After 5 g (0.1 mole) of NH_4Cl had been added, stirring was continued until all of the residual liq. NH_3 was evaporated to afford the residue, which was extracted with hot benzene several times. The extract was washed with water, 1N NaOH aq. solution, and water, dried over $CaCl_2$, and evaporated to give a brown residue, which was again extracted with hot *n*-hexane. Removal of the solvent afforded 2.8 g (28.5%) of the ketone (I) as colorless plates. Furthermore purification by silica gel chromatography using benzene as eluent gave the pure ketone, mp 124—125° (lit.,[6] mp 124—125°), whose IR and NMR spectra were completely identical with those of an authentic sample. Mixed melting point test also supports our product to be I.

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Coumarins from the Root of *Angelica gigas* NAKAI

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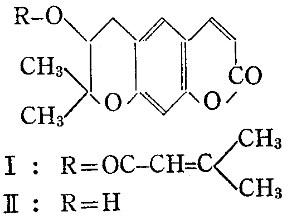
As a part of our continuing study of the coumarins from the Umbelliferous plants, we have investigated the root of *Angelica gigas* NAKAI which is used as "Danggui (当帰)" in Korea. The ether extract of the dried root of this plant upon chromatography over silica gel followed by elution with chloroform afforded a crystalline compound, $C_{19}H_{20}O_5$(I), mp 111°, and the column upon elution with a mixture of *n*-hexane and ethyl acetate (1:1) yielded another crystalline compound, $C_{14}H_{14}O_4$(II), mp 178°.



I : $R=OC\text{-}CH=C(CH_3)_2$
II : R=H

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 decursin, a new coumarin isolated previously from the root of *Angelica decursiva* FR. et SAV. whose structure was elucidated as 3′-hydroxy-3′,4′-dihydroxanthyletin senecioate.[2] From this fact and the mixed melting point deter-

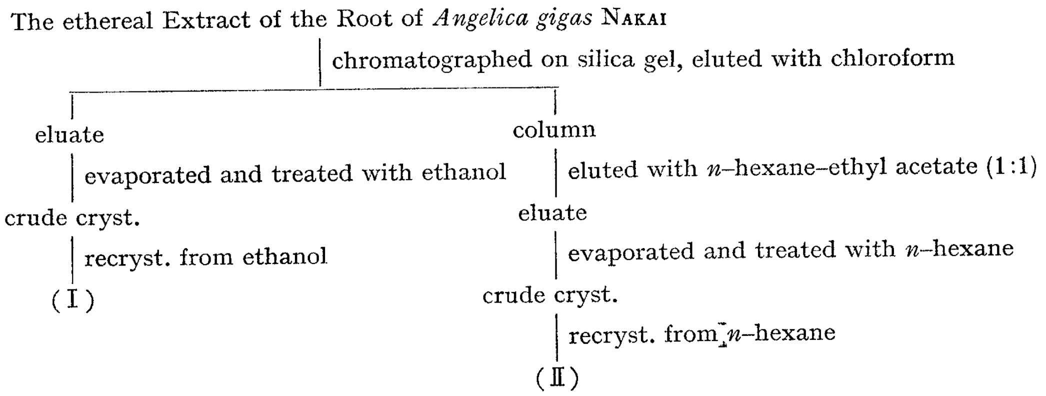


Chart 1. Isolation of the Compounds

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[1] Location: *Shimoadachi-cho, Sakyo-ku, Kyoto.*
[2] K. Hata and K. Sano, *Tetrahedron Letters*, **1966**, 1461.

mination with an authentic sample, I was confirmed to be identical with decursin. Similarly, the compound II was identified as decursinol,[2] a hydrolysis product of decursin.

During this investigation nodakenetin a known coumarin from the root of *Angelica decursiva* Fr. et Sav., was not isolated. However, from the fact that decursin is common to *Angelica gigas* Nakai and *A. decursiva* Fr. et Sav., it can be considered that the both species are closely related taxonomically to each other, although the latter was formerly regarded as a species of genus *Peucedanum*.

Experimental

Extraction and Isolation of the Compounds——The dried and crushed root (1.7 kg) of the plant cultivated in Kang won (江原) Province, Korea, was extracted with ether (15 liter) at a room temperature for 3 weeks. The ether solution was concentrated to yield brown colored viscid oil (50 g). The isolation of the compounds from the ether extract was carried out as shown in Chart 1.

Decursin (I)——Recrystallized from EtOH to colorless prisms, mp 111°, yield 0.8 g. *Anal.* Calcd. for $C_{19}H_{20}O_5$: C, 69.50; H, 6.14. Found: C, 69.75; H, 6.26. $[\alpha]_D^{33}$ +142° (c=1.3, $CHCl_3$), IR cm^{-1}: 1730, 1690 (C=O); 1650 (C=C); 1630, 1565, 1495 (aromatic C=C). NMR (τ)[3]: 2.55, 3.98 (2H, doublet J=9.5 cps, $C\underline{H}=C\underline{H}$); 2.93, 3.39 (2H, 2×aromatic H); 4.41 (1H, multiplet, $(CH_3)_2C=C\underline{H}$); 5.0, 7.0 (ABX pattern, $C\underline{H}-C\underline{H}_2$); 7.87, 8.12 (6H, doublet J=1.0 cps, $(C\underline{H}_3)_2C=CH$); 8.65 (6H, $2\times C-C\underline{H}_3$). Melting point was not depressed on admixture with an authentic sample of decursin.

Decursinol (II)——Recrystallized from n-C_6H_{14} to colorless needles, mp 178°. yield 0.5 g. *Anal.* Calcd. for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.23; H, 5.78. $[\alpha]_D^{33}$ +18° (c=1.0, $CHCl_3$). IR cm^{-1}: 3350 (OH); 1725 (C=O); 1630, 1565, 1495 (aromatic C=C). NMR (τ)[3]: 2.43, 3.83 (2H, doublet J=9.5 cps, $C\underline{H}=C\underline{H}$); 2.82, 3.15 (2H, 2×aromatic H); 6.12, 7.03 (3H, ABX pattern, $C\underline{H}-C\underline{H}_2$); 7.35 (1H, singlet $\underline{H}O-CH$); 8.60 (6H, $2\times C-C\underline{H}_3$). Melting point was not depressed on admixture with an authentic sample of decursinol.

Acknowledgement The authors are gratefully indebted to Dr. T. Shingu of this Faculty for the measurement of NMR spectra and to the members of the Institute of Elemental Analyses of Kyoto University for microanalyses.

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[3] Measured in $CDCl_3$ solution by Varian Associates Recording Spectrometer A 60, TMS was used as inner standard.

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Gas Liquid Chromatography of Steroids of Ch'an Su. II.[1] Reinvestigation on the Determination of Bufadienolides[2]

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In the previous paper,[1] the authors presented a gas chromatographic method for the determination of cinobufagin which is generally a major bufadienolide in Ch'an Su (Senso).[4]

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[1] Part I: K. Sakurai, E. Yoshii, and K. Kubo, *Yakugaku Zasshi*, 84, 1166 (1964).

[2] Presented at the 87th Annual Meeting of Pharmaceutical Society of Japan, Kyoto, April, 1967.

[3] Location: *a*) *Gofuku, Toyama*; *b*) *Umezawa-cho, Toyama*.

[4] J.P. Ruckstuhl and K. Meyer, *Helv. Chim. Acta*, 38, 883 (1955).