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Coumarins of *Angelica deccurens*J. Ganbaatar¹, E.E. Shults², L.D. Radnaeva³, V.V. Taraskin³¹*Institute of Chemistry and Chemical Technology, MAS, Peace avenue, Ulaanbaatar 13330, Mongolia*²*Novosibirsk Institute of Organic Chemistry SB RAS, Lavrentiev ave., 9, Novosibirsk 630090, Russia*³*Baikal Institute of Natural Management, SB RAS, Sakhyanovoy str., 8, Ulan-Ude 670047, Russia*

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Abstract: It was shown that the plant *Angelica deccurens* (Ldb.) B. Fedtsch might be serve as a source of valuable coumarins. Five linear furocoumarins – umbelliferon, isoimperatorin, imperatorin, psoralen and oxypeucedanin have been isolated from the roots of *Angelica deccurens* (Ldb.) B. Fedtsch growing in Mongolia. Molecular structures of these compounds were elucidated by spectroscopic methods. The coumarin psoralen has been isolated for the first time from this plant.

Keywords: Umbelliferae, *Angelica deccurens*, furocoumarins, spectroscopic method

INTRODUCTION

Plants of the Umbelliferae family are known to be a good source of naturally occurring coumarins. Natural coumarins, like other unsaturated lactones, may exert various effects on living organisms, both in plants and in animals. In view of their established low toxicity, relative cheapness, presence in the diet and occurrence in various herbal remedies, it is important to evaluate the properties and applications of coumarins [1].

A.deccurens (Ldb.) B. Fedtsch (Umbelliferae) has traditionally been used in oriental medicine as diuretic; remedy for colds, flu, hepatitis, arthritis, indigestion, coughs, chronic bronchitis, fever, rheumatism, bacterial and fungal infections and diseases of the urinary organs. The roots have been identified as containing a sweat-inducing agent, which is capable of countering harmful external influences on the skin, including cold, heat, dampness, and dryness [2 - 4].

The fruits of *A. deccurens* contain mono- and sesquiterpenoids as myrcene, β -fellandren, α -pinen, β -pinen, α -terpinen, p-cimol, α -bizabolol, β -bizabolen, β -elemen, γ -cadinen, ilangen and gumulen [5]. Coumarins (osthol, oxypeucedanin hydrate and oroselon) have been detected in the roots of *A. deccurens* [6]. Previously, a phytochemical investigation of *Angelica deccurens* growing in Mongolia has not been undertaken. Therefore in continuation of systematic phytochemical research of plants belonging to the Umbelliferae family we have investigated the roots of *Angelica deccurens*.

In this paper we are describing the isolation and characterization of coumarins from the roots of *A. deccurens* (Ldb.) B. Fedtsch growing in Mongolia.

EXPERIMENTAL

Plant material: The root of *A. deccurens* was collected in Dadal soum, Khentei province, Mongolia, during the butonization - flowering period. The voucher specimen was deposited at the Institute of Botany, MAS by Dr. Urgamal M.

The air-dried root (3 kg) was sliced and extracted three times with 70% of EtOH at room temperature. The combined extract was filtered and diluted with distilled water (1:1) and then concentrated *in vacuo* to yield an EtOH extract. The extract was fractionated by solvents with increasing polarity, i.e., *n*-hexane, diethyl ether, ethylacetate and *n*-butanol, respectively. Each fraction was evaporated by a rotary evaporator. Then, the fractions were separated by column chromatography over silica gel.

Melting points were determined on a Stuart SMF-38 instrument. The IR spectra were recorded on a Vector 22 spectrometer in KBr tablet. UV spectra were measured on a Specord UV-Vis spectrophotometer in ethanol ($c = 10^{-4}$ mol/l).

NMR spectra of compounds in $CDCl_3$ or CD_3OD were obtained on Bruker AV-300 (operating frequency (300.13 MHz) for 1H and 75.47 MHz for ^{13}C and AV-600 (600.13 and 150.96 MHz), respectively) spectrometers. Proton-proton and carbon-proton shift correlation spectroscopy COSY, COLOC, NOESY were used for structure elucidation of substances.

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The multiplicity of resonances in ^{13}C NMR spectra was determined by recording spectra in J-mode. A DFS ThermoScientific high-resolution mass spectrometer (ionizing electron energy 70 eV, vaporizer temperature 230-280°C) was used to record mass spectra and determine molecular weights and elemental compositions. Specific rotation $[\alpha]_D$ was measured on PolAAR3005 polarimeter.

RESULTS AND DISCUSSION

The greatest coumarin content was found in the ethylacetate and n-butanolic fractions of the ethanolic extract. The ethylacetate fraction was subjected to a silica gel column chromatography eluted using the solvent systems chloroform, chloroform-methanol 100:1[®]10:1. Umbelliferon (**1**), isoimperatorin (**2**), psoralen (**3**), imperatorin (**4**) and oxypeucedanin (**5**) were isolated from EtOAc and butanolic fractions by silica gel column chromatography with gradient elution using chloroform-methanol.

Molecular structures of the isolated compounds were elucidated by spectral methods. All isolated coumarins were belonged to simple or linear furocoumarins. Results of our study showed that *Angelica deccurens* might be serve as a source of furocoumarins **1-5** which were known that for possessing valuable biological properties [7-12]. Thus, the ultraviolet activity of umbelliferone **1** led to its use as a sunscreen agent, and an optical brightener for textiles [7]. Isoimperatorin **2** is an anti-inflammatory agent [8]. This compound also displayed chemopreventive effects against aflatoxin B-1 on H4IIE cells by increasing GST α activity [9]. Imperatorin **3** is reported to have anticonvulsant and anticancer effects [10]. *Psoralen 3 used for treatment of skin problems such as psoriasis, eczema and vitiligo* [11]. *The coumarin psoralen was isolated for the first time from the roots of the Angelica deccurens.*

Characterization of individual compounds

Umbelliferon (**1**)

White crystal, $\text{C}_9\text{H}_6\text{O}_3$, mp. 231-233°C, IR ν_{max} cm^{-1} : 3182, 1713, 1688, 1622, 1613, 1575, 1512. 821, $^1\text{H-NMR}$ (CDCl_3 , 300 MHz), δ : 6.15 (3H, d, H-3, $J = 9.5$ Hz), 7.79 (1H, d, H-4 $J = 9.5$ Hz), 6.84-6.88 (2H, m, H-6, H-8), 7.42 (1H, d, $J = 8$ Hz, H-5). $^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz), δ : 160.8 (C-2), 111.6 (C-3), 144.3 (C-4), 130.0 (C-5), 113.4 (C-6), 161.7 (C-7), 102.8 (C-8), 155.9 (C-9), 111.6 (C-10).

Isoimperatorin (**2**)

White crystal, $\text{C}_{16}\text{H}_{14}\text{O}_4$, mp. 105-107°C, IR ν_{max} cm^{-1} : 1729 (C=O), 1628, 1604 (aromatic ring, C=C), 1129 (benzofuran), 821, $^1\text{H-NMR}$ (CDCl_3 , 300 MHz), δ : 1.82 (3H, s, H-6''), 1.72 (3H, s, H-5''), 4.94 (2H, d, $J = 6.9$ Hz, H-2''), 5.56 (1H, t-like, $J = 6.9$ Hz, H-3''), 6.29 (1H, d, $J = 9.6$ Hz, H-3), 6.97 (1H, dd, $J = 0.9, 2.1$ Hz, H-3'), 7.17 (1H, br.s, H-8), 7.61 (1H, d, $J = 2.1$ Hz, H-2'), 8.17 (1H, d, $J = 9.6$ Hz, H-4), $^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz) δ : 18.6 (C-6''), 26.2 (C-5''), 70.2 (C-2''), 94.7 (C-8), 105.4 (C-3'), 108.0 (C-10), 113.0 (C-3), 114.7 (C-6), 119.5 (C-2''), 139.9 (C-4), 140.2 (C-4''), 145.3 (C-2'), 149.4 (C-5), 153.1 (C-9), 158.5 (C-7), 161.7 (C-2).

Imperatorin (**3**)

White crystal, $\text{C}_{16}\text{H}_{14}\text{O}_4$, mp. 102, IR ν_{max} cm^{-1} : 1722 (C=O), 1587 (aromatic ring, C=C), 1150 (benzofuran), 838, $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ : 1.74 (3H, s, H-6''), 1.76 (3H, s, H-5''), 5.02 (2H, d, $J = 6.9$ Hz, H-2''), 5.60 (1H, t-like, $J = 6.9$ Hz, H-3''), 6.37 (1H, d, $J = 9.6$ Hz, H-3), 6.83 (1H, dd, $J = 0.9, 2.1$ Hz, H-3'), 7.36 (1H, s, H-5), 7.70 (1H, d, $J = 2.1$ Hz, H-20), 7.76 (1H, d, $J = 9.6$ Hz, H-4). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ : 18.5 (C-5''), 26.2 (C-6''), 70.5 (C-2''), 107.1 (C-30), 113.1 (C-5), 115.1 (C-3), 116.9 (C-10), 120.2 (C-3''), (C-6), 132.1 (C-8), 140.1 (C-4''), 144.3 (C-9), 144.7 (C-4), 147.0 (C-2'), 149.0 (C-7), 160.9 (C-2).

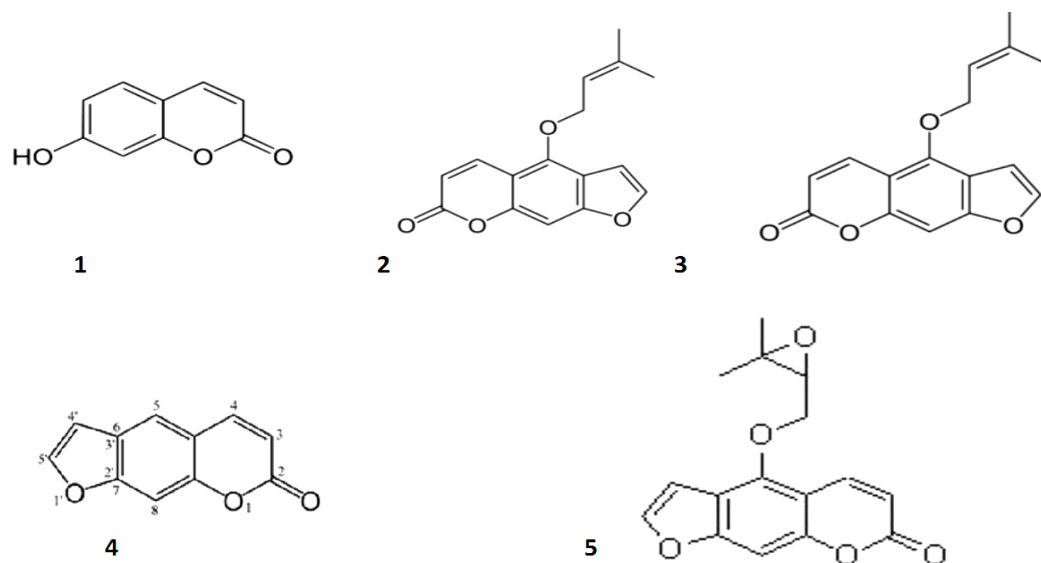


Fig. 1. Molecular structures of individual compounds

Psoralen (4)

Yellow crystal, C₁₁H₆O₃, mp. 164-165°C, IR ν_{\max} cm⁻¹: 1725 (C=O), 1635, 1577 (aromatic ring, C=C), 1136 (benzofuran), 824, ¹H-NMR (CDCl₃, 300 MHz), δ : 6.39 (1H, d, *J* = 9.6 Hz, H-3'), 6.85 (1H, dd, *J* = 0.9, 2.4 Hz, H-3'), 7.49 (1H, br.s, H-8), 7.70 (1H, s, H-5), 7.71 (1H, d, *J* = 2.4 Hz, H-2'), 7.81 (1H, d, *J* = 9.6 Hz, H-4), ¹³C-NMR (CDCl₃, 75 MHz), δ : 100.3 (C-8), 106.8 (C-3'), 115.1 (C-3), 115.8 (C-10), 120.2 (C-5), 125.3 (C-6), 144.4 (C-4), 147.3 (C-2'), 152.5 (C-9), 156.8 (C-7), 161.4 (C-2).

Oxypeucedanin (5)

White crystal, C₁₈H₁₆O₆, mp. 142-143°C, IR ν_{\max} cm⁻¹: 1720 (C=O), 1602 (aromatic ring, C=C), 1386, 1362 (C-O), ¹H-NMR (CDCl₃, 300 MHz) δ : 1.35 (3H, s, H-6"), 1.43 (3H, s, H-5"), (1H, dd, *J* = 4.5, 6.6 Hz, H-3"), 4.45 (1H, dd, *J* = 6.6, 10.8 Hz, H-2a"), 4.61 (1H, dd, *J* = 4.5, 10.8 Hz, H-2b"), 6.33 (1H, d, *J* = 9.6 Hz, H-3), 6.96 (1H, dd, *J* = 0.9, 2.4 Hz, H-3'), 7.22 (1H, br.s, H-8), 7.63 (1H, d, *J* = 2.4 Hz, H-2'), 8.22 (1H, d, *J* = 9.6 Hz, H-4), ¹³C-NMR (CDCl₃, 75 MHz), δ : 19.4 (C-6"), 25.0 (C-5"), 58.7 (C-4"), 61.5 (C-3"), 72.8 (C-2"), 95.4 (C-8), 104.9 (C-3'), 107.9 (C-10), 113.6 (C-3), 114.7 (C-6), 139.3 (C-4), 145.7 (C-2'), 148.8 (C-5), 153.0 (C-9), 158.6 (C-7), 161.4 (C-2).

CONCLUSIONS

1. Five linear furocoumarins – umbelliferon, isoimperatorin, imperatorin, psoralen and oxypeucedanin have been isolated from the roots of *Angelica deccurens* (Ldb.) B. Fedtsch growing in Mongolia. Molecular structures of these compounds were elucidated by spectroscopic methods.
2. The coumarin psoralen was isolated for the first time from the roots of the indicated plant.

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