

Coumarins from the Root of *Peucedanum insolens* Kitagawa

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왕산방풍의 쿠마린 성분

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Two coumarins were isolated from the dried roots of *Peucedanum insolens* Kitagawa (Umbelliferae) and identified as isoimperatorin (**I**) and (+)-oxypeucedanin methanolate (**II**).

As a part of our continuing studies on coumarins from the Umbelliferous plants, we have investigated the root of *Peucedanum insolens* Kitagawa. The dried roots "wang-san-fang-feng" (王山防風), have been used for medicinal purposes in Korea^{1,2)} for the treatment of diaphoresis, sedation and antipyresis.

This plant is a perennial herb distributing in middle Korea and chiefly related to *Peucedanum cervaria* (L.) Cusson. The leaflets are always petiolulate and all the dorsal ridages of mericarp splices up perfectly into two pieces in the unripe stage but connates with each other in the age of maturity³⁾.

The ether extract of the dried root of this plant was applied to silica gel column. Elution of the column with a mixture of *n*-hexane and ethyl acetate (1:1) afforded a crystalline compound, C₁₆H₁₄O₄ (**I**), mp 107° and continuing elution with a mixture of *n*-hexane and ethyl acetate (1:3) yielded another crystalline compound, C₁₇H₁₈O₆ (**II**), mp 126°.

The coumarin character of the compound **I** was suggested by the fluorescence under filtered

ultraviolet light. The IR and NMR spectra of the compound **I**, noted under Experimental, were identical with those of isoimperatorin, a furocoumarin isolated previously from the root of *Angelica koreana* Max. (Umbelliferae). From this fact and the melting point determination with an authentic sample, the compound **I** was confirmed to be identical with isoimperatorin^{4,5)}.

The structure of the compound **II** was indicated by the NMR spectrum, which in addition to furocoumarin resonances showed a two-proton multiplet at τ 5.54 (-OCH₂-C-), a one-proton signal at τ 6.07 (-CH(OH)-), a three-proton singlet at τ 6.72 (-OCH₃-) and a six-proton signal at τ 8.74 (-C(OCH₃)Me₂).

The furocoumarin nucleus is defined by the doublets at τ 2.41;2.98 and τ 1.78;3.74 having $J=2.5$ and 9.5 cps (-CH=) respectively. There is evidence of only one free position in the benzene ring and that this must be C-8 proton is shown by the singlet at τ 2.90 the resonance of the C-5 proton occurring usually at τ 2.6 to 2.75. This leaves position C-5 for attachment of the C-6 side chain. This side chain methoxyl is

indicated by the singlet at τ 6.72 and the geminal dimethyl group by the six-proton singlet at τ 8.74. D_2O exchange removes the doublet signal of hydroxylic proton at τ 7.16, presence of which is indicated by the absorption at 3350 cm^{-1} in the IR spectrum. Apart from these facts, the NMR spectrum shows a complex three-proton multiplet at τ 5.18–6.20 which can be attributed to the methylene and methine protons of the side chain as shown in the compound II. This multiplet can be analysed

in terms of an ABX system which results due to the asymmetry of the methine carbon, the proton on which is responsible for the typical X quartet centered at τ 5.75 of the ABX system.

The IR and NMR spectra of the compound II were identical with those of (+)-oxypeucedanin methanolate, a furocoumarin reported to be isolated previously from the leaves of *Skimmia japonica* Thunberg (Rutaceae) and the fruits and root of *Angelica glauca* Edgew (Umbelliferae) whose structure was elucidated as (+)-

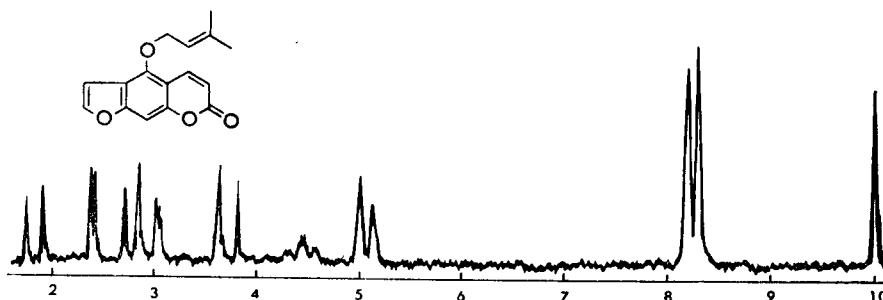


Fig. 1. NMR spectrum of Isoimperatorin (I)

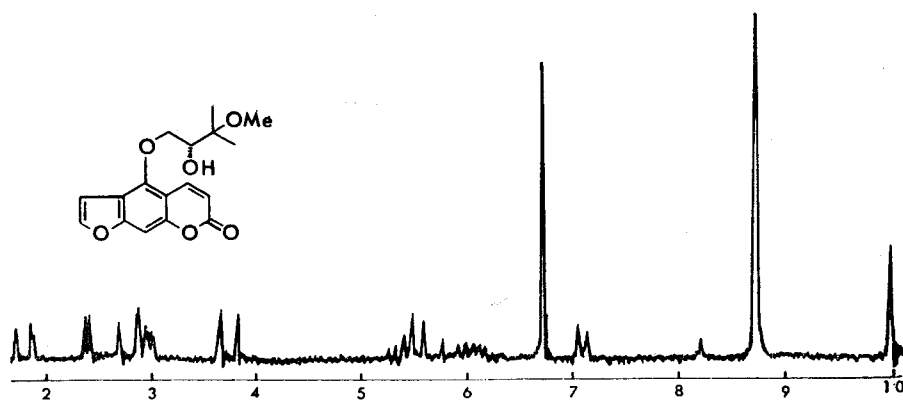


Fig. 2. NMR spectrum of (+)-Oxypeucedanin methanolate (II)

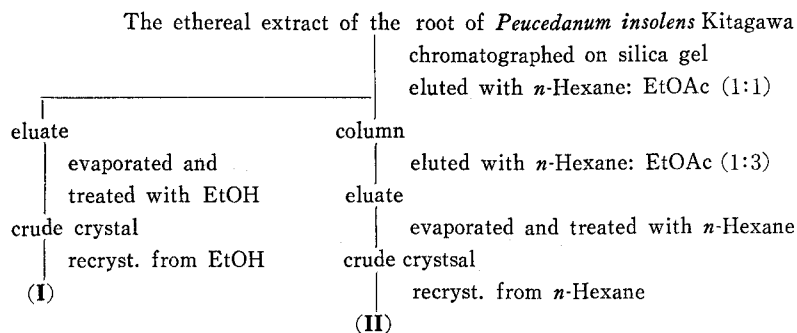
oxypeucedanin methanolate⁶⁻⁸⁾.

Experimental

The IR spectra were determined with a Japan Spectroscopic IR-S spectrometer and the NMR spectra (in $CDCl_3$) were determined with a Varian A-60 spectrometer using tetramethylsilane as internal standard.

Extraction and isolation of the compounds: The dried and crushed root (5.0 kg) of the plant collected in Kang-won Province, Korea, was extracted with ether (30 l) at room temperature for three weeks. The ethereal solution was concentrated to yield brownish oil (135 g).

The isolation of the compounds from the ether extract was carried out as shown in Scheme I.



Scheme I. Isolation of the Compounds

Isoimperatorin (I): Recrystallized from EtOH to colorless needles, mp. 107°, yield 0.7g
Anal. Calcd. for C₁₆H₁₄O₄: C, 71.10; H, 5.22. Found: C, 71.15; H, 5.29. IR cm⁻¹: 1720 (C=O); 1575 (aromatic C=C). NMR τ: 8.30, 8.20 (6H, doublet J=6.5 cps —CH=C $\begin{matrix} \diagup \text{CH}_3 \\ \diagdown \text{CH}_3 \end{matrix}$); 5.10 (2H, doublet J=7.0 cps —O—CH₂—C—); 3.75, 1.83 (2H, doublet J=9.5 cps aromatic H); 3.07 (1H, quartet J=2.5 cps furane H); 2.85 (1H, singlet aromatic H); 2.45 (1H, doublet J=2.5 cps furane H), Melting point were not depressed on admixture with an authentic sample of isoimperatorin (Cnidin).

(+)-Oxypeucedanin methanolate (II): Recrystallized from EtOH to colorless needles, mp. 126°, yield 0.8g. *Anal.* Calcd. for C₁₇H₁₈O₆: C, 64.14; H, 5.70. Found: C., 63.80; H, 5.59. [α]_D+12.5 (CHCl₃): IR cm⁻¹: 3350 (—OH); 1710 (C=O); 1610 (aromatic C=C). NMR τ: 8.74 (6H, singlet—C $\begin{matrix} \diagup \text{CH}_3 \\ \diagdown \text{OCH}_3 \end{matrix}$); 7.16 (1H doublet —OH removed with D₂O); 6.72 (3H, singlet—C $\begin{matrix} \diagup \text{CH}_3 \\ \diagdown \text{OCH}_3 \end{matrix}$); 6.07 (1H, multiplet —CH₂—C $\begin{matrix} \diagup \text{H} \\ \diagdown \text{H} \end{matrix}$ —); 5.54 (2H, multiplet —O—CH₂—C $\begin{matrix} \diagup \text{H} \\ \diagdown \text{OH} \end{matrix}$ —); 3.74, 1.78 (1H, doublet

J=9.5 cps aromatic H); 2.98 (1H, quartet J=2.5 cps furane H); 2.90 (1H, singlet aromatic H); 2.41 (1H, doublet J=2.5 cps furane H). The IR and NMR spectra are superimposable to those of (+)-oxypeucedanin methanolate (Alatol).

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