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A STUDY OF THE C3/C7 STEREOCHEMISTRY OF UNCARINES C, D, E AND F BY CIRCULAR DICHROISM

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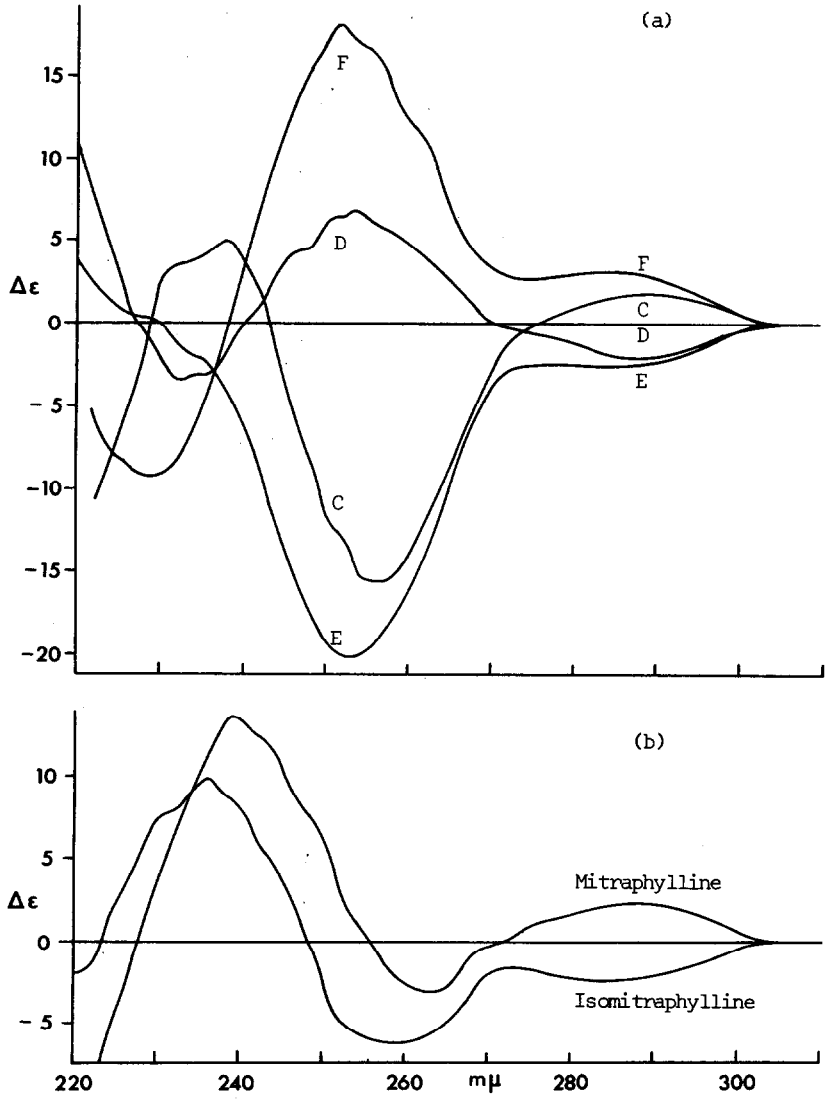
Uncarines C, D, E and F, the four 19α-methyl, 15,20 *cis* oxindoles epimeric at C3 and C7 and related to tetrahydroalstonine have been shown to have structures I-IV[1,2]. For uncarines D and F, which have 3βH, the complete stereochemistry was assigned as shown in III and IV respectively, but for uncarines C and E it was not possible to distinguish between the two structures (I and II) with 3αH and epimeric at C7. A study of circular dichroism (C.D.) spectra has now enabled specific structural assignments to be made for uncarines C and E.

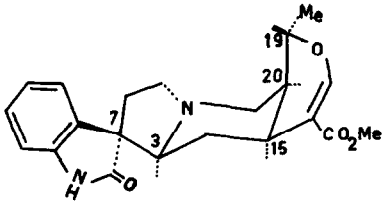
In the spectra of uncarines C and E (both 3α) the bands at 252 mμ are negative, and for uncarines D and F (both 3β) they are positive. The sign of the 252 mμ band system therefore reflects the known stereochemistry at C3[2]. For uncarines C and E the signs of the 290 mμ bands are opposed, as they are also for uncarines D and F. It follows that the 290 mμ band is governed by the stereochemistry at C7. At C7 uncarines D and E have the same configuration and are opposite to uncarines C and F. As the relative configuration at C7 of uncarines D (III) and F (IV) have been assigned from n.m.r. data[2], uncarines C and E must be II and I respectively, as II can be seen to have the opposite configuration to III at both C3 and C7 when models of II and III are viewed with the C3-H bond orientated in the same sense, while I bears a similar relationship to IV.

Comparison of the C.D. curves of the uncarines (Fig. 1a) with the C.D. curves (Fig. 1b) for mitraphylline and isomitraphylline (C15,20 ring junction *trans*, 3α configuration and epimeric at C7) supports this interpretation, as it is in accord with previous assignments of the C7 stereochemistry of mitraphylline and isomitraphylline based on consideration of pK values[3] and C.D. spectra[4].

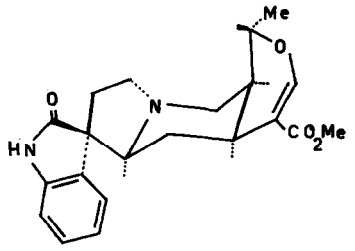
FIG. 1

C.D. curves of (a) uncarine C, D, E and F and of (b) mitraphylline and isomitraphylline. 0.001M in methanol.





I



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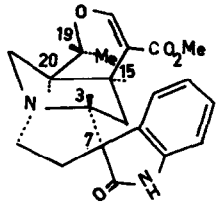
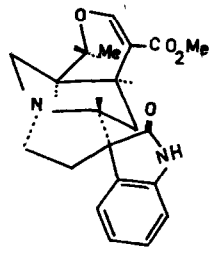


III



IV

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