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Toshiro Ibuka and Masahiko Kitano*1 : Studies on the Alkaloids of Menispermaceous Plants. CCXXXVIII.*2 Alkaloids of *Stephania japonica* Miers. (Suppl. 18).*2 Structure of Hasubanonine (Supplement 1).

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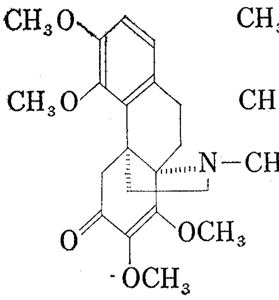
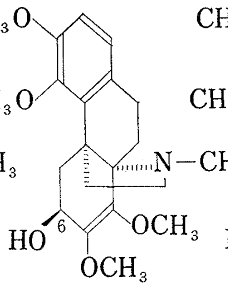
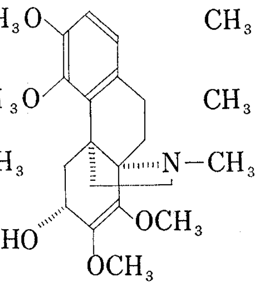
Hasubanonine (I) was first isolated from the basic fraction of *Stephania japonica* Miers by Kondo, *et al.*[1] and the early structural works of Kondo and his coworkers,[2] Watanabe and Matsumura,[3] and more recent degradative and spectroscopic investigations by Tomita and his colleagues[4] serve to establish the structural feature of the base.

The present paper describes a supplementary studies on the structure of hasubanonine derivatives.


I


IIa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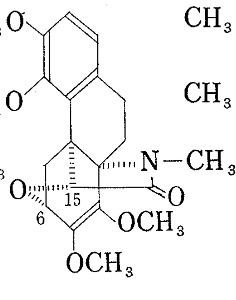
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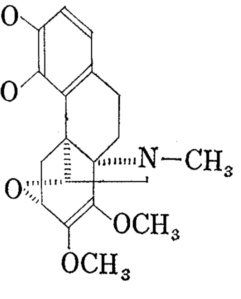
IV

Sodium borohydride reduction of hasubanonine (I), as reported previously,[4] yielded two epimeric alcohols, namely *quasi* axial hydroxyl compound (IIa) and *quasi* equatorial compound (IIb). On treatment of the alcohol (IIb) with activated manganese dioxide in chloroform gave a lactam (III), m.p. 152~156°, along with hasubanonine (I),[4] whereas oxidation of IIa with the same reagent afforded hasubanonine (I) as sole product.[4]

The configuration of the hydroxyl group of IIb and the structure of the lactam (III) was confirmed by following evidences. Elementary analysis and mass spectrometric determination of the lactam (III) demonstrated that the correct molecular formula is $C_{21}H_{25}O_6N$ (M^+ 387). The IR spectrum*3 of III showed five membered lactam carbonyl at $1688\ cm^{-1}$ and the NMR spectrum*4 revealed four methoxyl groups at 6.08, 6.19, 6.23 and 6.38 τ, one N-methyl group at 7.13 τ, C-6 proton at 5.38 τ as doublet (J=6.0 c.p.s.), and

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*2 This paper constitutes a part of a series entitled " Studies on the Alkaloids of Menispermaceous Plants " by Masao Tomita. Part CCXXXVII and Suppl. 17; T. Ibuka, M. Kitano : This Bulletin, in press.

*3 All IR spectra were taken in chloroform solution.

*4 All NMR spectra were taken on Varian Associates A-60 recording spectrometer in deuteriochloroform with tetramethylsilane as an internal standard.

1) H. Kondo, M. Satomi, T. Odera : Ann. Rep. ITSUU Lab., **2**, 35 (1951).

2) M. Satomi : *Ibid.*, **3**, 37 (1952); H. Kondo, M. Satomi, T. Odera : *Ibid.*, **4**, 45 (1953); H. Kondo, M. Satomi : *Ibid.*, **8**, 41 (1957).

3) Y. Watanabe, H. Matsumura : Yakugaku Zasshi, **83**, 991 (1963).

4) M. Tomita, T. Ibuka, Y. Inubushi, Y. Watanabe, M. Matsui : Tetrahedron Letters, No. 40, 2937 (1964); *Idem* : This Bulletin, **13**, 538 (1965).

C–15 proton at 5.58 τ as singlet. Lithium aluminum hydride reduction of Ⅲ gave the basic product (Ⅳ), m.p. 174°, $C_{21}H_{27}O_5N$ (M^+ 373). The IR spectrum of Ⅳ showed enolic double bond band at 1668 cm^{-1} and the NMR spectrum revealed four methoxyl groups at 6.09, 6.20, 6.30 (6H) τ, one N-methyl group at 7.72 τ, C–6 proton at 5.49 τ as doublet ($J=6.0$ c.p.s.), and C–15 proton at 5.26 τ as quartet ($J_A=3.0$ c.p.s., $J_B=7$ c.p.s.).

The configuration, α or β, of an equatorial hydroxyl group at C–6 of dihydrohasubanonine–B (Ⅱb) is determined by the nature of formation of ether bridge between C–6 and C–15 on treatment with manganese dioxide and the hydroxyl group must have α-configuration, and accordingly an axial substituent at C–6 of dihydrohasubanonine–A (Ⅱa) is β-oriented.

Experimental[*5]

Lactam (III)[4)]——Repeated recrystallization from ether gave the lactam (Ⅲ) as colorless flakes, m.p. 152~156°. *Anal.* Calcd. for $C_{21}H_{25}O_6N$: C, 65.10; H, 6.50. Found: C, 65.14, 65.18; H, 6.59, 6.75.

Lithium Aluminum Hydride Reduction of the Lactam (III)——To a solution of Ⅲ (28 mg.) in tetrahydrofuran (15 ml.) was added 250 mg. of $LiAlH_4$ and the mixture was refluxed for 8 hr. and after cooling the excess reagent was decomposed with water, and extracted with $CHCl_3$. The $CHCl_3$ extract was washed, dried over $MgSO_4$ and evaporated to give a crystalline solid. Recrystallization from MeOH gave pure compound (Ⅳ) as colorless needles, m.p. 174°. *Anal.* Calcd. for $C_{21}H_{27}O_5N$: C, 67.54; H, 7.29. Found: C, 67.84; H, 7.23.

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[*5] All melting points were determined on Yanagimoto Micro Melting Point Apparatus and uncorrected.