

THE STRUCTURE OF ECHITAMINE
(ADDENDUM)

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(Received 23 April 1960)

A recent letter¹ mentioned work on the chemistry of echitamine undertaken by the three first-named authors since 1955 [thesis (R. Ghose) Calcutta, 1957] and the postulated relationship with pseudo-akuammigine, also dating from before 1957. Our views on the structural aspect were largely in agreement with Conroy *et al*² and differed from those expressed by Govindachari³, Birch⁴ and (Mrs.) A. Chatterjee⁵ with their respective collaborators. In particular we rejected formulae^{3,4,5} containing $\overset{\cdot\cdot}{\text{MeN}}(\text{a}) \cdot \overset{\cdot\cdot}{\text{C}}(\text{OH})$ in favour of one containing $\overset{\cdot\cdot}{\text{MeN}}(\text{b}) \cdot \text{CH}(\text{OH})$ and we also considered that the pseudo-strychnine-like structure² should be replaced by one based on the N(b) methylajmaline model.

Further consideration of the evidence presented by Conroy *et al* and by Chatterjee *et al* (*loci cit*), the significance of which we had not fully appreciated, suggests that the $\overset{\cdot\cdot}{\text{MeN}}(\text{b}) \cdot \text{CHOH}$ group may not be in

¹ The present authors, Tetrahedron Letters No. 10, 10 (1960).

² H. Conroy, R. Bernasconi, P. R. Brook, R. Ikan, R. Kurtz and K. W. Robinson, Tetrahedron Letters No. 6, 1 (1960).

³ T. R. Govindachari and S. Rajappa, Proc. Chem. Soc. 134 (1959)

⁴ A. J. Birch, H. F. Hodson and G. F. Smith, Proc. Chem. Soc. 224 (1959)

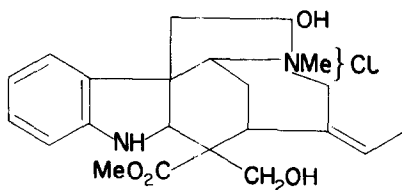
⁵ A. Chatterjee, S. Ghosal and S. G. Majumdar, Chemistry and Industry 265 (1960).

the same position as in methylajmaline salts but in the alternative position with the original tryptamine side-chain in the form
 $-\text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \overset{\cdot\cdot}{\text{N}}\text{Me} \} \text{Cl}$ (echitamine chloride).

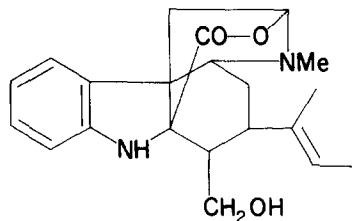
The superiority of this modification follows from the observation of Conroy et al that catalytic reduction of echitamine chloride affords the crystalline base echitinolide, $\text{C}_{21}\text{H}_{26}\text{O}_3\text{N}_2$, containing 2 Me(C) groups. This lactone is the result of hydrogenolysis of an allylic group and as the three oxygens are retained, the original salt cannot contain $\overset{\cdot\cdot}{\text{N}}\text{N}(\text{b}) \cdot \text{CH}(\text{OH}) \cdot \overset{\cdot}{\text{C}} = \text{CHMe}$. Therefore the $-\text{CH}(\text{OH})$ must be on the other side of N(b) in the group $\cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \overset{\cdot\cdot}{\text{N}}\text{Me} \cdot \text{CH}_2 \cdot \overset{\cdot}{\text{C}} : \text{CHMe}$.

This small but important modification also accommodates the finding of Chatterjee et al.⁵ that the oxidation of echitamine with periodic acid affords indole-3-acetaldehyde.

The structure which we now propose for echitamine chloride is (I) and echitinolide would be a lactone with a 7-membered bridge (II).



I



II