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STUDIES ON ORCHIDACEAE ALKALOIDS IX*

A 1-phenyl-tetrahydroisoquinoline alkaloid from Cryptostylis fulva Schltr.

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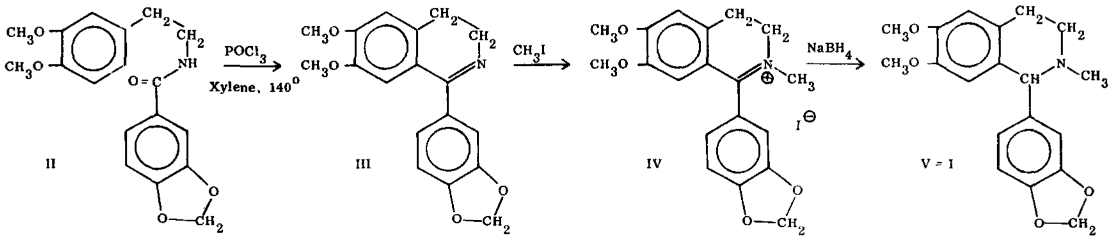
A crystalline alkaloid $C_{19}H_{21}NO_4$ (I) m.p. 101 - 102°; $[\alpha]_D + 54^{\circ}$ (c 2.7, $CHCl_3$), has been isolated from Cryptostylis fulva Schltr. The NMR spectrum (Fig. 1.) as well as the UV absorption at 286.5 mμ (ε_{max} 7800) and 235 mμ (ε_{infl} 12600) indicate that the alkaloid is a phenyl-tetrahydroisoquinoline carrying one N-methyl group, two methoxyl groups and one methylenedioxy bridge. The base peak m/e 206 in the mass spectrum shows that the phenyl group is attached to an α-position relative to the nitrogen atom and that the phenyl group carries the methylenedioxy bridge. The 1H singlet at τ 5.8 which is shifted to τ 4.1 in the methiodide shows that the phenyl group is attached at the 1-position of the tetrahydroisoquinoline system.

On biogenetic grounds the position of the oxygen functions was assumed to be identical with that of the benzylisoquinoline alkaloids and hence 1-(3,4-methylenedioxyphenyl)-2-methyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline was synthesized. In the synthesis, piperonyl chloride was condensed with homoveratryl amine to the amide $C_{18}H_{19}NO_5$(II), m.p. 113 - 114°. A Bischler-Napieralsky cyclization of II with phosphorus oxychloride in xylene afforded the corresponding 3,4-dihydroisoquinoline derivative $C_{18}H_{17}NO_4$(III), m.p. 109 - 110°. Sodium borohydride



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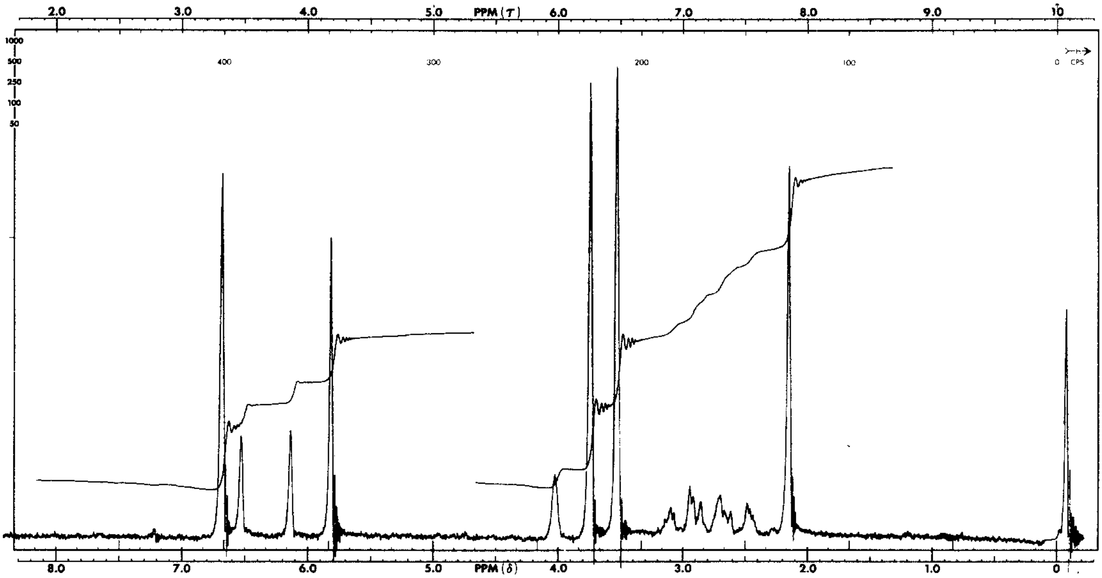
* For Paper VIII of this series see Ref. 1.

reduction of the methiodide of III, $C_{19}H_{20}INO_4$(IV), m.p. 208 - 209°, produced a base $C_{19}H_{21}NO_4$(V), m.p. 117 - 118°, which has all spectral properties identical with I.



I is easily racemized in boiling ether (racemate: m.p. 116 - 117°), most certainly by way of the planar immonium ion, which is also formed by oxidation of I by mercuric acetate.

I is the first 1-phenyl-tetrahydroisoquinoline alkaloid found in Nature. The plant contains at least two more alklaoids of the same class. A full report will be published later.

All crystalline compounds gave satisfactory elementary analyses. NMR-spectra were kindly measured by Dr. K.I. Dahlquist and the mass spectra by Dr. R. Ryhage. This work has been supported by the Swedish Natural Science Research Council.

The plant material was collected in New Guinea together with the staff of Lae Botanic Garden, who operates on grants from Smith, Kline and French Inc., Philadelphia, Pa.

REFERENCES

1. K. Leander and B. Lüning, *Tetrahedron Letters* **1968** in press.