NOTE

Chemotaxonomic Significance of Oregonin in *Alnus* Species

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A diarylheptanoid, (5S)-1,7-bis-(3,4-dihydroxyphenyl)-5-hydroxyheptane-3-on-5-O- β -D-xylopyranoside, named as oregonin (**1**), was isolated from the bark of *Alnus pendula* Matsumura which is a species of the genus *Alnus* species, growing throughout Korea. The structure elucidation was accomplished by various spectroscopic methods including negative FAB-MS, ^1H NMR and ^{13}C NMR techniques or comparison with authentic samples.

Key Words: *Alnus pendula*, Betulaceae, Diarylheptanoid, Chemotaxonomy.

Genus *Alnus* refers to deciduous broad-leaved trees or shrubs found in damp areas and mountains and comprises of more than 17 species, *Alnus borealis* Koidzumi, *Alnus firma* Sieb. et Zucc., *Alnus hirtella* Koidz., *Alnus hirsuta* Turcz., *Alnus hirsuta* Turcz. var. *sibirica* Fischer, *Alnus japonica* Steudel, *Alnus maritima* var. *arguta* Regel., *Alnus japonica* Thunb. var. *koreana* Callier, *Alnus japonica* Thunb. var. *reginosa* Nakai, *Alnus japonica* Thunb. var. *serrata* Nakai, *Alnus mandshurica* Callier, *Alnus mandshurica* Thunb. for. *barbinervis*, *Alnus mandshurica* Thunb. for. *pubescens* Kitagawa, *Alnus maximowiczii* Call, *Alnus mayrii* Call, *Alnus pendula* Matsum., *Alnus vermicularis* Nakai are growing in Korea¹. The bark of *Alnus pendula* (bar code; PB 2368.2) as well as MeOH extracts of *Alnus pendula* (leaf, bar code; PB 2368.1), *Alnus firma* (fruit, stem, leaf, flower, bar code; PB 2366.1-4) and *Alnus maximowiczii* (flower, bark, leaf, bar code; PB 2364.1-3) were purchased from the Korea Plant Extract Bank in October 2008.

Diarylheptanoids are characteristic components of the *Alnus* species^{2,3}. Several interesting biological activities of diarylheptanoids including their antiinflammatory⁴⁻⁷ and antioxidant properties⁸ have previously been reported. In a previous study conducted in our lab, quantitative analysis of diarylheptanoids including oregonin (**1**) was conducted using HPLC on *Alnus japonica*, *Alnus hirsuta* and *Alnus hirsuta* var. *sibirica*⁹. Here, as part of our continuous search for diarylheptanoids from new natural sources, we describe the isolation and identification of oregonin (**1**) from the bark of *Alnus pendula* and screening of oregonin (**1**) from some other

Alnus species [*Alnus firma* (fruit, stem, leaf, flower) and *Alnus maximowiczii* (flower, bark, leaf)].

Chemical structures of compound **1** isolated from *Alnus pendula* Matsumura

Extraction and isolation: The dried and powdered bark (300 g) of *Alnus pendula* was extracted using 80 % aqueous acetone at room temperature for 3 days. The filtrate was concentrated and applied to a Sephadex LH-20 column (25-100 μm , 8 $\times$ 150 cm, Pharmacia, Uppsala, Sweden) containing increasing proportions of MeOH (60-100 %) afforded 5 fractions (1-5). Repeated column chromatography of fraction 2 on the MCI-Gel CHP 20P (75-150 μm , 5 $\times$ 80 cm, Mitsubishi Chemical Co., Tokyo, Japan) and then fraction 2-2 on Disogel (40-60 μm , 3 $\times$ 50 cm, Daiso CO., Osaka, Japan) with 30-80 % methanol gradient in middle pressure liquid chromatography (MPLC) system (5 mL/min, 280 nm) resulted in oregonin (**1**).

Oregonin (1): Brown amorphous powder, Negative FAB MS: m/z 477 $[\text{M}-\text{H}]^-$, ^1H NMR (600 MHz, $\text{DMSO}-d_6 + \text{D}_2\text{O}$): δ 6.67-6.60 (4H in total, H-2', 2'', 5', 5''), 6.48-6.45 (2H in total, H-6'', 6'), 4.19 (1H, br d, $J = 7.8$ Hz, xyl-1), 4.03 (1H, m, H-5), 3.76 (1H, dd, $J = 11.4, 6$ Hz xyl-5e), 3.35 (1H, m, xyl-4), 3.08-2.56 (8H in total, H-1, 2, 4, 7), 1.74-1.68 (2H in total, m, H-6)¹⁰⁻¹². ^{13}C NMR (150 MHz, $\text{DMSO}-d_6 + \text{D}_2\text{O}$) (Table-1)¹⁰⁻¹².

TABLE-1
¹³C NMR SPECTRA OF COMPOUND 1

Carbon No.	Compound 1	Carbon No.	Compound 1
C-1	28.7	C-3"	145.1
C-2	45.1	C-4'	143.2
C-3	209.6	C-4"	143.4
C-4	47.5	C-5'	116.0
C-5	76.9	C-5"	116.0
C-6	39.7	C-6'	119.2
C-7	30.5	C-6"	119.3
C-1'	132.4	Xyl-1	102.8
C-1"	133.3	Xyl-2	74.7
C-2'	115.8	Xyl-3	77.0
C-2"	115.8	Xyl-4	69.8
C-3'	145.1	Xyl-5	66.0

 *150 MHz (DMSO-*d*₆ + D₂O)

Quantitative analysis of oregonin (1) of *Alnus pendula* using high pressure liquid chromatography (HPLC): HPLC was used for the quantitative analysis of the oregonin (1) contents. An Waters 600 series HPLC system (Milford, MA, USA), was employed and equipped with a vacuum degasser, a binary pump, a UV detector and column compartment. Oregonin (1) was separated on Kromasil 100-5 C18 (4.6 × 250 mm, 5 μm particle) with an linear gradient water:acetonitrile = 90:10 to 60:40 for 24 min. The column temperature was maintained at room temperature and the flow rate was 1.0 mL/min. The system was monitored at 280 nm ($\lambda_{\max}$ of 1) eluting at 19.09 min. Oregonin (1) was detected in the extracts of only the bark of *Alnus pendula* but not in the leaf extracts of *Alnus pendula*, as well as the extracts of *Alnus firma* (fruit, stem, leaf, flower) and *Alnus maximowiczii* (flower, bark, leaf). We were able to quantify oregonin (1) from the bark extract of *Alnus pendula* (7.69 ± 0.079 %) using a calibration equation ($y = 5201.9x - 47967$; $R^2 = 0.9985$).

Chemotaxonomic significance: This is report on the isolation and identification of oregonin (1) from *Alnus pendula*.

Since the initial isolation of oregonin (1) from *Alnus rubra*¹³ and oregonin (1) has only been distributed among *Alnus hirsuta*³, *Alnus cordata*, *Alnus incana*, *Alnus viridis* and *Alnus glutinosa*¹⁴, *Alnus japonica*¹⁵, *Alnus serrulatoidea*^{11,12} and *Pinus flexilis*¹⁰.

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