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SYNTHESIS OF 1,2,9,10-BISMETHYLENEDIOXYDIBENZO[de,g]QUINOLINE-7-ONE. (CASSAMERIDINE).

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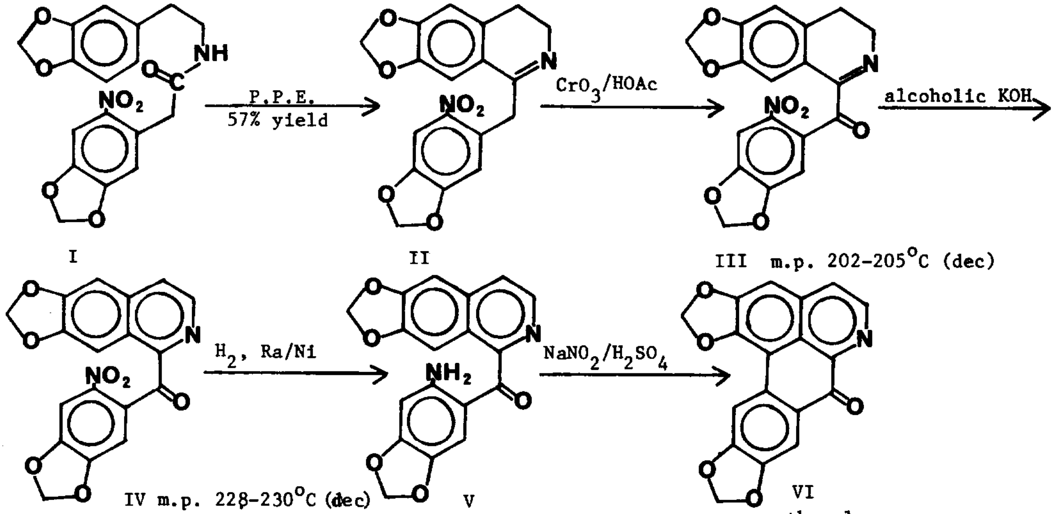
Recently M. P. Cava et al(1) isolated from Cassytha americana (C. filiformis L., Lauraceae) a new oxoaporphine, Cassameridine. This was assigned structure VI on the basis of its ultra-violet and mass spectra. In the course of our synthetic studies, we have synthesized the oxoaporphine 1,2,9,10-bismethylenedioxydibenzo[de,g]quinoline-7-one, corresponding to cassameridine. In our work, we have confirmed the effective use of polyphosphate ester (P.P.E.) as a reagent for the Bischler - Napieralski reaction.(2, 3)

The synthetic scheme for the above oxoaporphine is illustrated below:-



I

II

III m.p. 202-205°C (dec)

IV m.p. 228-230°C (dec)

V

VI

The ultra-violet spectrum of the synthetic product exhibits $\lambda_{max}^{ethanol}$ 249 mμ (log ε 4.55), 272 (4.45), 320 (4.11), 350 (4.00), 388 (3.93) and 434 (3.79); $\lambda_{max}^{ethanol-HCl}$ 261 mμ (log ε 4.74), 290 (4.68), 381 (4.37), 499 (3.97). The infra-red spectrum shows a band at 1640 cm^{-1} indicative of a conjugated carbonyl group while other bands occurred at 1510, 1410, 1340, 1240, 1040 and 960 cm^{-1} considered diagnostic for the methylenedioxy group.(4)

The mass spectrum(5) is consistent with a completely aromatic structure having no ready skeletal fragmentation and shows the molecular ion peak (M^+ 319) as the base peak. The n.m.r. spectrum(6) of the synthetic product shows two unsplit methylenedioxy groups at 3.34 τ and 3.75 τ and five aromatic protons at 2.43, 2.10, 1.71, 1.54 (doublets J = 6.5 Hz) and 1.24 (doublets J = 6.5 Hz). The assignments for these signals were carried out by comparison of these data with those quoted for the following oxoaporphines. All values are in τ units.

Compound	$-OCH_2O-$ 1,2	C_3 - H	C_4 - H	C_5 - H	C_8 - H	$-OCH_2O-$ 9,10	C_{11} - H
Cassamedine(1)	3.28 (S)	-	2.17	1.15	1.81	3.77 (S)	1.15 (S)
Liriodenine(7)	3.28 (S)	2.37 (S)	C_4 - H to C_{11} - H 1.1 to 2.3 (6H aromatic, m)				
Atherospermidine(7)	3.28 (S)	-	C_4 - H to C_{11} - H 1.1 to 2.3 (6H aromatic, m)				
Lanuginosine(8)	3.25 (S)	2.33 (S)	2.3 (d)	1.30 (d)	1.74 (d)	-	0.97 (d)
Oxoxylopine(9)	3.35 (S)	2.47 (S)	1.55 (d)	1.22 (d)	1.93 (d)	-	1.22 (d)

The signals at 3.34 τ and 3.75 τ are assigned to the two methylenedioxy groups at 1.2 and 9,10 positions respectively by analogy to those observed in the spectrum of cassamedine. Similarly by comparison, the 2.43 τ singlet is assigned to the proton C - 3, while the two doublets centred at 1.54 τ and 1.24 τ (J = 6.5 Hz) are attributed to the protons at C - 4 and C - 5. The remaining two one-proton singlets at 2.10 τ and 1.71 τ are assigned to C - 8 and C - 11 since C - 11 proton occurs at lower field than C - 8.

A direct comparison of our synthetic product with cassameridine is not possible as an authentic sample is not available. The U.V. spectra of the two compounds, however, are very similar.

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5. We are grateful to Dr. J. Macleod of Australian National University, Canberra, Australia for the measurement of the mass spectrum.
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