The Stereochemistry of Formosanine (Uncarine B) and Uncarine A

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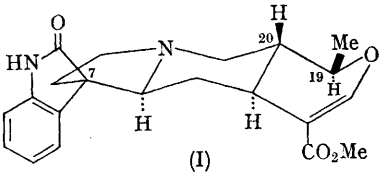
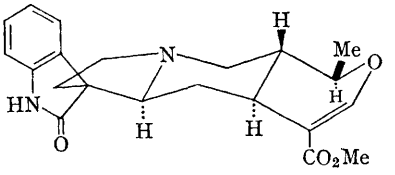
STUDY of the 100 Mc./sec. n.m.r. spectrum and circular dichroism (c.d.) of formosanine (uncarine B) has shown the need for revision of the previously assigned stereochemistry,[1] and formosanine and its C-7-epimer, uncarine A, are now represented by (I) and (II) respectively. Formosanine was previously assigned the stereochemistry indicated in (III) because of the resemblance of its 60 Mc./sec. n.m.r. spectrum to that of mayumbine.[1] The estimated value (J = 2·9 c./sec.) for the C-19–H, C-20–H coupling constant is consistent with the pseudo-axial–equatorial configuration shown in (III)[1] but the overlapping of the C-19–H multiplet and the signal from the CO_2Me methyl group makes the determination of the coupling constant difficult. However, in the 100 Mc./sec. spectrum, these signals are completely resolved, and the value (J = 9 c./sec.), determined by first-order analysis of the multiplet and confirmed by spin–spin decoupling, is consistent with the pseudo-*trans*-diaxial configuration for the C-19–H and C-20–H shown in (I).

The close resemblance of the c.d. spectrum of formosanine (negative band at 263 mμ and positive band at 288 mμ) to that of mitraphylline,[2,3] on which it is virtually superimposable, confirms the *trans*-D/E ring junction indicated in (I). By contrast, if formosanine had the previously assigned *cis*-D/E ring junction, the c.d. spectrum would resemble that of uncarine D (speciophylline), the C-19–epimer of (III) (positive band at 252 mμ and negative band at 290 mμ).[2]

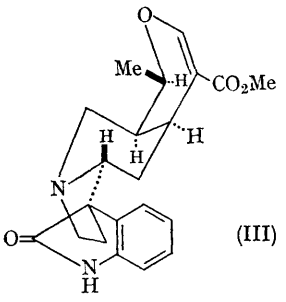
From the structures (I) and (II) now assigned, it is seen that formosanine and uncarine A are the C-19-epimers of mitraphylline and isomitraphylline respectively. The upfield shift of the C-19–H multiplet in the spectrum of formosanine (δ 3·79) relative to the position in the spectrum of mitraphylline (δ 4·38) is in accord with the shielding of the pseudo-axial C-19–H by the C-16,C-17-double bond in (I). Moreover, only two stereoisomers are formed on equilibration of either mitraphylline or formosanine by heating in pyridine or acetic acid, compared with the four stereoisomers produced from any one of the stereoisomers having a D/E-*cis* ring junction.[4] The respective assignments of the C-7 stereochemistry of (I) and (II) to formosanine and uncarine A are in accord with both the c.d.



(I)



(II)



(III)

spectrum of formosanine (positive band at 288 mμ)[2,3] and the relative basic strengths (pK_a 5·5 and 4·2 respectively).[5] Authentic formosanine used in our study was supplied by Dr. Raymond-Hamet.

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[3] J. L. Pousset, J. Poisson, and M. Legrand, *Tetrahedron Letters*, 1966, 6283.
[4] N. K. Hart, S. R. Johns, and J. A. Lamberton, *Chem. Comm.*, 1967, 87.
[5] N. Finch and W. I. Taylor, *J. Amer. Chem. Soc.*, 1962, **84**, 1318, 3871.