ALKALOID OCCURRENCE IN *DISCARIA TOUMATOU*

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Alkaloids of the cyclopeptide type have been isolated from two South American *Discaria* spp. (family Rhamnaceae) (1,2) and also from *D. pubescens* (3), the only Australian member of the genus. A Chilean species, *D. serratifolia*, however, has been found to contain benzylisoquinoline-type alkaloids (4). We now report an examination of *D. toumatou* (Maori name: matagouri), the sole New Zealand representative, from which R(−)-*N*-methylcoclaurine, one of the bases present in *D. serratifolia*, has been isolated. This alkaloid has been identified by comparison of its physical properties, and those of its derivatives, with data reported in the literature.

A previous examination of *D. toumatou* had indicated the absence of alkaloids (5); however, in preliminary experiments, we found that the plant gave strong alkaloid tests (6) in the field, but the intensity diminished fairly rapidly after collection and was reduced practically to zero after a few days. However, it was found that if the freshly collected material were immersed as soon as possible in hot methanol, the alkaloid content was stabilized, possibly due to the inactivation of plant enzymes which otherwise destroy it. The plant material could then be exhaustively extracted and the alkaloid isolated and purified by standard procedures.

EXPERIMENTAL

Leaves and terminal twigs of *D. toumatou* (9 kg), collected around the eastern foot of Porter's Pass, Canberbury, New Zealand, on May 10, 1981, and authenticated in the Division of Botany, DSIR, Lincoln, were immersed as soon as possible in boiling methanol for an hour. The plant material was then removed, air-dried, and milled to a coarse powder (5 kg), which was continuously extracted by cold percolation with methanol until tests showed that the alkaloid content was exhausted. All the methanol extracts were then combined and concentrated almost to dryness under vacuum at a temperature below 40°. The residue was treated with glacial acetic acid (2.5 liters) and water (1 liter), and the whole was warmed to 30° and thoroughly mixed. The homogeneous liquid was then poured into water (3 liters), and the suspension was agitated briskly for 2 hours.

The precipitate formed was filtered off through Hi-Flo Supercell and washed with 25% acetic acid until tests showed no alkaloid remained. The combined filtrates were evaporated to dryness under reduced pressure at 25°, the residue was dissolved in water (3 liters), and the solution was evaporated as before in order to remove as much acetic acid as possible. The residue was again dissolved in water (5 liters), and the solution was basified with conc. ammonia (50 ml) to pH 8–9. The precipitate which appeared was filtered off through Hi-Flo Supercell, and the aqueous solution was thoroughly extracted with chloroform (4 liters). The precipitate was washed with 5% methanol-chloroform until no more alkaloid was removed. The combined chloroform, and 5% methanol-chloroform solutions were thoroughly extracted with 0.5% aqueous sulfuric acid (4 liters), and the acid extracts were basified with ammonia to pH 9, then extracted thoroughly with chloroform. The chloroform extracts were dried (Na_2SO_4) and evaporated under reduced pressure to yield a crude alkaloid fraction (3.1 g, 0.062%).

The crude bases (2 g) were separated on a column of silica gel (Merck G60, 100–200 mesh, 80 g, prepared in 5% methanol-chloroform) which was eluted with methanol-chloroform mixtures ranging from 5% to 15% in concentration. Two hundred 5 ml fractions were collected: fractions 1 to 122 did not contain alkaloid, and subsequent fractions contained only one alkaloid component. The latter fractions, when combined and concentrated *in vacuo*, yielded R(−)-*N*-methylcoclaurine. Recrystallized from chloroform, the crude base (1.1 g) yielded 800 mg of white needles, mp 181–183° [lit. (2b) 181–183°], $[\alpha]^{20}D$ −94.7 (C=11.8) [lit. (2b) $[\alpha]^{20}D$ −92°]. ^1H Nmr ($CDCl_3$): δ 2.48 (s, 3H, NCN_3), 2.5–3.8 (m), 3.80 (s, 3H, OCH_3), 4.6 (bs, 2H, OH), 6.0 (s, 1H, aromatic), 6.60–6.95 (m, A_2B_2, 4H, aromatic), 6.55 (s, 1H, aromatic); uv (EtOH): λmax 285, 228 nm (ϵ max 1495, 3887; (EtOH + 1 drop 5% NaOH: 300, 245, 220 nm; ms: *m/z* 299 (M^+, 1%), 298 (2.5), 192 (100), 178 (16), 277 (25), 148 (22), 107 (22); ir: γ max *inter*

alia: 3600, 2850 cm^{-1}. The methiodide and the O,O-diacetate, prepared by standard methods, had mp 202° and 77–78°, respectively [lit. (2b) 202–204° and 77–78° resp.].

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