# Fuhsioside, a New Phenylethanoid Glucoside from *Veronica fuhsii*

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

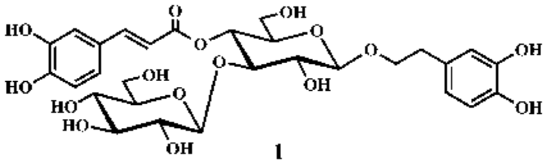
**Key words** *Veronica fuhsii*; Scrophulariaceae; phenylethanoid glycoside; fuhsioside

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)]

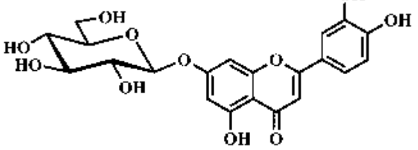
In the previous paper, we reported the structures of iridoid glucosides isolated from *Veronica fuhsii*, which is one of the endemic species distributed in Middle Anatolia.[11)] As a continuation of our studies on the same plant, we report here the isolation and structure elucidation of a new phenylethanoid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

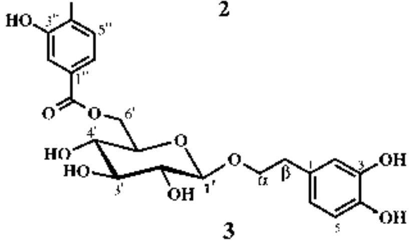
Compound **3** was obtained as a colourless, amorphous solid. UV spectra suggested its polyphenolic nature. The IR spectrum of **3** showed absorption bands for hydroxyl groups (3370 cm$^{-1}$), carbonyl (1698 cm$^{-1}$) and aromatic rings (1510 cm$^{-1}$). Compound **3** showed a $[M]^+$ peak at *m/z* 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 ($\delta_H$ 6.77, 7.44, 7.45) and a carbonyl carbon ($\delta_C$ 168.1), and one 2,3-dihydroxyphenethyl alcohol, confirmed by ABX-type aromatic groups ($\delta_H$ 6.48, 6.63, 6.64) and two methylenes which were coupled with each other ($\alpha$: $\delta_H$ 3.69, 3.93, $\delta_C$ 72.2; $\beta$: $\delta_H$ 2.76, $\delta_C$ 36.5).



**1**



**2**



**3**

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 $\delta_H$ 4.32 (d, $J$=7.9 Hz) and $\delta_C$ 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 $\delta_H$ 4.40 (dd, $J$=6, 12 Hz) and $\delta_H$ 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 $\delta_C$ 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) |
| $\alpha$ | 72.2 | 3.69 (m)<br>3.93 (m) |
| $\beta$ | 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)<br>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-$\alpha$ and H-$\alpha$/C-1′. Therefore, the structure of **3** was identified as 2-(3,4-dihydroxyphenyl)ethyl 6-*O*-protocatechuoyl-$\beta$-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 $\lambda_{max}^{MeOH}$ nm: 220, 242, 264, 290. IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3370 (OH), 1698 (C=O), 1600, 1510 (arom. ring). FAB-MS *m/z*: 452 $[M]^+$, 453 $[M+H]^+$. $^1$H- and $^{13}$C-NMR: Table 1.

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