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CATHARANTHUS ALKALOIDS. XXVIII[1].
THE STRUCTURE (CHEMICAL VERIFICATION) AND ABSOLUTE CONFIGURATION OF CATHANNEINE

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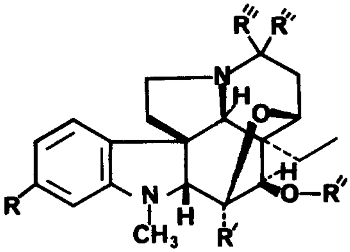
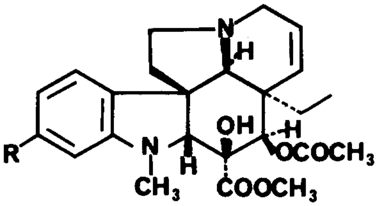
The alkaloid cathanneine has recently[3] been isolated from the leaves of *Catharanthus lanceus* (Boj. ex A. DC.) Pich. and structure I (without stereochemistry) was subsequently postulated for it on the basis of spectral analysis. We have now verified this structure and confirmed the absolute configuration to be as shown by the following chemical transformations.

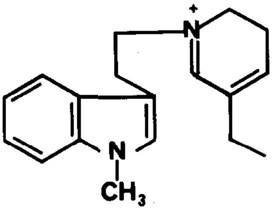
Lithium aluminum hydride reduction of cathanneine in ethereal solution afforded compound II, m.p. 144-146°. The mass spectrum of this compound exhibited major significant peaks at m/e 356 (molecular ion), 267, 212, 158 (base peak) and 144, the latter four peaks being due to ions a-d respectively (*cf.* the mass spectrum of cathanneine[4]; the molecular formulae of these ions were confirmed by high resolution measurements).



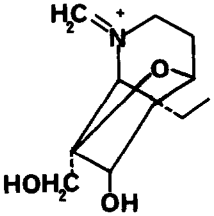
I, R = R''' = H; R' = $COOCH_3$; R'' = $COCH_3$
II, R = R'' = R''' = H; R' = CH_2OH
V, R = H; R' = $COOCH_3$; R'' = $COCH_3$; R''' + R''' = O
VI, R = OCH_3; R' = $COOCH_3$; R'' = $COCH_3$; R''' + R''' = O



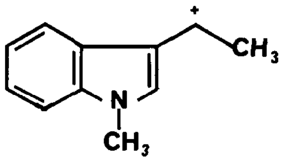
III, R = H
IV, R = OCH_3



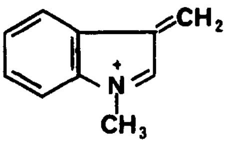
ion a



ion b



ion c



ion d

The structure and absolute configuration of this reduction product (and hence those of cathanneine) were confirmed by its synthesis from vindorosine (III)[5], the absolute configuration of which has been related[6] to that of vindoline (IV)[7], which has been established from X-ray studies on leurocristine[8]. After oxidation with chromic acid in pyridine, this alkaloid afforded a mixture consisting of two major components [R_f 0.75 and 0.85 after TLC on silica gel G using ethyl acetate-absolute alcohol (3:1) as developing solvent], one of which was assumed to have structure V by analogy with the recently reported[9] oxidation under similar conditions of vindoline (IV) to a mixture consisting of compound VI as one component. Without separation, the present oxidation product was reduced with lithium aluminum hydride in a mixture of tetrahydrofuran and ether as solvent. The reduction product was subjected to preparative TLC on silica gel G using methanol as the developing solvent and the area having R_f 0.32, after extraction with ether, afforded compound II, whose identity with the above cathanneine reduction product was confirmed by m.p., mass spectral and TLC comparisons.

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