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THE RELATIVE CONFIGURATIONS BETWEEN VIROSECURININE, SECURININE AND ALLOSECURININE

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IN our previous papers,[1] it was shown that virosecurinine, an alkaloid of Formosan Securinega virosa, has structure (I) and that it is antipodal with securinine isolated from S. suffruticosa by Russian chemists[2] and also by two groups of Japanese workers.[3] We have now established the absolute configuration of C_6 in virosecurinine and also the relative configurations between virosecurinine and its related alkaloids.

Virosecurinine (I), when reduced with amalgamated aluminum in ether-methanol, yielded the liquid unsaturated amino lactone (IIa), $\lambda_{max}^{CHCl_3}$ 2.85, 3.02, 5.69 (α,β-unsaturated γ-lactone), 6.04 and 11.86 μ, λ_{max}^{EtOH} 210.5 mμ. The U.V. absorption spectrum of this compound indicates that it is an α,β-unsaturated γ-lactone[1] which has no ethylenic double bond extending the conjugation of this system. It formed a picrate, m.p. 217° (decomp.), $[\alpha]_D$ -86° (acetone), λ_{max}^{Nujol} 3.11 and 5.73 μ, λ_{max}^{EtOH} 211 mμ (log ε 4.57). Acetylation of IIa with acetic anhydride and pyridine led to the acetate (IIb), m.p. 136°, $[\alpha]_D$ -227°, $\lambda_{max}^{CHCl_3}$ 5.71, 6.06, 6.13 and 11.74 μ, λ_{max}^{EtOH}

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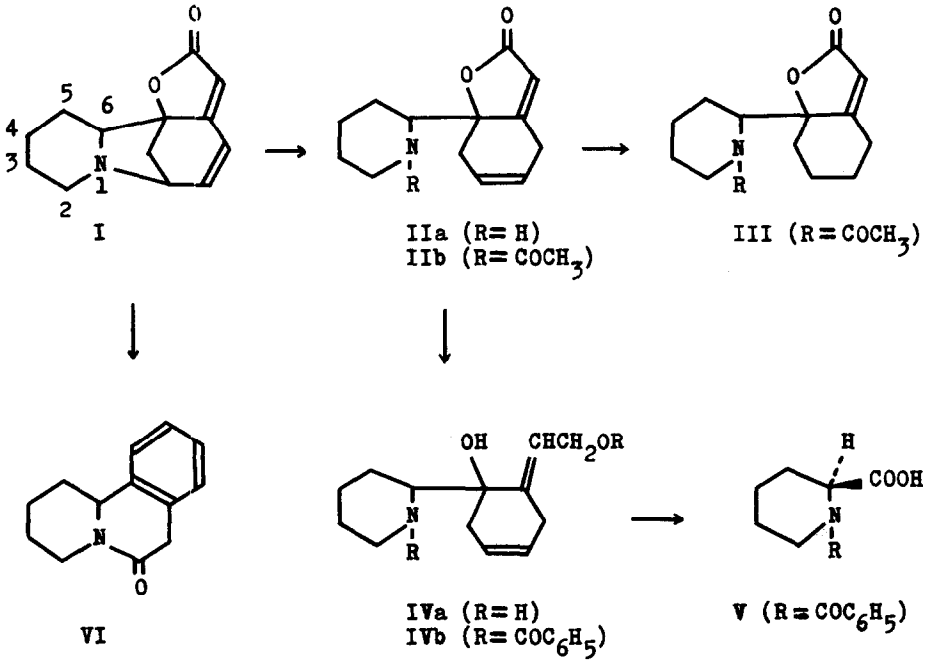
1 T. Nakano, T. H. Yang and S. Terao, Chem. & Ind. 1651 (1962); Ibid., Tetrahedron, 19, 609 (1963).

2 V. I. Murav'eva and A. I. Ban'kovskii, Doklady Akad. Nauk S.S.S.R. 110, 998 (1956).

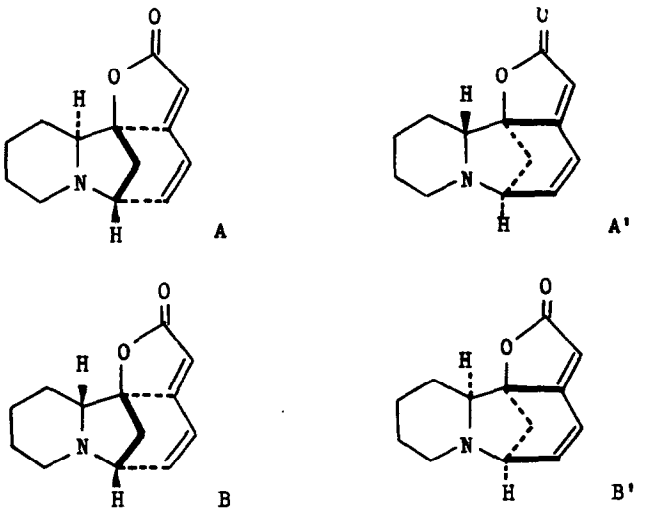
3 I. Satoda, M. Murayama, J. Tsuji and E. Yoshii, Tetrahedron Letters, No. 25 1199, (1962); S. Saito, K. Kodera, N. Sugimoto, Z. Horii and Y. Tamura, Chem. & Ind. 1652 (1962).

205.5 mμ (log ε 4.18) and 230 mμ (shoulder) (log ε 3.94). Catalytic hydrogenation of IIb with palladized charcoal in ethanol resulted in the rapid uptake of one molar equivalent of hydrogen and afforded III, the identity of which was proved by direct comparison (I.R., $[\alpha]_D$, U.V. and mixture m.p.) with the sample obtained previously by a different sequence of reactions.[1]



Reduction of IIa with lithium aluminum hydride led to the unsaturated amino diol (IVa), m.p. 94°, $[\alpha]_D$ +152°, $\lambda_{max}^{CHCl_3}$ 2.77, 2.95, 6.03 and 6.22 μ, no selective U.V. absorption; Picrate, m.p. 168-169°, $[\alpha]_D$ +22°. Benzoylation of IVa with benzoyl chloride and pyridine gave the benzoate (IVb). On oxidation of IVb with potassium permanganate in aqueous acetone in the presence of magnesium sulfate, there was obtained N-benzoyl-L-(-)-pipecolic acid

(V),[4] m.p. 128.5-129°, $(\alpha)_D$ -46°, $\lambda_{max}^{CHCl_3}$ 5.85 and 6.16 μ, whose infrared spectrum was shown to be identical in chloroform with that of the DL-compound.[5]



Turning now to the configuration of virosecurinine, four isomers (A and B are antipodal with A' and B', respectively.) are possible. By the isolation of N-benzoyl-L-(-)-pipecolic acid, it is clear that virosecurinine corresponds to either A or B'.

Satoda et al.[3] reported the isolation of another alkaloid, allosecurinine, from the mother liquor of securinine, and showed that it is a diastereoisomer of securinine. By treatment of these two alkaloids with zinc dust and sulfuric acid, they obtained two antipodal lactams corresponding to VI. One (from securinine) has m.p. 74-75°, $(\alpha)_D$ +13.9°, and the other (from allosecurinine), m.p. 69°, $(\alpha)_D$

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[4] Reported m.p. 133° and $(\alpha)_D$ -72° (J. W. Clark-Lewis and P. I. Mortimer, J. Chem. Soc. 189-201 (1961).

[5] N-Benzoyl-DL-pipecolic acid was prepared according to the method of F. E. King, T. J. King and A. J. Warwick, J. Chem. Soc. 3590 (1950).

-32.7°. The latter compound corresponds to the lactam (VI), m.p. $75-76^{\circ}$, $(\alpha)_D$ -35.7°, which we previously obtained from virosecurinine by the same reaction, and hence virosecurinine and allosecurinine must have identical absolute configuration at C_6 in their molecule. It follows, therefore, that if virosecurinine is postulated to be A, then allosecurinine should be B', or vice versa. Since securinine and virosecurinine are mirror-images of each other, securinine should be either A' or B dependent upon whether virosecurinine is A or B', respectively.

All melting points are uncorrected; $(\alpha)_D$ was measured in 95 % ethanol unless indicated otherwise; all crystalline compounds described gave correct analyses.

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