dl-threo-**1-Phenyl-2-benzoylamino-1, 3-diacetoxypropane (III)**—a) From (II) : 1) A solution of 250 mg. of (II) and 250 mg. of anhyd. AcOK in 2.5 cc. of Ac_2O was boiled for 1 hr., cooled, and poured into ice-water to deposit a solid. Recrystallization from ether-petr. ether gave colorless prisms, m.p. 140~142°; yield, 330 mg. *Anal.* Calcd. for $C_{20}H_{21}O_5N$ (III) : C, 67.59; H, 5.96; N, 3.94. Found: C, 67.75; H, 5.80; N, 3.84.

2) A solution of 200 mg. of (II) and 200 mg. of anhyd. AcOK in a mixture of 1 cc. of Ac_2O and 3 cc. of AcOH was boiled for 10 hrs., cooled, and poured into ice water to deposit a solid precipitate. Recrystallization from AcOEt gave colorless needles, m.p. 141~143°; yield, 120 mg.

b) From (I) ; Simultaneous Formation of a Mixture of *dl-threo*- and *-erythro*-1-Phenyl-2-benzoylamino-1, 3-diacetoxypropane (V) : A solution of 1 g. of (I) and 1 g. of anhyd. AcOK in a mixture of 5 cc. of Ac_2O and 15 cc. of AcOH was boiled for 14 hrs. and concentrated *in vacuo* to leave a solid, m.p. 120~150°. Recrystallization from AcOEt deposited colorless short needles, 166~167.5°; yield 520 mg. *Anal.* Calcd. for $C_{20}H_{21}O_5N$ (V) : C, 67.59; H, 5.96; N, 3.94. Found : C, 67.37; H, 6.14; N, 3.97.

The AcOEt mother liquor was concentrated to give colorless long needles. After recrystallization from benzene it melted at 141~143°, alone and on admixture with a sample of (III) obtained by procedure (a); yield 110 mg. *Anal.* Calcd. for $C_{20}H_{21}O_5N$ (III) : N, 3.94. Found : N, 4.01.

c) From *dl-threo*-2-Phenyl-4-phenylacetoxymethyl-Δ^2-oxazoline (IV). A solution of 65 mg. of (IV) and 65 mg. of anhyd. AcOK in a mixture of 0.4 cc. of Ac_2O and 1.2 cc. of AcOH was boiled for 10 hrs. and concentrated *in vacuo* to give an oily residue. The AcOEt extract of the residue was washed with water, dried over anhyd. Na_2SO_4, and concentrated to leave a solid residue. Recrystallization from benzene gave colorless needles, m.p. 137~139°, alone and on admixture with a sample of (III), yield 30 mg.

dl-threo-**2-Phenyl-4-phenylacetoxymethyl-Δ^2-oxazoline(IV)**—A solution of 270 mg. of (I) and 270 mg. of anhyd. AcOK in 5 cc. of Ac_2O was boiled for 1 hr. and concentrated *in vacuo* to leave an oily residue. The benzene extract was washed with water, dried over anhyd. Na_2SO_4 and concentrated *in vacuo* to leave an oily residue which crystallized upon addition of a small volume of ether. After recrystallization from MeOH, it melted at 143~145°, yield 240 mg. *Anal.* Calcd. for $C_{18}H_{17}O_3N$ (IV) : C, 73.20; H, 5.80; N, 4.75. Found : C, 73.39; H, 5.65; N, 4.71. I.R. : λ_{max}^{Nujol} 5.76, 8.07 μ(-OCOCH$_3$); 6.05 μ(-C=N-); 6.32, 6.67 μ(-C_6H_5).

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U. D. C. 547. 94 : 582. 675. 1 Thalictrum

Eiichi Fujita and Toshiaki Tomimatsu : Studies on the Alkaloids of *Thalictrum Thunbergii* DC. I. A Quaternary Base in the Root.

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Doassans,[1] Vashistha, *et al.*,[2] Nakajima,[3] Norkina, *et al.*,[4] and Yunusov, *et al.*[5] reported on the alkaloids of Thalictrum genus plants. They named 10 alkaloids and suggested three structural formulae among them. All of those alkaloids are tertiary bases and their studies are still incomplete. The present authors began systematic study of the alkaloids of *Thalictrum Thunbergii* DC. (Japanese name "Aki-karamatsu"), found a quaternary base from the root, and clarified its structure.

Thalictrum Thunbergii is a perennial herb belonging to Ranunculaceae family, and grows wild in fields or hilly districts. Studies on the components of this plant were

* Sho-machi, Tokushima (藤田栄一, 富松利明).

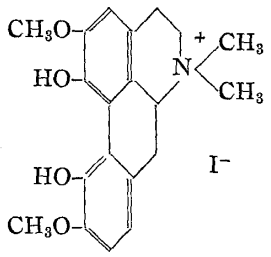
1) Doassans : Bull. soc. chim. France, **36**, 85(1880).
2) S. K. Vashistha, S. S. Siddiqui : J. Indian Chem. Soc., **18**, 641(1941).
3) T. Nakajima : J. Pharm. Soc. Japan, **65**, 422(1945).
4) S. S. Norkina, N. A. Pakhareva : J. Gen. Chem. U. S. S. R., **20**, 1720(1950) (C. A., **45**, 1306(1951)).
5) S. Yunusov, V. N. Progressov : J. Gen. Chem. U. S. S. R., **20**, 1197(1950); *Ibid.*, **22**, 1095(1952) (C. A., **45**, 1608(1951); **47**, 8084(1953)).

reported by Toyoda and Sekiguchi,[6] besides by the afore-mentioned Nakajima. The presence of two tertiary bases was clarified by these three Japanese investigators, though their structures have not yet been established.

The present authors, using the root of this plant collected in Tokushima City, separated only one quaternary base by means of Nakano's method[7] employed in the studies on Magnolia alkaloids. Its iodide, m.p. 252°(decomp.), corresponded to $C_{20}H_{24}O_4NI$ and showed the presence of two methoxyl groups.

The ultraviolet spectrum was identical with that of magnoflorine iodide (I). As described in the experimental part, other qualities were also analogous to those of (I), and the infrared spectra of both were quite identical. Moreover, the infrared spectrum of O, O-dimethyl ether iodide of this base was identical with that of O, O-dimethyl magnoflorine iodide.

Thus, it was established that the quaternary base obtained from *Thalictrum Thunbergii* is magnoflorine iodide (I), 11.1 g. of magnoflorine being obtained as a picrate from 381 g. of a methanol extract of 4.8 kg. of dried root. No other quaternary bases were found.



(I)

Magnoflorine has hitherto been separated from the plants of Magnoliaceae, Berberidaceae, and Menispermaceae families. It was found for the first time in a Ranunculaceous plant, which is an interesting fact.

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Experimental[8]

(1) Extraction and Isolation of the Quaternary Base—4.8 kg. of coarsely ground root of *Thalictrum Thunbergii* DC., collected in October, 1955, in Tokushima City, was extracted several times with hot MeOH and the extract was evaporated under reduced pressure. The syrupy residue (381 g.) was digested at 40° with about 5 volumes of 5% tartaric acid. After filtration, the acid extract was freed by means of ether from extraneous acidic and neutral substances. After making alkaline with aq. NH_3, it was extracted with ether. NH_3-alkaline mother liquor was slightly acidified with HCl and the quaternary base was precipitated as the reineckate (92 g.) by adding saturated solution of ammonium reineckate.

The reineckate of the quaternary base was decomposed with Ag_2SO_4 and then converted into the chloride, but it did not readily crystallize and was led to the picrate by adding conc. aq. sodium picrate solution. The precipitate here obtained was recrystallized from acetone to 11.1 g. of picrate crystals, m.p. 230~231°(decomp.). *Anal.* Calcd. for $C_{20}H_{24}ON_4 \cdot C_6H_2O_7N_3$: C, 54.73; H, 4.59; N, 9.82. Found: C, 54.68; H, 4.59; N, 9.79.

(2) Magnoflorine Iodide—Two g. of the above picrate was dissolved in a small amount of acetone and treated with 1% HCl to form the chloride, to which aq. KI was added to precipitate the iodide.

6) M. Toyoda, Y. Sekiguchi: Repts. Pharm. Lab. Toyama Pref., **1**, 1(1954).
7) T. Nakano: This Bulletin, **2**, 321(1954).
8) Melting points are all uncorrected.
9) T. Nakano: This Bulletin, **2**, 326, 329(1954).

It crystallized from MeOH in the form of colorless pillars, m.p. 252°(decomp.). Yield, 0.7 g. $[\alpha]_D^{12}$ +214°(c=0.254, MeOH, l=1 dm.). *Anal.* Calcd. for $C_{20}H_{24}O_4NI$: C, 51.18; H, 5.15; N, 2.98; OCH_3, 13.22. Found: C, 50.98; H, 5.25; N, 3.11; OCH_3, 13.50.

This substance gave a blue color with the Gibbs reagent, red color with the Millon reagent, and in an aq. solution, a dark yellowish brown color with $FeCl_3$. It gave a negative test for a methylenedioxy group with the Gaebel reagent. With conc. H_2SO_4 it produced a brown color, changing to blood red on addition of KNO_3. U.V. $\lambda_{max}^{H_2O}$ mμ(log ε): 226, 271, 310(4.60, 3.92, 3.85). The infrared spectrum of this substance, as well as its ultraviolet spectrum, was identical with those of magnoflorine iodide (Nujol mull).

(3) **O, O-Dimethylmagnoflorine Iodide**—0.5 g. of the iodide was methylated with MeI and alkali following the same procedure as described for the preparation of O, O-dimethylmagnoflorine iodide.[9] The O, O-dimethyl ether iodide here obtained crystallized from MeOH as colorless needles, m.p. 243~244°(decomp.), which was shown by infrared spectrum to be identical with O, O-dimethylmagnoflorine iodide. Yield, 0.34 g. *Anal.* Calcd. for $C_{22}H_{28}O_4NI$: C, 53.12; H, 5.48. Found: C, 52.98. H, 5.70. U.V. $\lambda_{max}^{H_2O}$ mμ(log ε): 223, 270(4.68, 4.14).

This substance gave no depression in m.p. when mixed with O-methylmenisperine iodide (O, O-dimethylmagnoflorine iodide), m.p. 224°(decomp.).

(4) **O, O-Dimethylmagnoflorine Chloride**—0.15 g. of O, O-dimethylmagnoflorine iodide was dissolved in a mixture of MeOH and a little water, and shaken with freshly prepared AgCl (from 0.2 g. of $AgNO_3$). After 1 hr. AgI was filtered off and the mother liquor was evaporated to dryness under reduced pressure. The residue was recrystallized from a very small amount of EtOH and the colorless needles, m.p. 237~238°(decomp.), were obtained. The substance gave no depression in m.p. when mixed with O, O-dimethylmagnoflorine chloride m.p. 236~237°(decomp.).

(5) **O, O-Diethylmagnoflorine Iodide**—The ethylation of the iodide was effected with EtI and alkali in a similar manner for the O, O-dimethyl ether, and the O, O-diethyl iodide was obtained from MeOH as colorless needles, m.p. 230~231°. *Anal.* Calcd. for $C_{24}H_{32}O_4NI$: C, 54.86; H 6.14. Found: C, 54.25; H, 6.32.

(6) **Another Method of Isolating the Quaternary Base**—i) Ammonia alkaline mother liquor, which was freed from tertiary bases, was acidified with AcOH and aq. KI solution was added into this solution. The resinous precipitate was recrystallized from MeOH. Thus, colorless pillars, m.p. 251~252°(decomp.), of magnoflorine iodide were directly obtained. The mother liquor freed from resinous precipitate was treated with aq. ammonium reineckate, and magoflorine alone was recovered.

ii) Ammonia alkaline mother liquor freed from tertiary bases was acidified with aq. HCl and set aside, but no crystals separated. The conc. aq. sodium picrate solution was added, and the precipitate produced was recrystallized from acetone. Thus, magnoflorine picrate, m.p. 231~232° (decomp.), was directly prepared.

Summary

A quaternary base magnoflorine was isolated from the root of *Thalictrum Thunbergii* DC. of the Ranunculaceae family.

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