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PILOCEREINE FROM *LOPHOCEREUS SCHOTTII* FORMAE *MONSTROSUS* AND *MIECKLEYANUS**

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Key Word Index—*Lophocereus*; Cactaceae; cactus alkaloids; pilocereine.

Plants. Cuttings of *Lophocereus schottii* (Engel.) Br. & R. (the "senita cactus"), *L. schottii* forma *monstrosus* Gates (the "totem pole cactus"), and *L. schottii* forma *mieckleyanus* G. Lindsey, as described by Lindsey [1]. *Source.* From authenticated plants growing in the Desert Botanical Garden of Arizona, Papago Park, in Phoenix, Arizona. *Previous work.* The presence of tetrahydroisoquinoline alkaloids in the genus *Lophocereus* is well documented [2–6].

Present work. A re-examination of *L. schottii*, using previously reported TLC screening [7,8], indicated no appreciable amounts of new alkaloids. Similar screening of two previously uninvestigated monstrose forms, *L. schottii* forma *monstrosa* and *L. schottii* forma *mieckleyanus*, showed identical alkaloid content. However, *L. schottii* forma *mieckleyanus* was quantitatively richest in alkaloids. $CHCl_3$ extraction and ion-exchange chromatography [7] of 775 g of freeze-dried, pulverized, and defatted *L. schottii* forma *monstrosus* yielded 74 mg of pilocereine (m.p. 175–176°, m.m.p. 174–175°; lit. 174–175°, IR, 0·01% yield) after refrigeration of the phenolic alkaloids in Et_2O and recrystallization from EtOAc. Surprisingly the non-phenolic fraction also contained pilocereine which substantiates the earlier reports of the cryptophenolic nature of this compound [3].

An identical extraction was conducted with 885 g of *L. schottii* forma *mieckleyanus*. Separating the alkaloids on neutral alumina (activated for 2 hr at 137°) with C_6H_6–Et_2O (1 : 1). Crystallization from EtOAc yielded 23 mg of pilocereine (m.p. 174–175°, m.m.p. 173–174°, reference m.p. 174–175°, IR, 0·005% yield). Lophocerine and traces of unidentified alkaloids were observed by TLC in the phenolic alkaloid fractions of all three plants. Due to the small quantities observed, attempts to crystallize additional alkaloids were not made.

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* Part XXV in the series "Cactus Alkaloids". For Part XXIV see Vanderveen, R. L., West, L. G. and McLaughlin, J. L. (1974) *Phytochemistry* **13**, 866.

Biological significance. The presence of alkaloids in these spineless monstrose plants imparts a disagreeable bitter taste, as well as known pharmacotoxic effects [9], and quite likely has a protective value to the plants in repelling hungry rodents and other animals.

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IDENTIFICATION AND C-13 N.M.R. SPECTRUM OF STACHYDRINE FROM *CADABA FRUTICOSA*

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Key Word Index—*Cadaba fruticosa*; Capparidaceae; cadabine; stachydrine.

Abstract—Cadabine, a compound isolated from the leaves of *Cadaba fruticosa* has been identified as stachydrine and its C-13 NMR studied.

In 1971, Ahmad and Basha [1] isolated hygroscopic crystalline needles, m.p. 98–100 from the leaves of *Cadaba fruticosa*, a straggling shrub found around Karachi. The compound contained nitrogen and from its ionic properties was presumed to be a betaine. It did not show any absorptions in the UV region and did not respond to mass spectrometry because of its low volatility. The IR spectrum afforded peaks at 1625 cm^{-1} (COO^{-}) and 3450 cm^{-1} (–OH).

NMR spectroscopy of a solution of the picrate in CF$_3$ COOD afforded peaks at 4·56 δ (*m*, 1H), 3·78 δ (*m*, 2H), 3·37 δ (*S*, 3H), 3·54 δ (*S*, 3H) and broad multiplets in the region 2·3—3·08 (4H). The multiplet at 3·78 δ collapsed to a singlet on spin–spin decoupling when irradiated at 2·5 δ. The above signals were assigned to the C-2, C-5, N–CH$_3$, N–CH$_3$, and C-3 and C-4 protons respectively. This spectrum was similar to that reported [2] for stachydrine (**1**) in D$_2$O. Since no C-13 NMR spectra of any betaines have previously been reported, such a spectrum was recorded at 25·2 MHz in D$_2$O using dioxan as internal standard. The fully decoupled spectrum afforded six sharp singlets at 75·3, 68·2, 52·7, 46·8, 24·8 and 19·2 ppm relative to TMS, which were assigned to C-2, C-5,