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Two Minor Furanocoumarins of *Angelica dahurica*

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Abstract □ Two minor constituents were isolated from the roots of *Angelica dahurica* and identified as isooxypeucedanin and gosferol, respectively.

Keywords □ *Angelica dahurica*, Umbelliferae, furanocoumarins, isooxypeucedanin, gosferol

Angelica dahurica Benth. et Hook. (Umbelliferae) is a perennial herb, mainly grown in Korea and Japan, the roots of which are most frequently prescribed as a sedative and an analgesic in Chinese medicine under the local name of "Baik-Chi", while two varieties such as *A. dahurica* Benth. et Hook. var. *formosana* Yen and *A. dahurica* Benth. et Hook. var *Pai-Chi* Kimura Hata et Yen are occasionally prescribed as the same name and the same use. With regard to the constituents of Baik-Chi, various linear furanocoumarins have been extensively studied[1-4], and further their potent hepatic enzyme inhibitory activities have recently been demonstrated[4].

During the course of a chromatographic screening of the roots of *A. dahurica* Benth. et Hook, the presence of two distinct fluorescent compounds not previously reported from this plant were noticed. This paper deals with the isolation and characterization of these minor compounds.

The first compound (**1**), mp. 105-108° was identified as isooxypeucedanin by direct comparison of spectral data, co-TLC and mixed melting point with an anthentic sample[5].

The second compound (**2**), mp. 128-131°, showed the UV spectrum exhibiting three strong bands at 252, 269 and 310 nm, typical of 5-substituted linear furanocoumarin and IR spectrum showing the presence of hydroxyl (3430 cm^{-1}), α-pyrone (1715 cm^{-1}) and an aromatic ring system (1620 cm^{-1}). Its NMR spectrum showed two one proton doublets at δ 6.28 and 8.18 attributable to the protons of the pyrone ring and two one proton doublets at δ 6.96 and 7.60, assignable to the protons of furan ring. The appearance of the signal for H-4 in rather lower field and further splitting of the doublet arising from H-3′ by long-range coupling strongly suggested the presence of an oxygen atom at C-5 position. Inspection of the high-field signals indicated the presence of 2-hydroxy-3-methyl but-3-enyl unit.

The three proton multiplet at ca δ 4.45 has been assigned to the two methylene protons (H-1″) and the adjacent methine proton (H-2″) and the signal at δ 5.37 disappearing in D_2O to the hydroxyl proton. A three proton singlet at δ 1.83 has been attributed to the vinyl methyl and the signals at δ 5.07 and δ 5.19 to terminal CH_2 group. The presence of the hydroxyl group as -CH-OH was corroborated from the analysis of the NMR spectrum of its acetate (Compound **3**), in which the carbinol methine proton appeared down field at δ 5.65. All these spectral data together with its optical data led to the conclusion that compound **2** was gosferol, which was first isolated from *Prangos ferulacea* root[6].

EXPERIMENTAL

Melting points were determined on a Mitamura-Riken apparatus and uncorrected. IR spectra were recorded on a Perkin-Elmer 283 B spectrophotometer. Optical rotations were measured on a Rudoloph Autopol III polarimeter. NMR spectra were obtained on a varian FT-80A spectrometer. EIMS were determined on a Hewlett-Packard 5985B GS/MS system.

Plant material

The roots of *Angelica dahurica* Benth. et Hook were purchased from local market and were botani-

cally identified by prof. H.J. Chi of this Institute, where a voucher specimen has been deposited.

Extraction and isolation

Coarsely powdered plant material (3 kg) was extracted three times with methanol under reflux. The extract was concentrated under reduced pressure and partitioned between hexane: methanol: H_2O (10: 1:9). The hexane extract (28.4 g) obtained by removal of the solvent was chromatographed on silica gel column. Gradient elution with n-hexane-ether with increasing proportions of ether gave isoimperatorin (1.58 g), imperatorin (2.47 g), phellopterin (0.73 g), isooxypeucedanin (**1**) (0.11 g) and gosferol (**2**) (0.05 g).

Isooxypeucedanin (1)

Pale greenish yellow fluorescence under UV light; mp. 105-108° (MeOH); MS *m/z* (rel. int.): 286 (M^+, 44.4), 215 (M-C_4H_7O, 35.1), 201 (M-C_5H_9O, 22.7), 187 (215-CO, 42.6), 145 (20.5), 89 (C_7H_5, 17.9), 71 (C_4H_7O, 48.3); UV λ_{max}^{MeOH} nm (log ε): 250 (4.57), 266 (4.54), 311 (4.45); IR ν_{max}^{KBr}: 1740, 1720, 1620, 1580, 1460 cm^{-1}; ^{1}H-NMR (80 MHz, $CDCl_3$) δ: 1.18 (6H, d, J=7 Hz, CH_3×2), 2.86 (1H, m, H-3″), 5.05 (2H, s, H-1″), 6.25 (1H, d, J=9.8 Hz, H-3), 6.80 (1H, dd, J=2.4 & 1 Hz, H-3′), 7.20 (1H, d, J=1 Hz, H-8), 7.57 (1H, d, J=2.4 Hz, H-2′), 8.25 (1H, d, J=9.8 Hz, H-4).

Gosferol (2)

Yellow fluorescence under UV light; mp. 128-131° (MeOH); $[\alpha]_D^{25}=0$ (c=1, EtOH); UV λ^{MeOH} nm (log ε), 252 (3.86), 269 (3.78), 310 (3.72); IR ν_{max}^{KBr} (cm^{-1}): 3430, 1715, 1695, 1620, 1455, 890; ^{1}H-NMR (80 MHz, $CDCl_3$) δ; 1.83 (3H, bs, H-4″), 5.07 (1H, bs, H-5a″), 5.19 (1H, bs, H-5b″), 4.45 (3H, m, H-1″, and H-2″), 6.28 (1H, d, J=9.8 Hz, H-3), 6.96 (1H, dd, J=1 & 2.3 Hz, H-3′), 7.17 (1H, bs, H-8), 7.60 (1H, d, J=2.3 Hz, H-2′), 8.18 (1H, d, J=9.8 Hz, H-4); MS *m/z* (rel. int.): 286 (M^+, 8.9), 215 (M-C_4H_7O, 2.7), 202 (M-C_5H_8O, 100), 174 (202-CO, 43.3), 145 (174-CHO, 8.0).

Gosferol acetate (3)

A soln of gosferol (20 mg) in a mixture of pyridine (1 m*l*) and acetic anhydride (1 m*l*) was kept to stand at room temp. for 24 hr. The reaction mixture was treated in the usual way and the product purified by prep TLC to afford gosferol acetate as needles, mp. 81-85°; IR ν_{max}^{KBr} (cm^{-1}): 1740, 1625, 1460, 1240, 890; ^{1}H-NMR (80 MHz, $CDCl_3$) δ: 1.83 (3H, bs, H-4″), 2.10 (3H, s, OAc), 5.08 (1H, bs, H-5a″), 5.13 (1H, bs, H-5b″), 4.52 (2H, d, J=5.5 Hz, H-1″), 5.65 (1H, t, J=5.5 Hz, H-2″), 6.28 (1H, d, J=9.8 Hz, H-3), 6.92 (1H, dd, J=1 & 2.3 Hz, H-3′), 7.15 (1H, bs, H-8), 7.60 (1H, d, J=2.3 Hz, H-2′), 8.10 (1H, d, J=9.8 Hz, H-4); MS *m/z* (rel. int.): 328 (M^+, 0.9), 215 (M-$C_6H_9O_2$, 1.5) 202 (M-$C_7H_{10}O_2$, 23.4), 174 (202-CO, 7.1), 145 (174-CHO, 7.3).

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