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A Flavone Glycoside from *Angelica gigas* Roots

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Abstract – A flavone glycoside was isolated from the roots of *Angelica gigas* (Umbelliferae) and identified as diosmin [diosmetin-7-*O*-α-L-rhamnopyranosyl (1 → 6)-β-D-glucopyranoside] by spectroscopic methods. This is the first report of a flavone gylcoside from *Angelica* species.
Key words – *Angelica gigas*, Umbelliferae, flavone glycoside, diosmin.

Introduction

Angelica gigas is genus of the family Umbelliferae. *A. gigas* grows on moist soils of Korea. The roots of this plant were used under the Korean name Zam Dang Gui. *A. gigas* has been used as traditional medicine not only for treatment anemia but also as a sedative, an anodyne or a tonic agent (Yook, 1990).

A. gigas has been studied extensively and are shown to contain a variety of substances including coumarins (Chi, 1969; Jung *et al.*, 1991; Konoshima *et al.*, 1968; Pachaly *et al.*, 1996; Ryu *et al.*, 1990), essential oils (Chi and Kim, 1988) and polyacetylenes (Choi *et al.*, 2000).

In the previous paper, we reported the isolation of coumarins and uracil from *A. gigas* roots (Lee *et al.*, 2002).

Our continuing phytochemical investigation from the roots of *A. gigas* has resulted in the isolation of a flavone glycoside, which was isolated for the first time from this plant.

Experimental

Instruments and reagents – Positive FAB- and EI-MS spectra were measured with Jeol JMS-AX505WA mass spectrometer. ^{1}H-, ^{13}C-NMR and HMBC spectra were recorded with Bruker AVANCE 400 NMR spectrometer in DMSO-d_6 using TMS as an internal standard. IR spectrum was recorded with Jasco FT/IR-300E instrument on KBr disc. Other reagents were commercial grade without purification.

Plant materials – The roots of *Angelica gigas* Nakai were purchased from Kyung Dong market in March 2001, Korea and verified by Prof. Emeritus H. J. Chi, Seoul National University, Korea. A voucher specimen has been deposited at the Herbarium of Natural Products Research Institute, Seoul National University, Korea.

Extraction and isolation – The air-dried powdered roots (5 kg) of *A. gigas* were extracted and subfractionated by same method described as earlier (Lee *et al.*, 2002). The portion of *n*-BuOH fraction (20 g) was chromatographed on silica gel eluting with a gradient of $CHCl_3$-MeOH to afford compound **1** (15 mg).

Compound **1**; FAB-MS, *m/z* 609 $[M + H]^+$; ^{1}H-NMR, (400 MHz, DMSO-d_6) δ: 12.93 (1H, *s*, 5-OH), 7.57 (1H, *dd*, 8.5, 2.1, H-6'), 7.45 (1H, *d*, 2.1, H-2'), 7.14 (1H, *d*, 8.5, H-5'), 6.83 (1H, *s*, H-3), 6.77 (1H, *d*, 2.1, H-8), 6.46 (1H, *d*, 2.1, H-6), 3.88 (3H, *s*, 4'-OCH_3); ^{13}C-NMR, (100 MHz, DMSO-d_6) δ: 181.9 (C-4), 164.2 (C-2), 162.9 (C-7), 161.2 (C-5), 156.9 (C-9), 151.3 (C-4'), 146.8 (C-3'), 122.9 (C-1'), 118.9 (C-6'), 113.1 (C-2'), 112.2 (C-5'), 105.4 (C-10), 103.8 (C-3), 100.5 (C-1'''), 99.9 (C-1''), 99.5 (C-6), 94.8 (C-8), 76.2 (C-3''), 75.6 (C-5''), 73.1 (C-2''), 72.0 (C-4'''), 70.7 (C-2'''), 70.3 (C-3'''), 69.5 (C-4''), 68.3 (C-5'''), 66.0 (C-6''), 55.8 (4'-OCH_3), 17.8 (C-6'''); IR, ν_{max} (KBr) cm^{-1}: 3424 (OH), 1733 (CO).

Acid hydrolysis of 1 – A MeOH soln. of **1** in 2 N HCl heated at 100° for 1 hr gave diosmetin, L-rhamnose and D-glucose identified by EI-MS, ^{1}H- and ^{13}C-NMR analysis (Han *et al.*, 1987; Son *et al.*, 1994).

Results and Discussion

The roots of *A. gigas* were extracted with MeOH. The MeOH extract was suspended in water, and then fractionated successively with equal volumes of Et_2O and *n*-BuOH. The *n*-BuOH extract was purified by chromatography on silica gel to afford compound **1**.

Compound **1** was obtained as white-yellow crystals from

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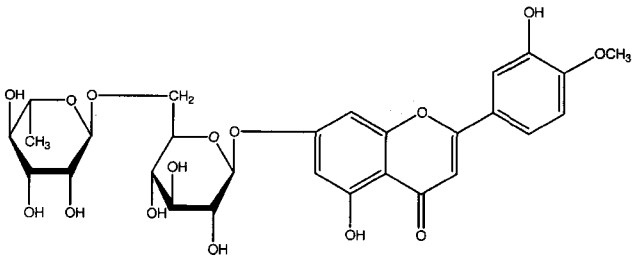

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MeOH. The positive FAB-MS of **1** showed an ion $[M + H]^+$ at *m/z* 609. In the ^{1}H-NMR spectrum, the typical flavonoid signals were observed. The singlet at δ 12.62 assigned the aromatic 5-OH of (A) ring of a flavonoid. The proton signals at δ 8.02 (d, J = 1.9 Hz), δ 7.50 (dd, J = 1.9, 8.4 Hz) and δ 6.90 (d, J = 8.4 Hz) showed ABX splitting pattern of (B) ring of a flavonoid. The singlet signal at δ 3.85 was 4'-OCH_3 by HMBC assignments and the proton signals at δ 3.00-5.00 showed glycosides. Its ^{13}C-NMR spectrum of **1** showed C=O at δ 177.8 and OCH_3 at δ 56.4. The anomeric protons of glucose and rhamnose showed at δ 5.51 (d, J = 7.7 Hz) and δ 4.55 (s), respectively. According to the coupling constant of an anomeric proton, glucose attached to 7-OH of aglycone, diosmetin. And in the ^{13}C-NMR spectrum, the terminal sugar was determined as a rhamnose by lowfield chemical shift of glucose C-6 methylene (δ 66.0). The carbon signals at δ 99.9 and δ 100.5 showed glucosyl C-1" and rhamnosyl C-1"', respectively. The IR spectrum of **1** indicated the presence of hydroxy at 3424 cm^{-1} and carbonyl group at 1733 cm^{-1}. The acid hydrolysis of **1** yielded diosmetin, L-rhamnose and D-glucose identified by EI-MS, ^{1}H- and ^{13}C-NMR analysis. Consequently, the structure of **1** was established as diosmin [diosmetin-7-*O*-α-L-rhamnopyranosyl (1 →)-β-D-glucopyranoside].

There have been no previous reports of flavone glycosides from *Angelica* species. To our knowledge, this is the first report of a flavone gylcoside from *Angelica* species. It is reported the isolation of diosmin from *Evodia rutaecarpa* (Kang *et al.*, 1997).

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References

Chi, H-J. and Kim, H. S., Studies on the essential oils of plants of *Angelica* genus in Korea (I). Essential oils of *Angelicae gigantis* Radix. *Kor. J. Pharmacogn.* **19**, 239-247 (1988).

Chi, H-J., Studies on the components of Umbelliferous plants in Korea (IV). *Yakhak Hoeji* **13**, 47-50 (1969).

Choi, Y. E., Ahn, H. and Ryu, J-H., Polyacetylenes from *Angelica gigas* and their inhibitory activity on nitric oxide synthesis in activated macrophages. *Biol. Pharm. Bull.* **23**, 884-886 (2000).

Han, Y. N., Noh, D. B. and Han, D. S. Studies on the monoamine oxidase inhibitors of medicinal plants I. Isolation of MAO-B inhibitors from *Chrysanthemum indicum. Arch. Pharm. Res.* **10**, 142-147 (1987).

Jung, D. J., Porzel, A. and Huneck, S., Gigasol and other coumarins from *Angelica gigas. Phytochemistry* **30**, 710-712 (1991).

Kang, S. S., Um, B. H., Kim, J. S. and Ahn, B. T., Isolation of flavonoids from Evodiae Fructus. *Kor. J. Pharmacogn.* **28**, 9-14 (1997).

Konoshima, M., Chi, H-J. and Hata, K., Coumarins from the root of *Angelica gigas* Nakai. *Chem. Pharm. Bull.* **16**, 1139-1140 (1968).

Lee, S., Kang, S. S. and Shin, K. H., Coumarins and a pyrimidine from *Angelica gigas* roots. *Nat. Prod. Sci.* **8**, 58-61 (2002).

Pachaly, P., Treitner, A. and Sin, K. S., Neue Cumaringlykoside aus *Angelica gigas. Pharmazie* **51**, 57-61 (1996).

Ryu, K. S., Hong, N. D., Kim, N. J. and Kong, Y. Y., Studies on the coumarin constituents of the root of *Angelica gigas* Nakai. Isolation of decursinol angelate and assay of decursin angelate and decursin. *Kor. J. Pharmacogn.* **21**, 64-68 (1990).

Son, K. H., Kim, J. S., Kang, S. S., Kim, H. P. and Chang, H. W. Isolation of flavonoids from *Lonicera japonica. Kor. J. Pharmacogn.* **25**, 24-27 (1994).

Yook, C. S., Coloured medicinal plants of Korea, Academy Book Co. Seoul, Korea, 1990, p. 390.

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