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Studies on Orchidaceae Alkaloids

XVI.* A New Alkaloid, 2-Hydroxydendrobine, from *Dendrobium findlayanum* Par. *et* Rchb. f.

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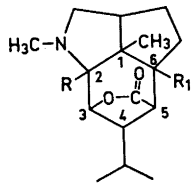
Dendrobine, nobiline and a new alkaloid, 2-hydroxydendrobine (I), have been found in *Dendrobium findlayanum* Par. *et* Rchb. f. The isolation procedure and structural determination of I are described.

Dendrobine [2–10] and a new alkaloid, 2-hydroxydendrobine, have been isolated from *Dendrobium findlayanum* Par. *et* Rchb. f., a species closely related to *Dendrobium nobile* Lindl. A small amount of nobiline [4,11] was also detected. The only hydroxydendrobine hitherto known was dendramine,[12,13] isolated from *D. nobile*.



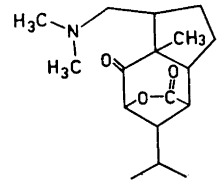


Fig. 1. R=OH, R_1=H, 2-hydroxydendrobine; R=R_1=H, dendrobine; R=H, R_1=OH, dendramine.

nobiline

Alkaloids with an oxygen function in the 2-position, *i.e.* dendroxine [14] and 6-hydroxydendroxine,[13] have been found previously in *D. nobile*.

* Number XV of this series, see Ref. 1.

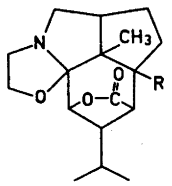


Fig. 2. R=H, dendroxine;
R=OH, 6-hydroxydendroxine.

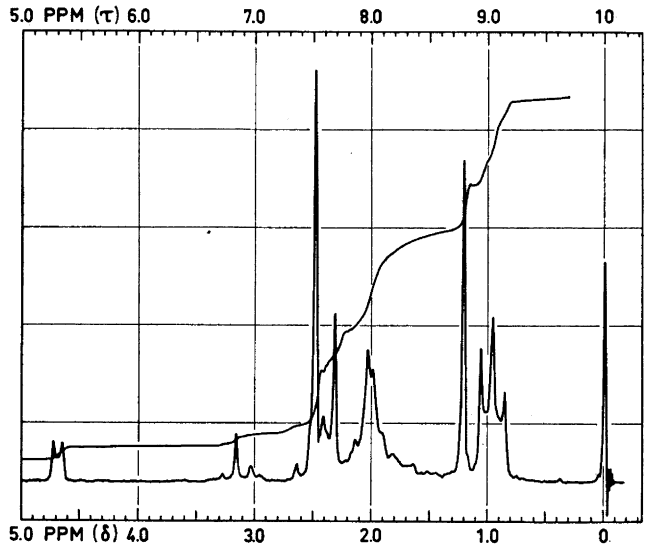


Fig. 3. NMR spectrum of 2-hydroxydendrobine (I) in $CDCl_3$.

From the parallelism of the IR and NMR spectra of I ($C_{16}H_{25}NO_3$) and those of dendramine,[12,13] it would be anticipated that the two alkaloids have the same skeleton. The most marked difference between the NMR spectra is the signal due to the proton in the 3-position appearing as a doublet (τ 5.30) in that of I and as a quartet in that of dendramine, implying the presence of a substituent in the 2- or 4-position of I. An IR absorption at 3470 cm^{-1} (in KBr), and the disappearance of a 1 H singlet at τ 7.7 in the NMR spectrum of I (in $CDCl_3$) upon the addition of deuterium oxide, indicate that I bears a hydroxyl group. Hydrogenolysis of I in glacial acetic acid at room temperature and atmospheric pressure afforded dendrobine quantitatively. The facile transformation of I into dendrobine confirms that the hydroxyl group is situated in the 2-position, and hence I is 2-hydroxydendrobine. The correlation of I with dendrobine also reveals the absolute configuration of I, since that is known for dendrobine.[8]

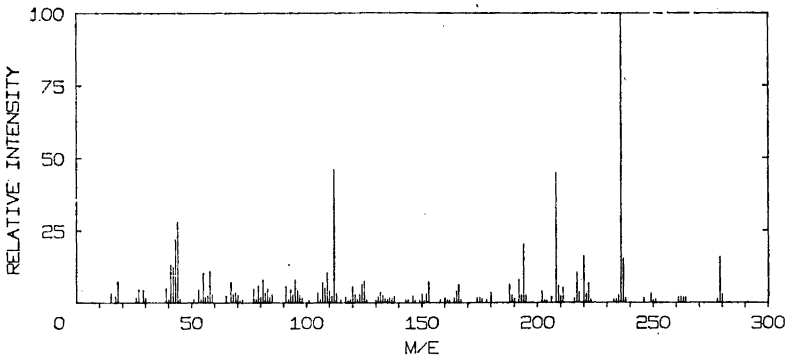


Fig. 4. Mass spectrum of 2-hydroxydendrobine (I.)

The fragmentation pattern in the mass spectrum of I is analogous to that of other dendrobine alkaloids.[12] The structure of the most abundant ions give further support to the position of the hydroxyl group.

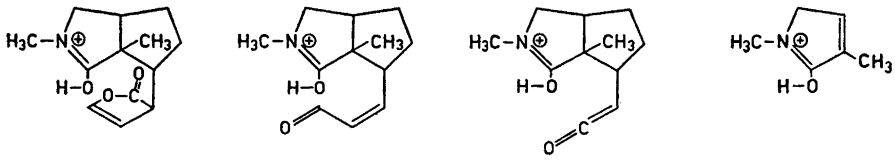
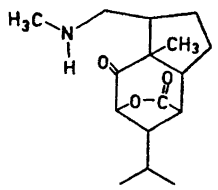


Fig. 5.

It was not possible, by IR, to demonstrate the existence of the tautomeric form (II) of I.



II

EXPERIMENTAL

All melting points are corrected. Mass spectra were measured on an LKB 9000 spectrometer (ionization energy 70 eV), and with a double focussing Atlas SM 1 mass spectrograph. IR spectra were recorded on a Perkin Elmer 257 instrument and the NMR spectra on a Varian A60-A spectrometer.

Isolation of the alkaloids. Fresh plants of *Dendrobium findlayanum* Par. *et* Rchb. f. (12 kg) were extracted with methanol (20 l). The methanol solution was concentrated to 0.5 l, acidified and washed with chloroform (4 × 0.5 l). The aqueous solution was made alkaline with sodium hydroxide (pH 9) and extracted with ether (8 × 0.5 l). The combined ether solutions were dried (Na_2SO_4), concentrated to 20 ml and filtered through neutral alumina (3 × 15 cm) using ether as eluent. Concentration of the eluate gave a crystalline residue. Two recrystallizations from ether afforded dendrobine (1.3 g), indistinguishable from an authentic sample (m.p. IR, NMR, MS and optical rotation) obtained from *D. nobile.*

The combined mother liquors were chromatographed on silica gel (3 × 30 cm, 30–70 mesh) using chloroform as eluent. The first fraction contained 2-hydroxydendrobine (I). Evaporation of the solvent and recrystallization of the residue twice from hexane gave I (0.8 g). The second fraction consisted of dendrobine and a small amount of nobiline, the latter being indistinguishable from an authentic sample (TLC, GLC–MS).

Characterization of 2-hydroxydendrobine (I). M.p. 103–105°, $[\alpha]_D^{26}$ −45° (*c* 0.73, chloroform). (Found: C 69.4; H 9.02; N 4.92; O 16.5. M.wt. 279.186. Calc. for $C_{16}H_{25}NO_3$: C 68.8; H 9.02; N 5.02; O 17.2. M.wt. 279.183. $^{12}C=12.0000$). IR spectrum: ν_{max} (CCl_4) 3600(m) and 1790(s) cm^{-1}; ν_{max} (KBr) 3470(m) and 1770(s) cm^{-1}. NMR spectrum, see Fig. 3. Mass spectrum, see Fig. 4.

Hydrogenolysis of I. A solution of I (40 mg) in glacial acetic acid (10 ml) was hydrogenolyzed over Adams catalyst (25 mg) at room temperature and atmospheric pressure. After 5 h the catalyst was filtered off and the solution concentrated, made alkaline and extracted with chloroform. The chloroform solution was dried and evaporated leaving dendrobine (35 mg), identified by its m.p., IR, NMR, MS, and optical rotation.

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