U.D.C. 547.837.1 : 582.675.4

Tatsuhiko Nakano and Mikio Uchiyama : Studies on the Alkaloids of Menispermaceous Plants. CXXXVIII.[1] Alkaloids of *Cocculus laurifolius* DC. (Suppl. 9).[2] Isolation of Magnoflorine.*

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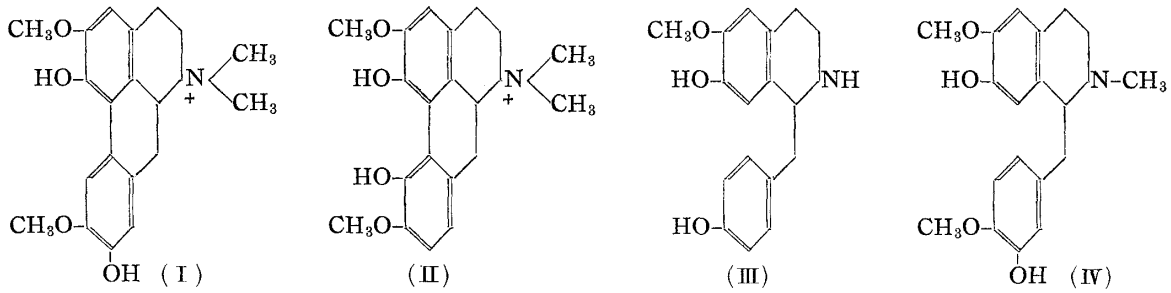
At an earlier date, Tomita and Kusuda[3] recorded the isolation of quaternary alkaloids, laurifoline (I) and a base (picrate, m.p. 88°), from *Cocculus laurifolius* DC. At that time, they obtained, after separating laurifoline as the crystalline chloride, the remaining uncrystallizable alkaloid as the mercuric salt, but left it unexamined. This investigation has been resumed using the material which was left by them.

Decomposition of this mercuric chloride of the quaternary base with hydrogen sulfide and subsequent conversion of the resulting chloride into the styphnate yielded yellow needles, m.p. 230~231°(decomp.). The iodide also crystallized in colorless pillars, m.p. 249°(decomp.). Their molecular formulae and melting points were found to be in accord with those given for the corresponding derivatives of magnoflorine[4](II), and this similarity was also confirmed by infrared spectra.

Since it was known so far that *Cocculus laurifolius* DC. contains coclaurine (III) and coclanoline (IV), besides laurifoline (I), this proof as to the occurrence of magnoflorine (II) in the same plant is of significance in considering the biogenesis of these series of alkaloids.



We wish to express our appreciation to Prof. M. Tomita for his interest in this work, and to Messrs. Y. Matsui and M. Narisada of the Research Laboratory, Shionogi & Co. Ltd., for the measurement of the infrared spectra. The expenses of this investigation have been partly defrayed by a Grant in Aid of Fundamental Scientific Research from the Ministry of Education.

Experimental[5]

Isolation of Magnoflorine from *Cocculus laurifolius* DC.—2.0 g. of the quaternary base mercuric chloride was dissolved in MeOH and decomposed with H_2S. The filtrate from HgS precipitate was evaporated to dryness *in vacuo*, the residue was dissolved in a small portion of water, and treated with aq. sodium styphnate. The resulting precipitate, after crystallization from acetone, yielded 1.8 g. of yellow needles, m.p. 230~231°(decomp.), which was shown by infrared spectrum to be identical with magnoflorine styphnate. *Anal.* Calcd. for $C_{20}H_{24}O_4N \cdot C_6H_2O_8N_3$: C, 53.24; H, 4.47.

* This constitutes a part of a series entitled "Studies on the Alkaloids of Menispermaceous Plants" by Masao Tomita.

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1) Part CXXXVII. M. Tomita, T. Kugo : J. Pharm. Soc. Japan, **76**, 857(1956).
2) (Suppl. 8). M. Tomita, I. Kikkawa : This Bulletin, **4**, 230(1956).
3) M. Tomita, F. Kusuda : *Ibid.*, **1**, 1, 5, 55(1953).
4) T. Nakano : *Ibid.*, **2**, 326, 329(1954).
5) All melting points are uncorrected. We are indebted to Dr. K. Hozumi, Mr. K. Imaeda, and Miss F. Tanase of the Central Analysis Room of this Institute for the microanalytical data.

Found : C, 53.18; H, 4.70. The iodide formed colorless pillars, m.p. 249°(decomp.), from MeOH, whose infrared spectrum was shown to be identical with that of magnoflorine iodide. *Anal.* Calcd. for $C_{20}H_{24}O_4NI$: C, 51.18; H, 5.15. Found : C, 51.26; H, 5.31.

Summary

The quaternary base magnoflorine (II) was identified from *Cocculus laurifolius* D.C besides laurifoline (I).

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Tatsuhiko Nakano and Mikio Uchiyama : Studies on the Alkaloids of Magnoliaceous Plants*. XVII.[1] Alkaloids of *Magnolia parviflora* SIEB. ET ZUCC.

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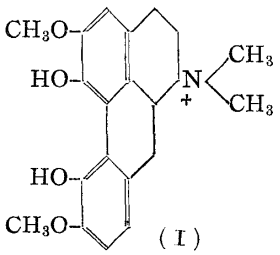
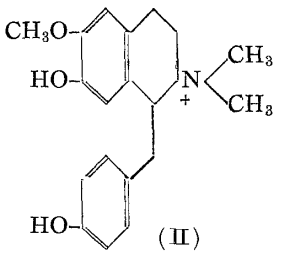
Surveys of the alkaloidal constituents of Magnolia plants have in recent years been the subject of chemical research in our laboratory and their scope was so far extended to nearly all species of the Magnolia genus which occur in this country. The present paper describes the investigation dealing with *Magnolia parviflora* SIEB. ET ZUCC., which was collected in October, 1955, in the southern part of Kyushu.

Treatment of the methanolic extract of its bark by the usual method yielded two quaternary alkaloids. One was isolated as a styphnate of yellow microneedles, m.p. 230~231°(decomp.). Its empirical formula and melting point suggested a close similarity to magnoflorine[2] (I) styphnate, the identity of which was established by direct comparison of their infrared spectra. The other was obtained as a picrate of yellow needles, m.p. 180~181°, from the mother liquor left after separation of magnoflorine styphnate. The analyses gave values corresponding to the composition of magnocurarine[3] (II) picrate, and their identity was confirmed by mixed melting point determination.



(I)



(II)

We are indebted to Prof. M. Tomita for his encouragement in this work, to Mr. T. Kikuchi in our laboratory for helping us in the collection of the plant material used in this experiment, and to Messrs. Y. Matsui and M. Narisada of the Research Laboratory, Shionogi & Co. Ltd., for the infrared spectral determinations. This work was supported in part by a Grant in Aid for Fundamental Scientific Research from the Ministry of Education, to which we are also grateful.

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* This constitutes a part of a series entitled "Studies on the Alkaloids of Magnoliaceous Plants" by Masao Tomita.

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1) Part XVI. T. Nakano : This Bulletin, **4**, 67(1956).
2) T. Nakano : *Ibid.*, **2**, 326, 329(1954).
3) M. Tomita, T. Nakano : J. Pharm. Soc. Japan, **72**, 1260(1952).