Note

UDC 581.19 : 582.893

Yukio Akahori : Principles of *Peucedanum japonicum* THUNB. II. Studies on P-Acid.

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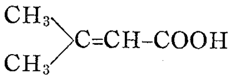
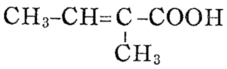
The isolation of p-acid was described in the preceding paper.[1] From its elemental analysis ($C_5H_8O_2$), molecular weight determination, and the bromine test, this acid agreed with unsaturated C_5-carboxylic acid. It also absorbed one mole of hydrogen on catalytic hydrogenation, giving dihydro-p-acid which showed no absorption peak in its ultraviolet spectrum. Ultraviolet spectrum of p-acid showed only one peak at 215 mμ. From this fact, the double bond should be in α,β-position. As the α,β-unsaturated C_5-carboxylic acid, the following five isomers can be considered : 3,3-Dimethylacrylic acid (I : senecioic acid), 2,3-dimethylacrylic acid (II, *trans* : angelic acid; II′, *cis* : tiglic acid), and β-ethylacrylic acid (III, *trans*; III′, *cis*).



$(CH_3)_2C{=}CH{-}COOH$

(I)



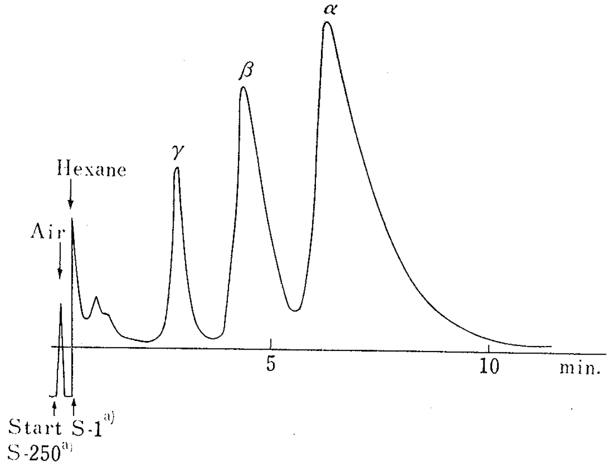
$CH_3{-}CH{=}C(CH_3){-}COOH$

(II : *trans*)
(II′ : *cis*)

$CH_3{-}CH_2{-}CH{=}CH{-}COOH$

(III : *trans*)
(III′ : *cis*)

Gas chromatography of methyl ester of p-acid (Fig. 1) showed three main peaks, α, β and γ. Peaks α and β were respectively identical with those of methyl senecioate[*2] and methyl angelate.[*3] The gas chromatography of dihydro-p-acid (Fig. 2) showed only



Compound^b)	Retention time (min.)^c)
P-Acid methyl ester	α 6.1
	β 4.3
	γ 2.8
Methyl senecioate	6.0
Methyl angelicate	4.3
Methyl tiglate	7.1

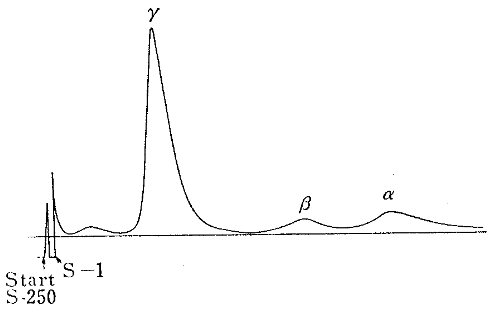
a) Sensitivity mv/full scale
b) Ca. 30% solution in hexane was injected.
c) Starting (injection) time was used as standard.

Fig. 1. Gas Chromatography of P-Acid

Conditions :

1. Apparatus : Aerograph Model 101-C (Wilkens Instrument and Research, Inc., U.S.A.)
2. Column : { Polyester of 1,4-butanediol and succinic acid 30% / Chromosorb, 60~80 mesh, 70% in 1/4×30 in. copper tube.
3. Temperature : 62°.
4. Helium flow rate : 57 cc./min.
5. Filament current : 149 mA.

[*1] Oshika, Shizuoka (赤堀幸男).
[1] Part I. This Bulletin, **9**, 921 (1961).
[*2] Org. Syntheses, **23**, 27 (1944). The methyl ester was prepared by the same method.
[*3] R.E. Bubkles : J. Org. Chem., **15**, 680 (1950); The methyl ester was prepared by the same method.



Compound	Retention time (min.)
Dihydro-p-acid methyl ester	α 12.0
	β 9.3
	γ 4.2
Methyl isovalerate	4.3
Methyl valerate	7.5
Methyl 2-methylbutyrate	4.2

All conditions were the same as in Fig. 1, except that the flow rate of helium was 30 cc./min.

Fig. 2. Gas Chromatography of Dihydro-p-acid

one large peak, which was identical with those of methyl isovalerate and methyl 2-methylbutyrate. From those results, although peak γ (in Fig. 1) was not identified as yet, it seemed that p-acid was a mixture of (I) and (II).

These gas chromatographic data were re-confirmed by paper chromatography (Table I). Efforts to separate each component as such from p-acid failed, but *p*-bromophenacyl esters and *p*-phenylphenacyl esters of (I) and its dihydro compound were isolated.

TABLE I. Paper Chromatography

Compound	Rf	Compound	Rf
P-Acid	0.25 (small) 0.54 (broad)	Dihydro-p-acid	0.25? (not clear) 0.55 (broad)
Senecioic acid	0.54	3-Methylbutyrate	0.56
Angelic acid	0.55	Isovaleric acid	0.54
Tiglic acid	0.44		

Paper: Toyo Roshi No. 50 (2×40 cm.).
Elution solvent: 99% EtOH-H_2O-conc. NH_4OH (100:4:1).
Detection: Spray of Bromothymol Blue (40 mg. of B.T.B. in 100 cc. H_2O and NaOH solution added until the solution became slightly blue).
Temperature: 15~18°.

Ozonization of p-acid, followed by thermal decomposition, gave acetone and acetaldehyde as 2,4-dinitrophenylhydrazones which also re-confirmed the presence of (I) and (II) in p-acid. The nuclear magnetic resonance spectrum (Fig. 3) also ascertained the above results, when compared with the data already published.[2]

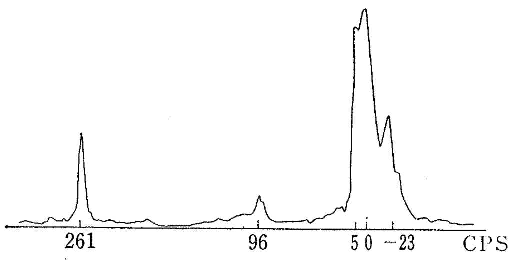


Fig. 3. NMR Spectrum of P-Acid

Apparatus: 27 mc. high-resolution spectrometer constructed in the laboratory of Dr. S. Fujiwara, University of Electro communication, Tokyo.
Solvent: Carbon tetrachloride
Temperature: 25°.
Standard: CH_3-group was used as reference.

Experimental

P-Acid——Colorless liquid, b.p$_{760}$ 167~175°. *Anal.* Calcd. for $C_5H_8O_2$: C, 59.98; H, 8.05; mol. wt., 100.1. Found: C, 59.61; H, 8.19; mol. wt. (titration), 104.1. The bromine test (double bond) and $NaHCO_3$ test (carboxylic acid) were positive.

Methyl Ester of P-Acid——To 100 mg. of p-acid dissolved in 2 cc. Et_2O, excess diazomethane in Et_2O was added and the mixture was kept in a cold room overnight. The solvent was carefully evaporated at room temperature in a slightly reduced pressure (ca. 100 mm. Hg) and 98 mg. of fra-

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[2] S. Fujiwara, H. Shimizu, Y. Arata, Y. Akahori: Bull. Chem. Soc. Japan, 33, 428 (1960).

grant, colorless liquid was obtained.

Dihydro-p-acid——A mixture of 110 mg. of p-acid in 5 cc. MeOH was shaken with 50 mg. of 5% Pd-C in H_2 current and 25.3 cc. (ca. 1 mol. equiv.) of H_2 was absorbed during 2 hr. After filtration, the solution was neutralized with 5% aq. NaOH and concentrated in a reduced pressure. After acidification with dil. HCl, this was extracted with Et_2O and Et_2O solution was carefully evaporated, leaving 106 mg. of colorless liquid. Its odor was like that of isovaleric acid and the bromine test was negative.

Methyl Ester of Dihydro-p-acid——100 mg. of dihydro-p-acid was treated with excess diazomethane in usual manner and 96 mg. of fragrant colorless liquid was obtained.

Gas Chromatography——Each sample was dissolved in two volumes of hexane. Apparatus and conditions are given in Fig. 1.

***p*-Bromophenacyl Ester of Senecioic Acid**——100 mg. of p-acid was esterified with 270 mg. of *p*-bromophenacyl bromide by the usual way. The reaction mixture was cooled, the deposited crystals were collected, washed with cold dil. EtOH, and recrystallized repeatedly from EtOH to 28 mg. of colorless leaflets, m.p. 101.0°. A mixed melting point with the authentic sample did not show any depression. *Anal.* Calcd. for $C_{13}H_{13}O_3Br$: C, 52.64; H, 4.41. Found : C, 52.52; H, 4.36.

***p*-Phenylphenacyl Ester of Senecioic Acid**——100 mg. of p-acid was treated with 270 mg. of *p*-phenylphenacyl bromide by essentially the same method as *p*-bromophenacyl ester. Colorless leaflets, m.p. 142~143°. A mixed melting point with the authentic sample did not show any depression. *Anal.* Calcd. for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16. Found : C, 77.43; H, 6.22.

***p*-Bromophenacyl Ester of Isovaleric Acid**——97 mg. of dihydro-p-acid was derived to its *p*-bromophenacyl ester by the usual way. After repeated recrystallisation from EtOH, 3 mg. of pure compound, m.p. 68.0~68.5°, was obtained which was identified as *p*-bromophenacyl ester of isovaleric acid by a mixed melting point with the authentic sample.

Ozone Oxidation of P-Acid——Through a solution of 50 mg. of p-acid dissolved in 5 cc. dehyd. $CHCl_3$, 2.4% O_3 in O_2 was passed at −50°. After 30 min., the blue solution was evaporated in vacuum at 0°, giving colorless oily ozonide. 1 cc. of 10% NaCl solution was added to this ozonide and the mixture was heated at 60° while bubbling N_2, and outlet of N_2 was led into 20 cc. of saturated 2,4-dinitrophenylhydrazine in 2*N* HCl. After 3 hr., 46 mg. of yellow crystals deposited in the hydrazine solution. This was dissolved in benzene-petr. ether (1:1) and chromatographed on 4 g. of Al_2O_3 (Merck, Brockmann). First elution with 12 cc. of benzene-petr. ether (1:1) gave orange crystals, which were recrystallized from a mixture of 2 cc. benzene and 10 cc. petr. ether, and then from EtOH to orange plates, m.p. 163.0~164.0°(in closed capillary), which was identified as acetaldehyde 2,4-dinitrophenylhydrazone by mixed melting point, and UV and IR spectra.

The above benzene-petr. ether mother liquor was chromatographed again on Al_2O_3(3 g., Merck, Brockmann) and 15-cc. elution by the same solvent (benzene-petr. ether 1:5) gave 3 mg. of orange prisms, m.p. 125.5~126.0°, after recrystallization from EtOH. UV and IR spectra of this compound were identical with those of acetone 2,4-dinitrophenylhydrazone, and the mixed melting point with the authentic sample did not show any depression. Further elution gave acetaldehyde 2,4-dinitrophenylhydrazone.

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Summary

The p-acid, which was isolated from *Peucedanum japonicum* THUNB., was proved to be a mixture of senecioic acid, angelic acid, and a small amount of unidentified compound. Gas chromatography, ozone oxidation, NMR spectrography, and paper chromatography were used for its identification. Senecioic acid was also identified as *p*-bromo- and *p*-phenyl-phenacyl esters.

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