The selenourea groups of an ion are planar and approximately parallel, the plane of the middle (Se_2) selenourea group making angles of 15° and 5°, respectively, with the planes of the terminal (Se_1 and Se_3) selenourea groups, in both compounds. The three selenium atoms and the carbon atoms of the terminal selenourea groups lie approximately in the same plane; this plane makes an angle of about 75° with the plane of the three selenium atoms and the carbon atom of the middle selenourea group.

There is a close non-bonded contact between the middle selenium atom Se_2 and a halide ion X^-, 3.46 Å in I and 3.53 Å in II, at a C—Se···X angle of 175°. A close non-bonded contact also occurs between Se_3 and a halide ion, 3.70 Å in I and 3.72 Å in II, at a C—Se···X angle of 165.°

A full account of the work will be published later.

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Studies on Orchidaceae Alkaloids

XIX.* Synthesis and Absolute Configuration of Dendrine

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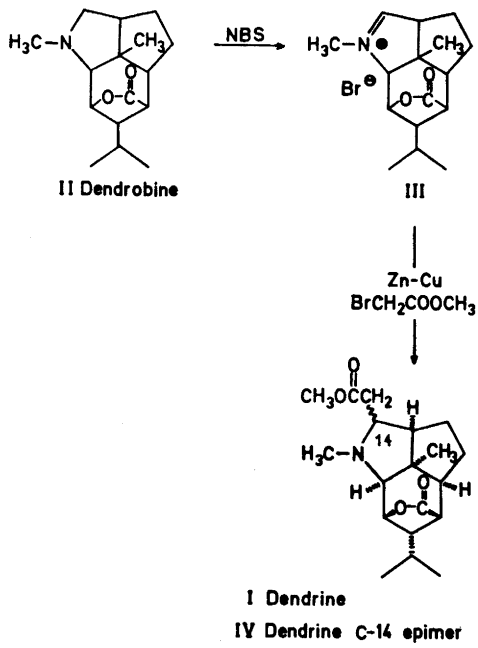
Dendrine,[1] a minor alkaloid from *Dendrobium nobile* Lindl., has been assigned the structure I, with only the configuration at C-14 undetermined. In the present communication a synthesis of dendrine (I) by a Reformatsky reaction on dendrobine immonium bromide (III) is reported.



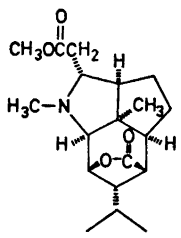
Oxidation of dendrobine (II) with *N*-bromosuccinimide in ether-acetone afforded the immonium salt III.[2] By reacting III with methylbromoacetate and zinc-copper couple in *N*,*N*-dimethylformamide at 100°, two bases were formed. The major product, m.p. 188—189°, $[\alpha]_D^{26}$ −80° (*c* 0.17, chloroform), has properties (NMR, IR, MS, GLC, TLC) indistinguishable from those of authentic dendrine (I), except for specific optical rotation which was previously reported to be $[\alpha]_D^{13}$ −114° (*c* 0.85, chloroform).[1] However, our measurement of optical rotation of authentic dendrine (I), $[\alpha]_D^{24}$ −81° (*c* 0.14, chloroform), was very close to the specific rotation of the synthetic product reported herein.

The minor product (IV) was obtained as a gum, $[\alpha]_D^{20}$ +23° (*c* 0.57, chloroform). Its mass spectrum was indistinguishable, except for small differences in intensities of some of the peaks, from that given by dendrine (I). The similarity of the mass spectra of I and IV suggests that the bases are epimers, which is further supported by their IR and NMR spectra.

In the synthesis, the epimers I and IV were formed in the ratio 15:1. The Reformatsky reagent preferably attacks the

* For No. XVIII of this series, see Ref. 1.

immonium salt (III) from the sterically less hindered side, as is shown in Fig. 1, and hence dendrine (I) should be the 14-*exo*-epimer. Since the absolute configuration of dendrobine (II) is known,[3] the transformation of dendrobine (II) into dendrine (I) establishes the absolute configuration of the latter.



Dendrine

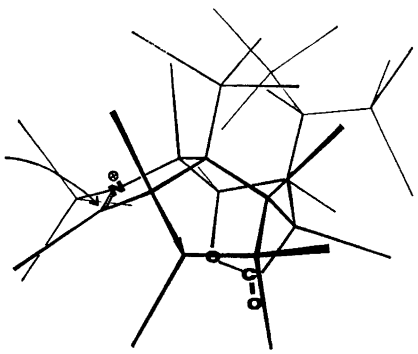


Fig. 1.

Experimental. Melting points are corrected. Mass spectra were measured on a Perkin-Elmer 270 instrument. IR spectra were recorded on a Perkin-Elmer 257 instrument, the optical rotations on a Perkin-Elmer 141 polarimeter (accuracy 0.001°), and the NMR spectra on a Varian A60-A spectrometer.

Dendrobine immonium bromide (III).[3] To a solution of dendrobine (II, 200 mg) in ether (40 ml) *N*-bromosuccinimide (200 mg) was added under stirring. During the addition, a yellow precipitate appeared. After 20 min, acetone (6 ml) was added and the reaction mixture was refluxed for 3 h, to give the crude immonium salt (III, 260 mg) as a white precipitate, m.p. 231–234°. Recrystallization of III from acetone gave needles, m.p. 236–239°. IR spectrum: σ_{max} (KBr) 1797(s), 1783(s) (γ-lactone); 1680(m) ($\diagdown\!\!\diagup C{=}\overset{+}{N}\diagdown\!\!\diagup$); 3460(s), 1631(w) (water of crystallization) cm^{-1}.

Reformatsky reaction on III. To zinc-copper couple[4] (100 mg) and methylbromoacetate (236 mg), crude III (260 mg) dissolved in *N*,*N*-dimethylformamide (1 ml) was added. The reaction mixture was heated (100°, 2 h), cooled and acidified with hydrochloric acid. The mixture was washed with ether (2 × 15 ml), made alkaline (pH 10) and extracted with ether (4 × 20 ml). The ether solution was dried (Na_2SO_4), evaporated to dryness and the residue was chromatographed on silica gel (2 × 15 cm) using ether as eluent.

The first fraction was evaporated to dryness, leaving IV (4 mg) as a gum, $[\alpha]_D^{20}$ +23° (*c* 0.57, chloroform). IR spectrum: σ_{max} (CCl_4) 1783(s) (γ-lactone); 1742(s) (ester). NMR spectrum ($CDCl_3$): τ 5.40 (t, 1 H), τ 6.32 (s, 3 H), τ 7.65 (s, 3 H), τ 8.63 (s, 3 H), τ 9.0 (d, 6 H). Pertinent mass spectral peaks *m/e* (rel. intensity): M^+ 335 (1), 320 (1), 292 (7), 262 (100), 168 (6), 108 (13).

The second fraction was evaporated to dryness and the residue was crystallized from ether giving dendrine (I, 60 mg), m.p. 188–189°, $[\alpha]_D^{26}$ −80° (*c* 0.17, chloroform) indistinguishable from an authentic sample (IR, NMR, MS, TLC, GLC).

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