(c) A mixture of (IV) (0.5 g.) and aniline (1 g.) was warmed on a water bath for a few mins. After cool, the solution was acidified with HCl and separated colorless needles, m.p. 235~236°, which was undepressed on admixture with diphenylurea. *Anal.* Calcd. for $C_{13}H_{12}ON_2$: C, 73.56; H, 5.70; N, 13.20. Found: C, 73.33; H, 6.06; N, 13.28.

Summary

4-Ethoxycarbonyl- (III) and 4-cyano-5-aminoisoxazole (IV) were prepared by reacting hydroxylamine and ethyl α-ethoxymethylenecyanoacetate (I) or α-ethoxymethylenemalononitrile (II), respectively. These 5-aminoisoxazoles were very unstable toward bases compared with a compound (XI) substituted in 3-position and the ring cleavage occurred at the nitrogen-oxygen bond with subsequent isomerisation to their corresponding nitriles, (V) and (VIII).

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Eiichi Fujita and Toshiaki Tomimatsu: Studies on the Alkaloids of *Thalictrum Thunbergii* DC. II.⁽¹⁾ A Quaternary Base in the Stem and Leaves.

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In the preceding paper,[1] it was shown that the quaternary base isolated from the root of *Thalictrum Thunbergii* DC. was only magnoflorine. The present paper deals with the evidence for the presence of magnoflorine in the stem and leaves of the same plant.

The stems and leaves of plant, which grew wild in Otani district of Tokushima City were collected and the presence of a quaternary base was examined by the method described below.

Crystals of m.p. 252° (decomp.) were isolated as the iodide, and the base was established as magnoflorine iodide by the comparison of general chemical properties and infrared spectra with the authentic specimen.

Furthermore, it was proved that no other quaternary bases are contained, and therefore that this plant, in its stem and leaves, as well as in its root, contains magnoflorine alone as the quaternary base. The stem and leaves, however, contain only 0.004% of magnoflorine, whereas the base is obtained in 0.08% yield from the root.

Recently, magnoflorine has been found in a fairy wide range of plant families, including Magnoliaceae, Menispermaceae, Berberidaceae, Rutaceae, Aristolochiaceae, and Ranunculaceae. The presence of magnoflorine in the plant of Ranunculaceae family was hitherto known only in one example[2] (*Coptis japonica* MAKINO), and this is the second case.

Examination of tertiary bases in *Thalictrum Thunbergii* DC. is now being continued by the authors.

The infrared spectra were measured by Mr. M. Narisada of the Research Laboratory, Shionogi & Co. Ltd., through the good offices of Prof. Dr. M. Tomita, University of Kyoto. The authors acknowledge their indebtedness to them. Their thanks are due to Mr. A. Takamatsu for the microanalyses.

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[1] Part I. E. Fujita, T. Tomimatsu: This Bulletin, **4**, 489(1956).

[2] M. Tomita, S. Kura: Yakugaku Zasshi, **76**, 1425(1956).

Experimental[3]

Isolation and Purification of Magnoflorine—2.4 kg. of the stem and leaves of *Talictrum Thunbergii* DC., collected in November, 1955, at Otani district of Tokushima City, and dried, were coarsely ground and their extraction with boiling MeOH for 7 hrs. was repeated 3 times. MeOH was evaporated *in vacuo* and 500 g. of crude extract was obtained. It was then extracted with about 4 parts of 2% AcOH, and the AcOH solution was freed from acidic and neutral substances by ether extraction. The mother liquor was made alkaline with NH_4OH, the tertiary base that precipitated was extracted exhaustively with ether, the mother liquor freed from the tertiary base was neutralized with AcOH, and was further acidified weakly with HCl. To this solution, the aq. solution of NH_4 reineckate was added, and the precipitate formed was collected by filtration (the filtrate gave a negative test with the Meyer reagent). The reineckate obtained here was dried by standing at room temperature, dissolved in acetone, and the insoluble resinous substance was filtered off. To the filtrate was added 0.6% Ag_2SO_4 to decompose the salt, $BaCl_2$ to convert the sulfate solution into the chloride solution, and Ag reineckate and $BaSO_4$ were filtered off. The chloride solution was concentrated *in vacuo*, but no crystalline product was obtained. The iodide, precipitated by adding aq. KI to this chloride solution, was treated once with a small amount of charcoal, repeatedly recrystallized from MeOH, and 0.1 g. of colorless pillars, m.p. 252°(decomp.), was obtained. *Anal.* Calcd. for $C_{20}H_{24}O_4NI$: C, 51.18; H, 5.15. Found : C, 50.94; H, 5.29.

It gave no depression of m.p. on admixture with magnoflorine iodide, m.p. 252°(decomp.), and furthermore, the absorption curve of its infrared spectrum agreed completely with that of magnoflorine iodide. The mother liquor from the iodide gave a negative test with the Meyer reagent.

Summary

From the part of the stem and leaves of *Thalictrum Thunbergii* DC., magnoflorine was isolated.

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[3] All melting points are uncorrected.