

TABLE V. Effect of Neutral Salt and Buffer Concentration

Surfactant	k (day ⁻¹) in buffer	k (day ⁻¹) in buffer contg. 0.1M NaCl	k (day ⁻¹) in buffer concn. × 2	pH
Em. 120 10%	0.428	0.434	—	0.99
	1.14	—	1.13	5.57
C. D. 5%	0.200	0.190	—	0.90
	0.478	—	0.450	6.50
S. L. S. 5%	0.143	—	0.136	2.08
	0.977	—	0.974	7.28

Temp. : 37°

is suppressed only by cationic surfactants (cetylethyldimethylammonium bromide and benzalkonium chloride). This relationship between charges contrasts with the results of the previous work.¹⁾

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Summary

1) Attempt was made to suppress the hydrolysis of acetylsalicylic acid with anionic (sodium laurylsulfate), cationic (cetylethyldimethylammonium bromide and benzalkonium chloride), and nonionic (Emulgen 120) surfactants. The hydrolysis of the undissociated form of acetylsalicylic acid is suppressed by the three kinds of surfactants and that of the anionic form is suppressed by cetylethyldimethylammonium bromide and benzalkonium chloride.

2) Through the ultraviolet spectra and the partition coefficient, it was ascertained that the undissociated form of acetylsalicylic acid is solubilized with the above three kinds of surfactants and the anionic form interacts with only a cationic surfactant.

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80. Hiroshi Mitsuhashi and Tsuneo Itoh : Studies on the Constituents of Umbelliferae Plants. V. Studies on the Constituents of *Angelica edulis* MIYABE. (1). Isolation of Edultin.

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Angelica edulis MIYABE (Japanese name "Amanyu" or "Marubaezonyu"—Umbelliferae) is widely distributed in the northern part of Japan, especially in Hokkaido, and is said to be used in the vegetable diet or as an antiseptic by mixing it with fishoil among the people of the Ainu race. Although it is well assumed by its flavor the root contains some essential oils, the presence of any other constituents in the root has not been reported so far.

The authors have investigated the constituents of the root as a part of the studies on the constituents of Umbelliferae²⁾ to see whether any biological active principle could

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1) A preliminary communication appeared in this Bulletin, 9, 170 (1961).

2) H. Mitsuhashi, *et al.*, : This Bulletin, 8, 245 (1960).

be isolated. This paper presents the separation of a new coumarin, edultin and the determination of its constitution.

The dried powdered roots were extracted with ethanol for 4 hours at room temperature in a macerator until the extracts became more like a faintly yellowish solution. Evaporation of the alcoholic extracts under a reduced pressure at 50~60° left a viscous dark brown residue, which was dissolved in ether, washed with alkali and, after addition of a suitable amount of hexane, the solution was kept in a refrigerator for several days. From the solution, crystalline compounds gradually precipitated. The mother liquor was decanted and the precipitated crystals were washed several times with methanol, then purified by means of column chromatography using silica gel as an adsorbent and benzene-acetone (9:1) as the original developing solvent. Attempts to prove the presence of the expected other analogs failed, and the complete absence of any contaminative substances was confirmed by paper- and glass stripchromatography. The eluted crystalline compound, edultin was recrystallized several times from methanol to form white needles, m.p. 136~142°. The infrared absorption spectrum did not exhibit any absorption of hydroxyl function. It gave negative ferric chloride and silver-mirror tests, and did not react with Fehling's solution and 2,4-dinitrophenylhydrazine. It was suggested, therefore, that edultin possesses a δ -lactone ring, an ester grouping, and a coumarin nucleus by its behavior towards alkaline solutions. The infrared and ultraviolet absorption spectra of this compound are shown in Fig. 1. and Fig. 2.

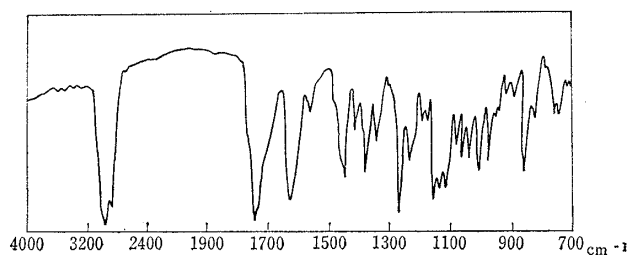


Fig. 1. Infrared Absorption Spectra of Edultin NaCl Cell, Nujol mull

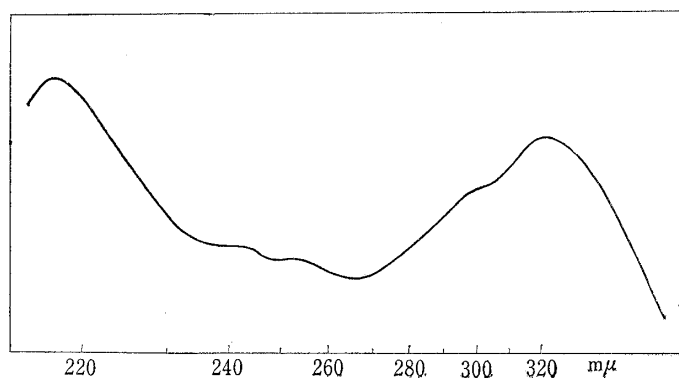


Fig. 2. Ultraviolet Absorption Spectra of Edultin (in 0.000021N EtOH)

Experimental*2

Isolation of Edultin from *Angelica edulis* MIYABE—The dried and milled root of Angelica (6 kg.), collected in the suburbs of Sapporo from July to August, just before and when in its full bloom, was treated according to the procedure as shown Chart 1.

Edultin was obtained as white needles m.p. 136~142° (uncor.), $[\alpha]_D^{20} +41.5$ ($c=26.8$, pyridine), easily soluble in benzene or CHCl_3 and sparingly soluble in MeOH. *Anal.* Calcd. for $\text{C}_{21}\text{H}_{22}\text{O}_7$: C, 65.27; H, 5.74; mol. wt. 386.6. Found: C, 65.47; H, 5.75; mol. wt. (Rast) 382.8. UV $\lambda_{\text{max}}^{\text{EtOH}}$ m μ (ϵ):

*2 The UV and IR spectra were measured with Shimadzu RS-27-type self-recording spectrophotometer, and Kōken DS-301-type infrared spectrophotometer, respectively.

Root of *Angelica edulis* MIYABE (Amanyu) (6 kg.)

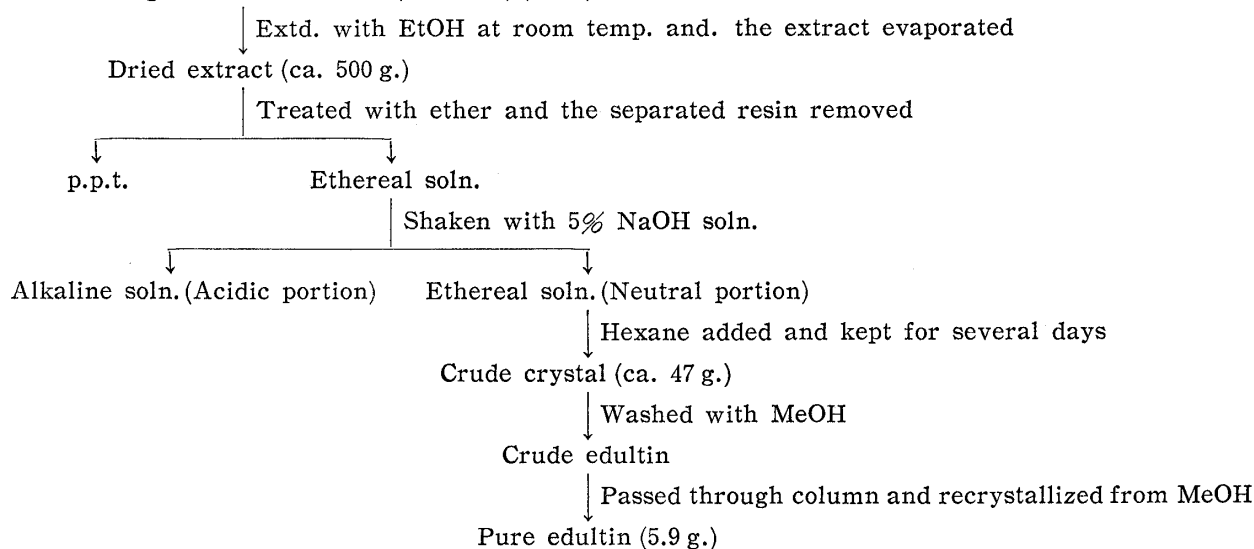


Chart 1. Isolation of Edultin

219 (31,430), 248 (6,770), 259 (5,710), shoulder 299 (9,350), 323 (21,000), $\lambda_{\text{min}}^{\text{EtOH}}$ m μ (ϵ): 245 (6,770), 254 (5,240), 266 (2,860).

Paper Partition Chromatography of Edultin—The above crude and pure crystals of edultin were submitted to paper partition chromatography, using a mixture of benzine–benzene–MeOH (5:4:2) as a solvent, and a single spot (R_f 0.95) was detected with color reagent (chameleon solution) on the paper chromatogram (at 23°, Toyo Roshi No. 50, time 4 hr., ascending method). The glass-strip-chromatographic analysis also revealed the presence of a single spot (migration distance of origin, 5.5 cm.), using hexane–AcOEt (85:15) as a developing solvent (at 20°, time 1.5 hr.).

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Summary

From the ethanolic extract of the root of *Angelica edulis* MIYABE a new compound $C_{21}H_{22}O_7$, named edultin was isolated.

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