

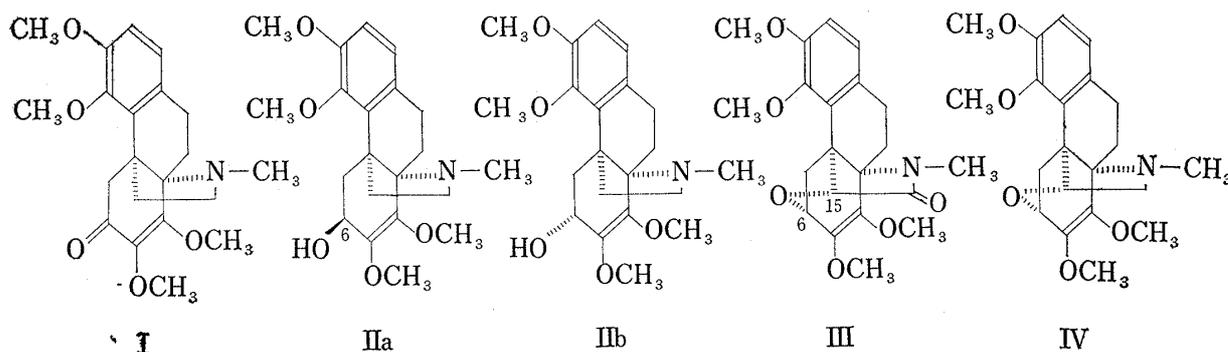
Toshiro Ibuka and Masahiko Kitano*¹: Studies on the Alkaloids
of Menispermaceous Plants. CCXXXVIII.*² Alkaloids of
Stephania japonica MIERS. (Suppl. 18).*³ Structure
of Hasubanone (Supplement 1).

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Hasubanone (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 colleagues⁴⁾ serve to establish the structural feature of the base.

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



Sodium borohydride reduction of hasubanone (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 hasubanone (I),⁴⁾ whereas oxidation of IIa with the same reagent afforded hasubanone (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 C₂₁H₂₅O₆N (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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*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 dihydrohasubanone-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 dihydrohasubanone-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.