Chemistry of Natural Compounds, Vol. 43, No. 5, 2007

A NEW FLAVONE GLUCOSIDE FROM *Stachys aegyptiaca*

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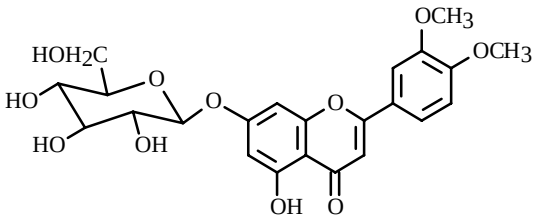
*In addition to 5,7,3′-trihydroxy-6,4′-dimethoxyflavone, 5,7,3′-trihydroxy-6,8,4′-trimethoxyflavone, isoscutellarein, luteolin, and luteolin-7-*O*-glucoside, the methanol extract of the aerial parts of* Stachys aegyptiaca *yielded a new flavone identified as luteolin 3′,4′-dimethylether-7-*O*-β-D-glucoside on the basis of chemical and spectroscopic methods.*

Key words: *Stachys aegyptiaca*, Lamiaceae, new flavone glucoside.

Stachys aegyptiaca is a perenninal plant growing wild in the Sinai desert [1] and proved to be a rich source for flavonoids. We have previously reported the isolation and structure elucidation of diapigenin 7-*O*-(6″-*trans*-6″-*cis*-p,p′-dihydroxy-μ-truxinyl)glucoside [stachysetin] [2] and hypoluetin 7-[6″-acetylallosyl-(1→2)-3″-acetyl-glucoside, along with 24 known flavonoid aglycones and glycosides [3]. Also, the acetylated isoscutellarein glucoside was reported [4]. In continuation of our study on the phenolic constituents of *S. aegyptiaca*, the present communication describes the further isolation and structure elucidation of a new flavone glycoside, the structure of which was identified as luteolin 3′,4′-dimethylether-7-*O*-glucoside from the aerial parts of the same plant.



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The methanol extract of the aerial parts of *S. ageyptiaca* was fractionated on a polyamide column with H_2O as eluent with increasing amounts of MeOH. Isolation and purification were achieved by combination of PPC, TLC on silica gel and Sephadex LH-20.

Flavonoid **1** was isolated as a yellowish white amorphous powder. Acid hydrolysis of **1** afforded glucose, which was identified by co-chromatography with authentic samples and the aglycone **1a**. The UV spectral data of **1a** with diagnostic shift reagents [5] indicated a flavone, absence of a free *ortho*-dihydroxyl pattern, occupation at positions-3′ and -4′, and a free hydroxyl group at position-7. The UV spectral data of **1** indicated a flavone with occupation at positions-7,3′ and -4′ [5].

The EI-MS spectrum of permethylated [6] **1** gave a molecular ion peak at *m/z* 546 (66%) in accordance with fully methylated luteolin glucoside. A fragment at *m/z* 328 was due to the aglycone luteolin bearing three methoxyl groups. The identity of the glucose moiety was confirmed by the fragment at *m/z* 218 due to the ion $[glucose\text{-}H]^+$ and the fragment at *m/z* 187 for the ion $[glucose\text{-}MeOH]^+$.

The ^1H NMR spectrum of **1** showed that it is a monoglucoside of luteolin dimethylether on the basis of the signal H-1 glucose (δ 5.1), and the coupling constant (J = 7.5 Hz) is characterized for a β-linked glucose. Furthermore, the chemical shift (δ 5.1) confirmed that the glucose is directly attached to the aglycone [7]. The spectrum also showed signals at δ 7.4 and δ 6.9 (m; d, J = 8.0 Hz) assigned for H-2′,6′ and H-5′, confirming the disubstituted pattern at ring-B. Two doublets (J = 2.5 Hz) at

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 0009-3130/07/4305-0542

δ 6.8 and δ 6.4 were assigned for H-8 and H-6, while H-3 appeared as a singlet at δ 6.75. The two methoxyls groups appeared as two singlets at δ 3.95 and δ 3.90.

The ^{13}C NMR spectrum confirmed that **1** is a monoglucoside of luteolin on the basis of C-6 glucose (δ 61.0). The ^{13}C NMR shifts of the aglycone part of **1** correspond with the shifts of luteolin [8], the only difference being a downfield shift of the signal assigned to C-3′ and C-4′ by approximately 3.7 ppm, confirming the location of the –OCH_3 groups at C-3′ and C-4′. Also the signal assigned to C-7 was shifted upfield by approximately 2 ppm and there was a downfield shift of about 1.8 ppm for the *para*-related carbon (C-10). These shifts are analogue to those reported when the hydroxyl group is glycosylated at C-7 in flavonoids [9 – 11]. The assignments of the glucose carbons in **1** are based on those given in the literature [7, 11, 12]. From the above data, compound **1** is identified as luteolin 3′,4′-dimethylether-7-*O*-*β*-D-glucoside.

EXPERIMENTAL

Plant Material. *S. aegyptiaca* aerial parts were collected around the Suez Canal University guest house at Saint Catherine, Sinai, in March 2004.

Extraction and Isolation. Dried plant (1.25 kg) was extracted with 80% MeOH. The concentrated extract was subjected to a polyamide column eluted with a H_2O-MeOH mixture with increasing amounts of MeOH. PPC using H_2O, 15% AcOH, BAW (*n*-BuOH–AcOH–H_2O, 4:1:5, upper phase) afforded pure samples of the known flavonoids and the aglycone **1a**. A combination of TLC ($CHCl_3$–MeOH–H_2O, 45:30:2) and Sephadex LH-20 (MeOH) afforded compound **1**.

Luteolin 3′,4′-dimethylether-7-*O*-*β*-D-glucoside (1). UV spectra (MeOH, λ_{max}, nm): 255, 267, 352; +NaOMe: 265, 397; +$AlCl_3$: 273, 297, 330sh, 422; $AlCl_3$+HCl: 260, 275, 297, 350, 385; NaOAc: 260, 370; NaOAc+ H_3BO_3: 260, 370. ^{1}H NMR (270 MHz, DMSO-d_6, δ, J/Hz): 7.40 (2H, m, H-2′,6′), 6.90 (1H, d, J = 8.0, H-5′), 6.80 (1H, d, J = 2.5, H-8), 6.75 (1H, s, H-3), 6.40 (1H, d, J=2.5, H-6), 5.1 (1H, d, J = 7.5 Hz, H-1 glu), 3.95 (3H, s, -OCH_3), 3.90 (3H, s, -OCH_3). ^{13}C NMR (270 MHz, DMSO-d_6, δ): 55.0 (-OCH_3), 55.8 (-OCH_3), 61.0 (C-6″), 69.6 (C-4″), 73.5 (C-2″), 76.2 (C-3″), 77.2 (C-5), 94.5 (C-8), 99.8 (C-6), 100.0 (C-1), 103.0 (C-3), 105.0 (C-10), 111.0 (C-2′),120.0 (C-6′), 124.5 (C-1′), 149.5 (C-3′), 151.5 (C-4′), 152.5 (C-5′), 158.9 (C-9), 161.0 (C-5), 162.7 (C-7), 164.4 (C-2),182.0 (C-4).

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