Table V. Effect of Neutral Salt and Buffer Concentration

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>k_{(day^{-1})} in buffer</th>
<th>k_{(day^{-1})} in buffer concn. \times 2</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Em. 120 10%</td>
<td>0.428</td>
<td>0.434</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>1.14</td>
<td>--</td>
<td>5.57</td>
</tr>
<tr>
<td>C. D. 5%</td>
<td>0.200</td>
<td>0.190</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td>0.478</td>
<td>--</td>
<td>6.50</td>
</tr>
<tr>
<td>S. L. S. 5%</td>
<td>0.143</td>
<td>0.136</td>
<td>2.08</td>
</tr>
<tr>
<td></td>
<td>0.977</td>
<td>--</td>
<td>7.28</td>
</tr>
</tbody>
</table>

Temp.: 37°C

is suppressed only by cationic surfactants (cetyltrimethylammonium 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 (cetyltrimethylammonium 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 cetyltrimethylammonium 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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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 fish oil 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 Kita-12-jo, Nishi-5-chome, Sapporo, Hokkaido (三遠 博, 伊束常男).
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-dinitrophenylhydrazone. 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 0.00021N 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.), [α]D +41.5 (c=26.8, pyridine), easily soluble in benzene or CHCl3 and sparingly soluble in MeOH. Anal. Calcd. for C25H20O7: C, 65.27; H, 5.74; mol. wt. 386.6. Found: C, 65.47; H, 5.75; mol. wt.(Rast) 382.8. UV $\lambda_{max}$ 360 mµ (ε):

*2 The UV and IR spectra were measured with Shimazu RS-27-type self-recording spectrophotometer, and Köken DS-301-type infrared spectrophotometer, respectively.
Root of Angelica edulis Miyabe (Amanyu) (6 kg.)

Extd. with EtOH at room temp. and. the extract evaporated

Dried extract (ca. 500 g.)

Treated with ether and the separated resin removed

\[ \downarrow \text{p.p.t.} \quad \downarrow \text{Etheral soln.} \]

Shaken with 5% NaOH soln.

\[ \downarrow \text{Alkaline soln. (Acidic portion)} \quad \downarrow \text{Ethereal soln. (Neutral portion)} \]

Hexane added and kept for several days

Crude crystal (ca. 47 g.)

\[ \downarrow \text{Washed with MeOH} \]

Crude edultin

\[ \downarrow \text{Passed through column and recrystallized from MeOH} \]

Pure edultin (5.9 g.)

Chart 1. Isolation of Edultin

219 (31,430), 248 (6,770), 259 (5,710), shoulder 299 (8,350), 323 (21,000), \( \lambda_{	ext{min}}^{	ext{EtOH}} \text{sp.} (\epsilon) : 245 (6,770), 254 (5,240), 266 (2,860). \)

Paper Partition Chromatography of Edultin—The above crude and pure crystals of edultin were submitted to paper partition chromatography, using a mixture of benzene-benzene-MeOH (5:4:2) as a solvent, and a single spot (Rf 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.).

The authors are indebted to Miss Oshibe of Hoshi College of Pharmacy and Mr. K. Narita of this Institute for the elemental analysis. The authors also express their deep gratitude to Mr. T. Yoshida for his kind help in collection of the plant material.

Summary

From the ethanolic extract of the root of Angelica edulis Miyabe a new compound \( \text{C}_{21}\text{H}_{27}\text{O}_{5} \), named edultin was isolated.

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