yellow needles, m.p. 128°; [α]$^{21}_{D}$: +47.5°(c=1.38 in $CHCl_3$). Yield : 0.1 g.

(−)Isodihydrousic acid, faint yellow needles (from MeOH), m.p. 128°; [α]$^{20}_{D}$: −48.4°(c=1.59 in $CHCl_3$), and (±)isodihydrousnic acid, faint yellow plates (from MeOH), m.p. 158°; [α]$_D$ 0, were obtained from (+) and (±)dihydrousnic acids, respectively, under the same procedure used for the preparation of (−)isodihydrousnic acid. *Anal.* Calcd. for $C_{18}H_{18}O_7$: C, 62.42; H, 5.24. Found ((+)Isodihydrousnic acid) : C, 62.60; H, 5.46. ((−)Isodihydrousnic acid) : C, 62.43; H, 5.36. ((±)Isodihydrousnic acid) : C, 62.54; H, 5.30.

On heating isodihydrousnic acid with anhyd. $CaCl_2$ under ordinary pressure, a small amount of acetylacetone distilled out and then yellowish needles, m.p. 127°, were obtained on sublimation *in vacuo*, which were identified with 3,5-dimethyl-6-hydroxy-7-acetylcoumaran-2-one by a mixed fusion (mixed m.p. 127°).

Summary

(−) and (+)Dihydrousnic acid were directly prepared from (+) and (−)usnic acid by catalytic hydrogenation using palladium black as a catalyst and tetrahydrofuran as a solvent. On heating *in vacuo*, (−) and (+)dihydrousnic acid were converted into isomeric (+) and (−)isodihydrousnic acid, respectively.

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Tatsuhiko Nakano : Studies on the Alkaloids of Magnoliaceous Plants. XVI⁽¹⁾. Alkaloids of *Magnolia denudata* Desr. (2).⁽²⁾*

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An earlier paper²⁾ of this series showed the presence of three quaternary bases, salicifoline, magnocurarine, and a new alkaloid of undetermined structure (picrate, m.p. 222~223°) in the bark of *Magnolia denudata* Desr. (Japanese name "Hakumokuren"). The new supply of the root of the plant material being now available, further investigation was continued, and this paper presents the isolation of another quaternary base from this root.

The treatment with a procedure so far described in this series yielded a quaternary base as the styphnate forming yellow aggregate crystals, m.p.230~231°(decomp.)³⁾, in a small quantity. The analyses were in accord with the composition, $C_{20}H_{24}O_4N \cdot C_6H_2O_8N_3$, in which two methoxyls and one $N(CH_3)_2$ group were confirmed. The picrate, crystallized as slightly brownish yellow microscopic pillars, m.p. 202~203° (decomp.). The iodide came in colorless pillars, m.p. 248~249°(decomp.). The methylation of the iodide with methyl iodide and alkali furnished the O,O-dimethyl ether iodide, as colorless needles, m.p. 243°(decomp.). On ethylation with ethyl iodide and alkali, the O,O-diethyl ether iodide was obtained as colorless needles, m.p. 235°.

The molecular formula and general properties of this alkaloid suggested a similarity to the aporphine bases, and this relationship became evident when these

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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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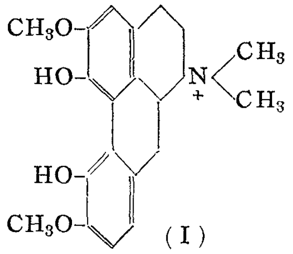
1) Part XV. T. Nakano : This Bulletin, **3**, 234(1955).

2) Part (1). M. Tomita, T. Nakano : J. Pharm. Soc. Japan, **72**, 1260(1952).

3) This decomposition point somewhat dependeds upon the rate of heating.


(I)

experimental data were compared with those given for the corresponding derivatives of magnoflorine[4] (I), a major alkaloid of *Magnolia grandiflora* L. (Japanese name "Daisanboku"). This identity was further confirmed by direct comparison of the infrared spectra of some of their derivatives. For convenience of comparison, the occurrence and distribution of the quaternary bases of *Magnolia denudata* Desr. are shown in Table I.

TABLE I.

	Organ	Quaternary alkaloids
M. denudata Desr.	Bark	Salicifoline, Magnocurarine, Picrate (m.p. 222~223°)
	Root	Magnoflorine

The author wishes to acknowledge his indebtedness to Prof. Dr. M. Tomita for his interest in this work; to Drs. Kato, Hiyama, Messrs. Tanno, Kawami, and Niki of the Osaka Factory of Dainippon Pharmaceutical Industries for according him facilities in the preparation of the methanol extract of the plant material, and to Messrs. Matsui and Narisada of Research Laboratory, Shionogi & Co., Ltd., for the measurement of the infrared spectra. This work has been supported partly by a Grant in Aid for Fundamental Scientific Research from the Ministry of Education, to which the author is also grateful.

Experimental[5]

(1) **Extraction and Isolation of Magnoflorine**—12 kg. of coarsely ground root of *M. denudata* Desr., collected in February, 1955, in Kyoto City, was extracted 3 times with hot MeOH, and the extract was evaporated *in vacuo*. The syrupy residue was treated in the usual manner, yielding only a trace of tertiary bases, too small to be worked up. On the other hand, the quaternary base was purified by reprecipitating as the reineckate, then as the $HgCl_2$ salt, and finally isolated as the crystalline styphnate. Yield, 1.9 g. It formed from a mixture of acetone and MeOH yellow aggregate crystals, m.p. 230~231° (decomp.), the infrared spectrum of which was identical with that of magnoflorine styphnate from *M. grandiflora* L. (Nujol mull). *Anal.* Calcd. for $C_{20}H_{24}O_4N \cdot C_6H_2O_8N_3$: C, 53.24; H, 4.47; N, 9.55; OCH_3, 10.58; NCH_3, 5.12. Found: C, 53.50; H, 4.58; N, 9.39; OCH_3, 10.77; NCH_3, 5.31.

The above styphnate was decomposed with HCl and the liberated styphnic acid eliminated by means of ether. The aqueous layer was evaporated *in vacuo* to dryness. A portion of the residue was converted into a picrate, which was induced to crystallize from a mixture of acetone and EtOH, yielding slightly brownish yellow microscopic pillars, m.p. 202~203° (decomp.). *Anal.* Calcd. for $C_{20}H_{24}O_4N \cdot C_6H_2O_7N_3$: C, 54.73; H, 4.59; N, 9.82. Found: C, 54.42; H, 4.77; N, 9.27. The major portion was treated with aq. KI, and the iodide obtained was recrystallized from MeOH to colorless pillars, m.p. 248~249° (decomp.). *Anal.* Calcd. for $C_{20}H_{24}O_4NI$: C, 51.18; H, 5.15. Found: C, 51.31; H, 5.01. The infrared spectrum was identical with that of magnoflorine iodide.

(2) **O,O-Dimethylmagnoflorine Iodide**—The above iodide was methylated with MeI and alkali following the same procedure as described for the preparation of O,O-dimethylmagnoflorine iodide.[4] The O,O-dimethyl ether iodide thus obtained crystallized from MeOH as colorless needles, m.p. 243° (decomp.), which was shown by infrared spectrum to be identical with O,O-dimethylmagnoflorine iodide. *Anal.* Calcd. for $C_{22}H_{28}O_4NI$: C, 53.12; H, 5.48; OCH_3, 24.96. Found: C, 53.20; H, 5.51; OCH_3, 24.70.

(3) **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 iodide. The O,O-diethyl ether iodide was obtained from EtOH as colorless needles, m.p. 235°. *Anal.* Calcd. for $C_{24}H_{32}O_4NI$: C, 54.86; H, 6.14. Found: C, 54.66; H, 6.31.

Summary

A quaternary alkaloid, magnoflorine (I) has been identified from the root of *Magnolia denudata* Desr. (Magnoliaceae).

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[4] T. Nakano: This Bulletin, **2**, 326, 329 (1954).

[5] All melting points are uncorrected. The author wishes to thank Messrs. K. Hozumi and K. Imaeda, and Miss F. Tanase of the Microanalytical Laboratory of this Institute for the microanalyses.