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STUDIES ON ORCHIDACEAE ALKALOIDS VIII*

An Imidazolium Salt from Dendrobium anosmum Lindl. and Dendrobium parishii Rchb. f.

Kurt Leander and Björn Lüning
Department of Organic Chemistry, University of Stockholm
Stockholm Va, Sweden

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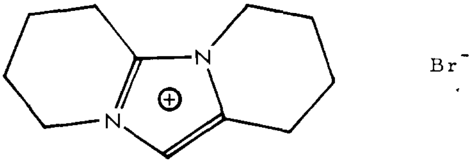
An optically inactive quaternary compund has been isolated from Dendrobium anosmum Lindl. and D. parishii Rchb. f. It was crystallized as the bromide (I), $C_{11}H_{17}BrN_2$. I is stable towards catalytic hydrogenation (PtO_2, 50 atm., 25°, 24 h) but reacts with Raney nickel alloy in the presence of hydroxide ion or with lithium aluminium hydride. In the latter reactions I affords a saturated base $C_{11}H_{20}N_2$ (II), thereby establishing the tricyclic nature of I. The UV and IR spectra, as well as the NMR spectrum (Fig. 1), showing one aromatic, eight allylic and eight almost equal aliphatic protons, suggest that I is an imidazolium salt. NMR double resonance measurements show that the aromatic proton couples (J = 1.1 cps) with a methylene group which is not attached to nitrogen. On basis of the above evidence, the following structure of I was indicated:



I

This structure was proved by synthesis of I. Catalytic hydrogenation of dipyrido [1,2-a:1 , 2'-c] imidazol-10-ium bromide afforded octahydrodipyrido [1,2-a:1', 2'-c] imidazol-10-ium bromide, indistinguishable from I. I is not structurally related to any compound previously found in nature. Attempts to elucidate the biosynthesis of I are in progress.

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* For number VII of this series see Ref. 1.

Isolation and characterization of I. Fresh plants of Dendrobium parishii Rchb. f. (2. 0 kg) were extracted with methanol (8 l, 24 h, 4°). The extraction procedure was repeated and the combined methanol extracts were concentrated to 0. 5 l, washed with chloroform (4 × 50 ml), evaporated to dryness and the residue extracted with methanol (400 ml). The methanol solution was concentrated and chromatographed on neutral alumina (5. 5 × 32 cm) using ethanol as eluant. The salts were transformed into the bromide by filtering an aqueous solution through a column (3 × 38 cm) of Dowex 1-X4 (Br^-). Concentration of the aqueous solution gave a brown solid (4. 1 g). Crystallization from acetone afforded white needles (3. 3 g) m.p. 162-164°. Two recrystallizations from acetone raised the m.p. to 164-165°. (Found: C 51. 4; H 6. 56; N 10. 8; Br 30. 9. Calc. for $C_{11}H_{17}BrN_2$: C 51. 4; H 6. 66; N 10. 9; Br 31. 1). UV spectrum:

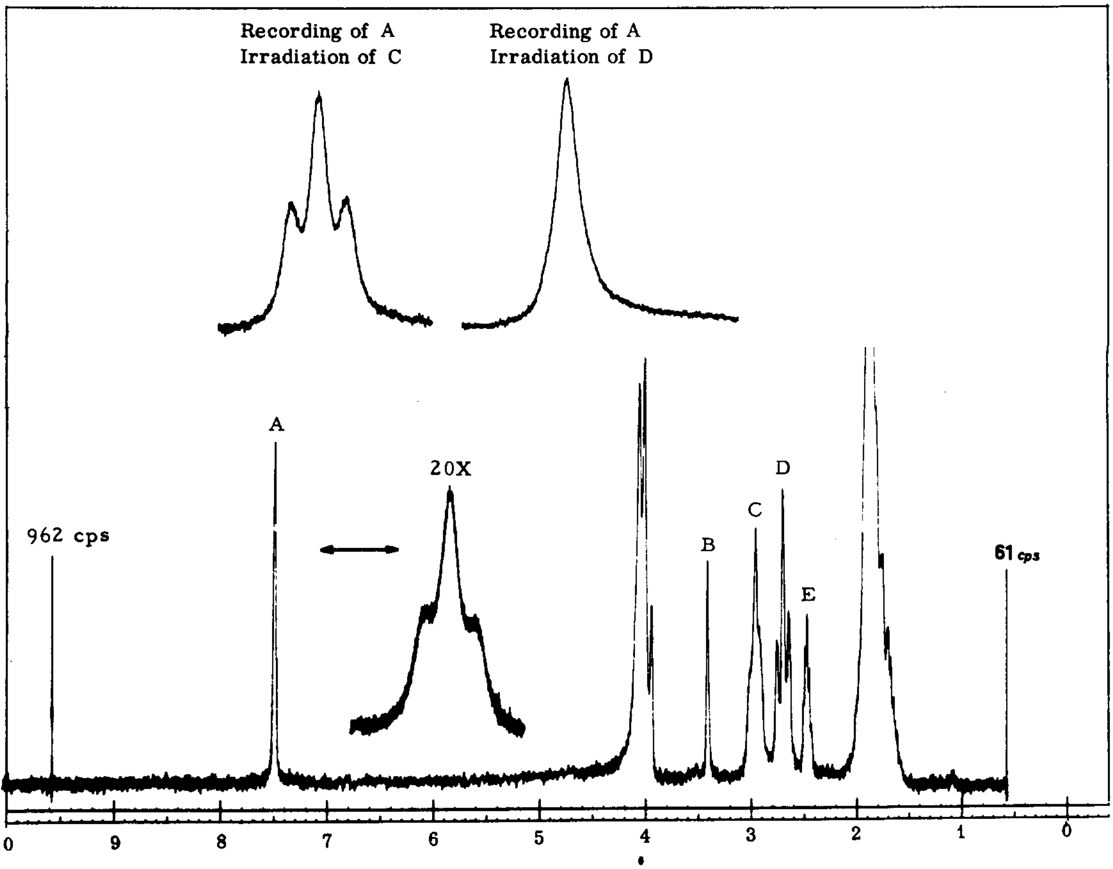

Fig. 1. 100 MC NMR spectrum of I in DMSO, B = HDO; E = DMSO (d_5).

$\lambda_{max}^{ethanol}$ 221 mμ (log ε 3.78). IR spectrum: $\nu_{max}^{CH_2Cl_2}$ 3040, 1610, 1550 and 1515 cm^{-1}. The chloride of I was prepared as hygroscopic crystals, which melted at 86-88.5°, solidified and melted again at 153-156°.

Reduction of I with lithium aluminium hydride. I (67 mg) was dissolved in a mixture of methylene chloride (1.4 ml) and ether (1 ml). Lithium aluminium hydride (100 mg) was added in portions with stirring over a period of 90 min. After 3 h sufficient water was added to form solid hydroxides but no aqueous phase. The ether solution was concentrated and the residue purified by preparative gas chromatography. (Column: 20 % SE-52 on Chromosorb AW DMCS, 60/80 mesh; 8 mm × 2.9 m. Retention time: 17 min; 175°; gas flow rate 80 ml/min.) Yield: 22 mg (47 %) of a diacidic base (II). (Found: M$^+$ 180.161 Calc. for $C_{11}H_{20}N_2$: 180.1626. ^{12}C 12.00000).

Dipyrido [1,2-a:1', 2'-c] imidazol-10-ium bromide (III).$^{(2)}$ 2-Bromomethylpyridine hydrobromide$^{(3)}$ (0.0050 mole) and 2-bromopyridine (0.15 mole) were heated together for 15 min at 190°. The reaction mixture was made alkaline with 0.5 M aqueous sodium hydroxide and extracted with chloroform (4 × 50 ml). The aqueous layer was neutralized with hydrobromic acid and evaporated to dryness. The residue was extracted with hot acetonitrile (2 × 20 ml). Treatment of the combined acetonitrile solutions with activated carbon yielded greenish yellow needles (0.0038 mole, 76 %) m.p. 220-227°. Three recrystallizations from ethanol afforded light yellow needles m.p. 226-229° (Hamana *et al.*$^{(2)}$ obtained a monohydrate m.p. 150-152°). (Found: C 53.0; H 3.58; N 11.3; Br 32.0. Calc. for $C_{11}H_9BrN_2$: C 53.0; H 3.62; N 11.3; Br 32.0). UV spectrum: $\lambda_{max}^{ethanol}$ 228, 237, 270, 283, 306, 319, 334, 363, 381 and 401 mμ; log ε 4.48, 4.42, 3.32, 3.26, 3.81, 4.09, 4.17, 3.70, 3.62 and 3.27 (*cf.* UV spectrum of the perchlorate$^{(4)}$).

Octahydrodipyrido [1,2-a:1', 2'-c] imidazol-10-ium bromide (I). A solution of III (0.0010 mole) in methanol (10 ml) was hydrogenated over platinum oxide (25 mg) at room temperature and atmospheric pressure. After 3.5 h 4 molar equivalents of hydrogen had been consumed. The catalyst was filtered off and the solution evaporated to give I in a quantitative yield, m.p. 164-165°. I was indistinguishable from the bromide of the natural product (m.p., UV, IR and NMR).

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