	104.4	4.32 (d, <i>J</i> =8 Hz)
2'	74.9	3.22 (t, <i>J</i> =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, <i>J</i> =6, 12 Hz)
		4.56 (dd, <i>J</i> =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, <i>J</i> =8 Hz)
6''	123.8	7.44 (dd, <i>J</i> =2, 8 Hz)
C=O	168.1	

a) Signal pattern unclear due to overlapping.



* To whom correspondence should be addressed.

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 trivial 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 CD₃OD 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 H₂O, followed by increasing concentrations of MeOH to yield four main fractions: A—D [fr.A, 9.2 g (H₂O); 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 CHCl₃-MeOH-H₂O (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 chro-

matographed over silica gel by stepwise elution with the CHCl₃-MeOH-H₂O (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 CHCl₃-MeOH-H₂O (80:20:1→70:30:3) solvent system and then rechromatographed over Sephadex LH-20 with MeOH to give **2** (5 mg).

Fuhsioside (3) [α]_D²⁴ -21.1° (*c*=1.2, MeOH). UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm: 220, 242, 264, 290. IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 3370 (OH), 1698 (C=O), 1600, 1510 (arom. ring). FAB-MS *m/z*: 452 [M]⁺, 453 [M+H]⁺. ¹H- and ¹³C-NMR: Table 1.

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