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TOTAL SYNTHESIS OF (±)-EPICRININE BY PHOTOLYSIS

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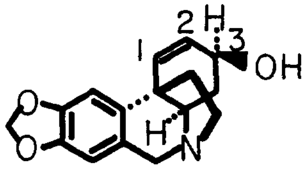
Among various Amarylidaceae alkaloids, epicrinine, which was totally synthesised by Muxfeldt,[1] is a representative of the widely occurring alkaloids which possess 5,10b-ethanophenanthridine ring system. The present report deals with the total synthesis of (±)-epicrinine (1) by photolytic cyclisation as follows.

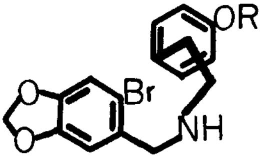
The Schiff base which was readily obtained by the condensation of 4-benzyloxyphenethylamine with 2-bromo-4,5-methylenedioxybenzaldehyde was reduced with sodium borohydride to give the *O*-benzyl derivative (2), which was debenzylated to afford 2-bromo-*N*-(4-hydroxyphenethyl)-4,5-methylenedioxybenzylamine (3). An ethanolic sodium hydroxide solution of (3) was irradiated with a Riko 400 W mercury lamp fitted with a Pyrex-filter at room temperature for 4 hr. Chromatography on the reaction mixture on silica gel, followed by sublimation *in vacuo*, gave (±)-oxocrinine (4), m.p. 175 - 178° (lit.,[1] 172 - 173°; lit.,[2,3] 177 - 178°), in 5 % yield. The compound (4), $C_{16}H_{15}NO_3$ (*M*$^+$, *m/e* 269) displayed a typical enone system in the i.r. spectrum ($\nu_{max.}$ 1675 and 1615 cm^{-1} in $CHCl_3$), and the n.m.r. spectrum (τ in $CDCl_3$) showed two aromatic protons (2.71, 3.46, 2H, each s), two olefinic protons (2.40, 1H, d, *J* 10 Hz; 3.91, 1H, d, *J* 10 Hz), methylene protons due to a methylenedioxy group (4.06, 2H, s), and two benzylic protons (5.53, 1H, d, *J* 17 Hz; 6.19, 1H, d, *J* 17 Hz). Lithium aluminium hydride reduction of (4) afforded (±)-epicrinine (1) as colourless needles, m.p. 235 - 239° (lit.,[1] 235.5 - 237°; lit.,[2,3] 239°), in 60 % yield. The n.m.r. spectrum (τ in $CDCl_3$) revealed two aromatic protons (3.20, 3.53, 2H, each s), two olefinic protons (3.60, 1H, d, d, $J_{1,2}$ 10 Hz, $J_{1,3}$ 2 Hz; 4.22, 1H, d, $J_{1,2}$ 10 Hz), methylene protons due to a methylenedioxy group (4.09, 2H, s), and two benzylic protons (5.58, 1H, d, *J* 17 Hz; 6.23, 1H, d, *J* 17 Hz). The i.r. spectrum (KBr) was superimposable upon that of an authentic sample, kindly donated by Professor Wildman.

Thus, we have accomplished the total photolytic synthesis of (±)-epicrinine by a simple method.

Acknowledgement. We are very grateful to Professor W. C. Wildman, Iowa State University, Iowa, U. S. A., for his gift of (±)-epicrinine.

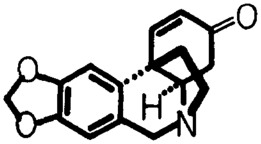


(1)



(2) $R=CH_2Ph$

(3) $R=H$



(4)

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2 (±)-Epicrinine of natural origin which was prepared by mixing (-)-epicrinine and (+)-epicrinine showed m.p. 239°. (±)-Oxocrinine was prepared by mixing (-)-oxocrinine and (+)-oxocrinine which were derived from natural origin respectively, and it showed m.p. 177 - 178°.

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