Natural Product Sciences
8(4) : 141-143 (2002)

Flavone Glucosides from the Leaves of *Helianthus tuberosus*

Sungwook Chae[1,2], Sanghyun Lee[2], Sam Sik Kang[2], and Ho Jin Lee[1]

[1]*School of Plant Science, Seoul National University, Suwon 441-744, Korea*
[2]*Natural Products Research Institute and College of Pharmacy, Seoul National University, Seoul 110-460, Korea*

Abstract – Two flavone glucosides have been isolated from the leaves of *Helianthus tuberosus* (jerusalem artichoke). Their structures were identified as kaempferol 3-*O*-glucoside (**1**) and quercetin 7-*O*-glucoside (**2**) by spectroscopic analysis and confirmed by comparison with reported data. These flavonoids were isolated for the first time from this plant part.
Keywords – *Helianthus tuberosus*, Compositae, kaempferol 3-*O*-glucoside, quercetin 7-*O*-glucoside.

Introduction

Helianthus tuberosus, which is native to North America, belongs to the family Compositae. It was called as 'Askipaw' or 'Skibwan' by America indian and cultivated to make so called Pottage soup or eaten raw as the word Skibwan means raw itself (Kosaric *et al.*, 1984).

H. tuberosus, one of the crops that native Americans cultivated in 17C, was introduced to Europe. *H. tuberosus* tolerates blight and grows in infertile soil. It has been appreciated that *H. tuberosus* produces and stores D-fructose polymer as nutrient. This fact raises interests in the usage of D-fructose polymer in food application. Previous phytochemical investigations on this plant have resulted in isolation of coumarins (Francisco *et al.*, 1998), sesquiterpene alcohols (Mitsuo and Hiromu, 1983), carbohydrates (Bacon, 1951), and a sesquiterpene lactone such as heliangine (Morimoto *et al.*, 1966; Shinobu *et al.*, 1967).

Thus, understanding of the chemical constituents from jerusalem artichoke could be the way for obtaining useful secondary metabolites.

This paper describes the chemical constituents from the leaves of *H. tuberosus*.

Experimental

General – The ^{1}H and ^{13}C-NMR spectra were recorded with Bruker AVANCE 400 NMR spectrometer. MS spectra were measured with Jeol JMS-AX505WA mass spectrometer. IR spectra were recorded with JASCO FT/IR-300E instrument on KBr disc.

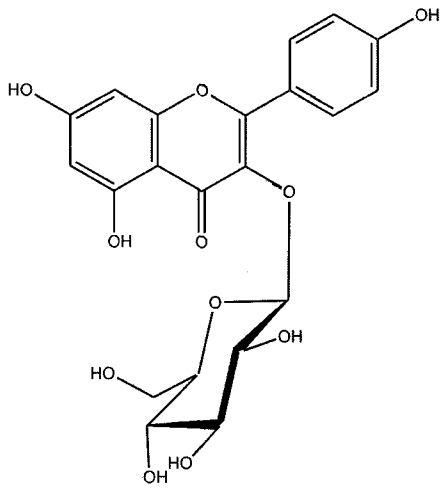
*Author for correspondence, E-mail address: hojinlee@snu.ac.kr

Plant Materials – The leaves of *Helianthus tuberosus* L. were collected at the College of Agriculture & Life Sciences, Seoul National University, Suwon, Korea.

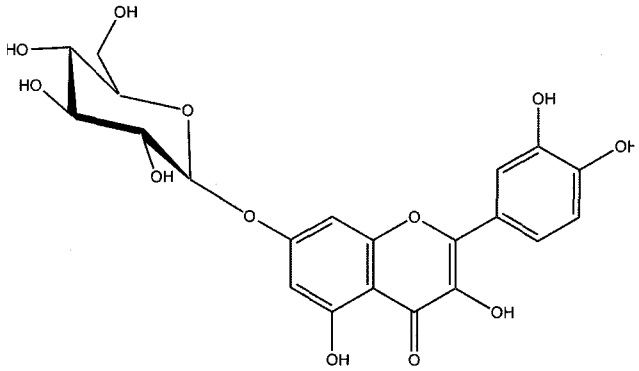
Extraction and Isolation – Two hundred grams of the dried leaves were ground and extracted with methanol for 3 hrs three times under reflux. The combined filtrate was evaporated under reduced pressure to dryness, which was partitioned with *n*-hexane, ethyl acetate and *n*-butanol to give 3 fractions. Ethyl acetate fraction was chromatographed over a column of silica gel (Kieselgel 60, Merck 7734). The column was eluted with a gradient of *n*-hexane : ethyl acetate and ethyl acetate : methanol to give 25 subfractions. Among them, compounds **1** (30 mg) and **2** (7 mg) were obtained from subfractions 16 and 17, respectively.

Compound 1 – (Kaempferol 3-*O*-glucoside): Yellow crystal; IR (KBr) cm^{-1}: 3432, 1654, 1605, 1499, 1266, 1180, 1017; ^{1}H-NMR (DMSO-d_6, 400 MHz) δ_H (ppm) : 12.61 (1 H, s, 5-OH), 10.23 (1 H, br s,-OH), 8.03 (2 H, d, J = 8.7 Hz, H-2' and 6'), 6.87 (2 H, d, J = 8.7 Hz, H-3' and 5'), 6.43 (1 H, d, J = 1.8 Hz, H-8), 6.20 (1 H, d, J = 1.8 Hz, H-6), 5.45 (1 H, d, J = 7.2 Hz, H-1"); ^{13}C-NMR (DMSO-d_6, 100 MHz) δ_c (ppm): 177.9 (C-4), 164.6 (C-7), 161.6 (C-5), 160.4 (C-4'), 156.8 (C-9 or C-2), 156.7 (C-2 or C-9), 133.6 (C-3), 131.3 (C-2'), 121.3 (C-1'), 115.5 (C-3' and 5'), 104.4 (C-10), 101.2 (C-1"), 99.1 (C-6), 94.1 (C-8), 77.9 (C-3"), 76.8 (C-5"), 74.6 (C-2"), 70.3 (C-4"), 61.0 (C-6"); EI-MS, *m/z* (rel. int., %) 286 [kaempferol]$^+$ (100), 153 (5), 134 (3), 105 (2.5); FAB-MS, *m/z* 449 [M + H]$^+$.

Compound 2 – (Quercetin 7-*O*-glucoside): Yellow crystal; IR (KBr) cm^{-1}: 3420, 1654, 1596, 1498, 1074; ^{1}H-NMR (DMSO-d_6, 400 MHz) δ_H (ppm) : 12.52 (1 H, s, 5-OH), 7.72 (1 H, d, J = 1.7 Hz, H-2'), 7.55 (1 H, dd, J = 1.7, 6.6 Hz, H-6'), 6.89 (1 H, d, J = 6.6 Hz, H-5'), 6.76 (1 H, d, J = 1.6 Hz,



1



2

H-8), 6.42 (1 H, d, J = 1.6 Hz, H-6), 5.04 (1 H, d, J = 7.4 Hz, H-1); ^{13}C-NMR (DMSO-d_6, 100 MHz) δ_c (ppm): 176.0 (C-4), 162.7 (C-7), 160.4 (C-5), 155.7 (C-9), 147.9 (C-2' or 4'), 147.6 (C-4' or C-2'), 145.0 (C-3'), 136.0 (C-3), 121.8 (C-1'), 120.0 (C-6'), 115.6 (C-2' or C-5'), 115.4 (C-5' or 2'), 104.6 (C-10), 99.8 (C-1"), 98.7 (C-6), 94.2 (C-8), 77.1 (C-3"), 76.4 (C-5"), 73.1 (C-2"), 69.5 (C-4"), 60.6 (C-6"); EI-MS, *m/z* (rel. int., %) 302 [quercetin]$^+$ (100), 153 (7); FAB-MS, *m/z* 465 [M + H]$^+$.

Results and Discussion

The chromatographic separation of the ethyl acetate fraction from *H.* tuberosus led to the isolation of two flavonoids: kaempferol 3-*O*-glucoside (**1**) and quercetin 7-*O*-glucoside (**2**).

The IR spectrum of **1** showed absorption bands for hydoxyl at 3432, α,β-unsaturated C=O at 1654, aromatic C=C stretching at 1605 and 1499, aromatic C-O at 1266 and phenolic OH at 1180 cm^{-1}. In the ^{1}H-NMR spectrum of **1**, the typical flavonoid signals were observed. The singlet at δ12.61 showed flavonoid chelated 5-OH. The proton signals at δ8.03 (2 H, d, J = 8.7 Hz), and 6.87 (2 H, d, J = 8.7 Hz) showed A_2B_2 splitting pattern of B ring. The proton signals at 3.0-5.5 showed glucose. Due to the chemical shift of C-3 of kaempferol changed from 135.6 to 133.6 and anomeric proton signal of glucose at 5.45 (1 H, d, J = 7.8 Hz), glucose was β-linkage at C-3 of aglycone. The ^{13}C-NMR spectrum of **1** showed C=O at δ177.9. The carbon signal at δ101.2 showed glucosyl C-1". In the EIMS of **1**, the aglycone peak showed at *m/z* 286 as a base peak. The characteristic fragment ion peaks at 105, 134 and 153 showed the *retro* Diels Alder fragmentation of flavonoid (Markham, 1982). The FABMS of **1** showed [M + H]$^+$ peak at *m/z* 449. The molecular formula of **1** was determined to be $C_{21}H_{20}O_{11}$. Accordingly, the structure of **1** was elucidated as kaempferol 3-*O*-glucoside.

Kaempferol (3,5,7,4'-tetrahydroxyflavone) and its 3-*O*-glucoside caused significant inhibition of HIV-1 infection at non-toxic concentration (Corrado, 2001).

The IR spectrum of **2** showed absorption bands for hydoxyl at 3420, α,β unsaturated C=O at 1654, aromatic C=C stretching at 1596 and 1498 cm^{-1}. In the ^{1}H-NMR spectrum of **2**, the typical flavonoid signals were observed. The singlet at δ12.52 showed 5-OH. The proton signals at δ7.72 (1 H, d, J = 1.7 Hz), δ7.55 (1 H, dd, J = 1.7, 6.6 Hz) and δ6.89 (1 H, d, J = 6.6 Hz) showed ABX splitting pattern of B ring. The proton signals at 3.0-5.5 showed glucose. Due to the chemical shift of C-7 of quercetin changed from δ164.5 to δ162.8 and anomeric proton signal of glucose at δ5.04 (1 H, d, J = 7.4Hz), glucose was β-linkage at C-7 of aglycone. The ^{13}C-NMR spectrum of **2** showed C=O at δ176.0. The carbon signal at δ99.8 showed glucosyl C-1". In the EIMS of **2**, the aglycone peak showed at *m/z* 302 as a base peak. The characteristic fragment ion peaks at 153 showed the *retro* Diels Alder fragmentation of flavonoid (Markham, 1982). The FABMS of **2** showed [M + H]$^+$ peak at *m/z* 465. The molecular formula of **2** was determined to be $C_{21}H_{20}O_{12}$. Accordingly, the structure of **2** was elucidated as quercetin 7-*O*-glucoside.

Quercetin 7-*O*-glycoside showed the antibacterial activity against *Pseudomonas maltophilia* and *Enterobacter cloacae* (Susan and Paul, 1984).

Kaempferol 3-*O*-glucoside and quercetin 7-*O*-glucoside were isolated for the first time from this plant.

References

Bacon, J. S. D. and Edelman, J., The carbohydrates of the jerusalem artichoke and other Compositae. *Biochem. J.*, **48**, 114 (1951).

Corrado, T., Bioactive compounds from natural sources, Taylor and francis, pp. 315-316 (2001).

Francisco, C. H., Francis, D., Jesus, V. J., and Daniele, W. R., Coumarins in *Helianthus tuberosus*: Characterization, induced accumulation and biosynthesis. *Phytochemistry*, **49**, 1029-1036 (1998).

Kosaric, N., Cosentiono, G. P., Wieczorek, A., and Duvnjak, Z., The jerusalem artichoke as an agricultural crop. *Biomass*, **5**, 1-36 (1984).

Markham, K. R., Techniques of flavonoid identification, Academic press, London, pp. 87-90 (1982).

Mitsuo, M. and Hiromu, K., Helianthol A, a sesquiterpene alcohol from *Helianthus tuberosus*. *Phytochemistry*, **22**, 1040-1042 (1983).

Morimoto, H., Sanno, Y., and Oshio, H., Chemical studies on heliangine: A new sesquiterpene lactone isolated from the leaves *of Helianthus tuberosus* L., *Tetrahedron*, **22**, 3173-3179 (1966).

Shinobu I., Nobutaka T., and Saburo T., Chemistry of heliangine: Part II. Analyses of an ABC system in the 60 and 100 Mc NMR spectra of helianginone. *Agr. Biol. Chem.*, **31**, 240-244 (1967).

Susan K. W. and Paul A. H., Biologically active flavonoids from *Gossypium arboreum*. *Phytochemistry*, **23**, 2509-2511 (1984).

(Accepted December 10, 2002)