

## 5(10 → 9)abeo-Ergolines from 9-Hydroxyergolines

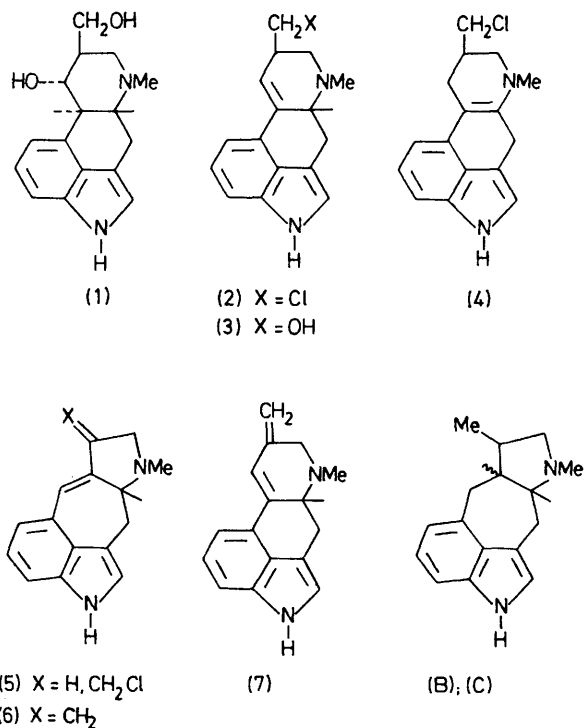
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**Summary** Treatment of 9-hydroxyergolines with  $\text{POCl}_3$ -pyridine yields 5(10 → 9)abeo-9,10-didehydroergolines.

LYSERGIC ACID (5 g) in tetrahydrofuran (200 ml) was treated overnight with diborane (0.55M; 135 ml), and 5% methanolic KOH (250 ml) was then added followed by 35%  $\text{H}_2\text{O}_2$  (25 ml). The solution was diluted with water and extracted with ether. The extract was evaporated *in vacuo* and the residue boiled for 3 h with methanol; on dilution with water the diol (1) (2.8 g), m.p. 275–278 °C, separated.<sup>1</sup> When a sample of (1) (2 g) was treated at 70 °C for 2 h with  $\text{POCl}_3$ -HCl-pyridine (3:3:20) a compound (A), m.p. 184 °C,  $[\alpha]_D^{20} - 148^\circ$  (pyridine), resulting from the replacement of a hydroxy-group by chlorine and loss of one molecule of  $\text{H}_2\text{O}$ , was obtained. Since its u.v. spectrum showed  $\lambda_{\text{max}}$  323 nm as in lysergic acid, (A) was assumed to have structure (2). However treatment of lysergol (3) with  $\text{POCl}_3$ -pyridine gave the known<sup>2</sup> chloromethylergolene derivative (2) which was different from (A) (m.p., optical rotation, and i.r. spectrum). The isomeric structure (4) could be ruled out since the u.v. spectrum was unchanged in strongly acid solution and moreover the presence in the  $^1\text{H}$  n.m.r. spectrum of (A) of a singlet at  $\delta$  6.26 suggested the existence of an isolated vinylic proton.

Finally, catalytic hydrogenation and dehalogenation of (A) in methanol (Pd-C; KOH) gave two isomeric compounds {(B), m.p. 255 °C;  $[\alpha]_D^{20} - 164^\circ$  (pyridine); (C) m.p. 178 °C;  $[\alpha]_D^{20} - 48^\circ$  (pyridine)} whose  $^1\text{H}$  n.m.r. spectrum showed the presence of the expected Me-CH doublet ( $\delta$  1.1 and 1.23, respectively). However neither (B) or (C) had physical constants in accord with those reported for the known 8-methylergolines<sup>3</sup> and therefore it must be concluded that the ergoline skeleton was no longer present in (A).

A Merweein-Wagner rearrangement involving the anti-periplanar C-9-OH and C-5-C-10 bonds followed by loss of a proton would give compound (5). Assignment of formula (5) to (A) is in accord with the  $^1\text{H}$  n.m.r. spectrum:  $\delta$  [( $\text{CD}_3$ )<sub>2</sub>SO] 2.26 (s, 3H, NMe), 3.96 (m, 2H,  $\text{CH}_2\text{Cl}$ ), 6.26 br (s, 1H, 10-H), 6.4–7.1 (m, 4H, indole-H), and 10.5 (s, 1H, NH), and is further substantiated by the formation of the diene (6) (m.p. > 300 °C) by treatment of (A) in benzene



with 1,5-diazabicyclo[5.4.0]undec-5-ene at 80 °C for 6 h. Comparison of the u.v. spectra of (6) [ $\lambda_{\text{max}}$  (MeOH) 357 nm;  $\log \epsilon$  3.81] and lysergenine (7)<sup>2</sup> [ $\lambda_{\text{max}}$  (MeOH) 337 nm;  $\log \epsilon$  4.11] confirms the *cisoid* diene structure of (6), since it is known<sup>4</sup> that these absorb at longer wavelength but with a lower intensity in comparison with *transoid* dienes. We therefore conclude that compound (A) has structure (5).

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<sup>3</sup> A. Stoll and A. Hofmann, in 'The Alkaloids,' ed., R. F. Manske, Vol. 8, Academic Press, New York, 1965, p. 725.

<sup>4</sup> A. I. Scott, 'Interpretation of the Ultraviolet Spectra of Natural Products,' Pergamon, Oxford, 1964, p. 46.