Total Synthesis of (±)-Methoxycarbonyldihydrocleavamines

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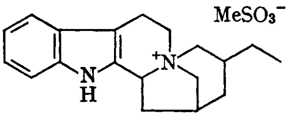
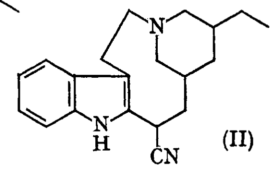
WE have recently described[1] the synthesis of the pentacyclic quaternary salt (I) and its conversion into α- and β-dihydrocleavamines. Treatment of (I) with potassium cyanide[2] yielded a crystalline mixture of stereoisomeric cyano-compounds (II) which with methanolic hydrogen chloride gave a mixture of stereoisomeric methoxycarbonyldihydrocleavamines (III), easily separated by layer chromatography (l.c.) into all four possible racemates. One of these proved identical (l.c. in several solvent systems and mass spectrum) with authentic (optically active) methoxycarbonyldihydrocleavamine prepared from catharanthine and kindly supplied by Prof. G. Büchi. More vigorous hydrolysis of (II) gave, as expected, a mixture of α- and β-dihydrocleavamines.

Alternative rather longer routes to (I), (II), and (III) have recently been briefly reported.[3]

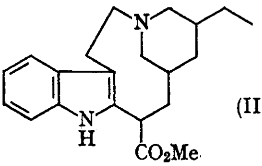
Optically active (III) has previously[4] been converted into the Iboga-type alkaloids coronaridine and dihydrocatharanthine.



(I)



(II)



(III)

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[1] J. Harley-Mason, Atta-ur-Rahman, and J. A. Beisler, *Chem. Comm.*, 1966, 743.

[2] *Cf.* G. H. Foster, J. Harley-Mason, and W. R. Waterfield, *Chem. Comm.*, 1967, 21.

[3] J. P. Kutney, W. J. Cretney, P. Le Quesne, B. McKague, and E. Piers, *J. Amer. Chem. Soc.*, 1966, **88**, 4756.

[4] J. P. Kutney, R. T. Brown, and E. Piers, *Canad. J. Chem.*, 1965, **43**, 1545.