

was chondrofoline (1) or a stereoisomer thereof. The stereochemical coidentity of the alkaloid from *U. ovata* was ascertained by comparison of the ORD spectrum [1, 5] with that of authentic chondrofoline and the structure was finally confirmed by direct comparison (UV, IR, mmp, TLC).

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PHENETHYLAMINES FROM *ECHINOCEREUS CINERASCENS* AND *PILOSOCEREUS CHRYSACANTHUS**

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Key Word Index—*Echinocereus cinerascens*; *Pilosocereus chrysacanthus*; Cactaceae; alkaloids; *N,N*-dimethyl-3,4-dimethoxyphenethylamine; *N*-methyl-3,4-dimethoxyphenethylamine; *N*-methyl-3,4-dimethoxyphenethylamine.

In a field screening of Mexican cacti for the presence of alkaloids, *Echinocereus cinerascens* (DC.) Rümpler and *Pilosocereus chrysacanthus* (Web.) Byl. et Rowl. were found to give positive tests with the Dragendorff reagent [1]. Plants were collected and the alkaloids extracted and studied. The present report describes the isolation and identification of the major phenethylamine alkaloids of these two cactus species.

Although several alkaloid screening papers have listed various *Echinocereus* species [2–4], only one species, *E. merkeri*, has been investigated in more detail. *N,N*-dimethyl-3,4-dimethoxyphenethylamine was isolated for the first time from *E. merkeri*, which contains several additional phenethylamines and the tetrahydroisoquinoline salsoline [5, 6].

We have now identified the major alkaloid of *E. cinerascens* as *N,N*-dimethyl-3,4-dimethoxyphenethylamine. Alkaloid extraction followed by fractionation on an alumina column led to the isolation of this compound, as well as small amounts of *N*-methyl-3,4-dimethoxyphenethylamine. *E. cinerascens* has an edible fruit [7] and dry plants are used as fuel [8], but no medicinal uses seem to have been recorded for *E. cinerascens* or *Pilosocereus chrysacanthus*. The major alkaloid of the latter species was identified as *N*-methyl-3,4-dimethoxyphenethylamine.

The alkaloids now isolated were identified by comparison with synthetic reference materials using TLC, GC, IR, and MS. A part of the *N,N*-dimethyl-3,4-dimethoxyphenethylamine isolated from *E. cinerascens* was oxidized to the corresponding 3,4-dimethoxybenzoic acid, identified by IR and mp comparison with an authentic sample.

*Cactaceae Alkaloids. 27.

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N-Methyl- and *N,N*-dimethyl-3,4-dimethoxyphenethylamine have been reported from *E. merkeri* [5], and are also found in other genera of the Cactaceae, e.g. *Coryphantha* [9] and *Ariocarpus* [10].

EXPERIMENTAL

Plant material. *Echinocereus cinerascens* (DC.) Rümpler (4.1 kg) was collected north of Pachuca, Hidalgo, and *Pilosocereus chrysacanthus* (Web.) Byl. et Rowl. (3.0 kg) near San Antonio Texcala, Puebla, by the authors.

Alkaloid extraction. Fresh plant material was homogenized in EtOH. The filtered extracts were evaporated to dryness and dissolved in 3% HOAc. The aq. phases were extracted with CHCl₃ and the CHCl₃ discarded. Aq. phases were basified with NH₃ conc (pH 10) and alkaloids extracted with CHCl₃ and CHCl₃-EtOH (3:1). Crude alkaloids were purified on an acid diatomaceous earth column (Celite 545). Yield of alkaloids. *E. cinerascens* 585 mg; 0.014%; *P. chrysacanthus* 684 mg; 0.02%.

Isolation and identification. The alkaloid extract of *E. cinerascens* (525 mg) was fractionated on an aluminium oxide column (Merck, act. II–III acc. to Brockmann) as earlier described [5]. The eluates were analyzed by TLC and GC (5% SE-30 and 5% XE-60 columns, col. temp. 150°) [11]. MS were obtained with a combined GC–MS instrument (ion source 2.5 kV, electron energy 70 eV, and ionization current 60 µA). *N,N*-Dimethyl-3,4-dimethoxyphenethylamine was eluted with CHCl₃-C₆H₆ (1:2) and crystallized as the hydrochloride (292 mg) mp 193–197°; lit. mp 194–196° [4]. Alkaline permanganate oxidation of 50 mg of this compound gave 10 mg of 3,4-dimethoxybenzoic acid, mp 178–181°; lit. mp 181° [12]. *N*-methyl-3,4-dimethoxyphenethylamine was isolated from the CHCl₃-MeOH (4:1) fractions as the hydrochloride (yield 8 mg), mp 134–136°; lit. mp 136–137° [4]. Preparative TLC on Si gel GF plates in CHCl₃-EtOH-NH₃ conc (80:20:0.4) of 80 mg of the *P. chrysacanthus* alkaloids yielded *N*-methyl-3,4-dimethoxyphenethylamine, which was crystallized as the hydrochloride (yield 21 mg), mp 134–135°; lit. mp 136–137° [4].

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THE C₁₉-DITERPENOID ALKALOIDS FROM *ACONITUM FALCONERI*

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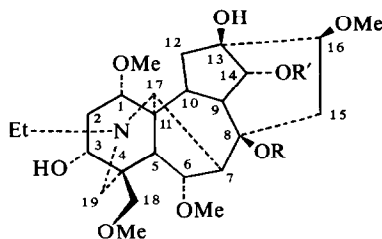
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Key Word Index—*Aconitum falconeri*; Ranunculaceae; aconitine alkaloids; veratroylpseudoaconine; pseudoaconitine; indaconitine.

In 1966, Singh *et al.* [1] made a preliminary study of two new diterpenoid alkaloids designated as bishatisine and bishaconitine from the indigenous crude drug known as Bish, Bikh or Mitha telia. This drug was identified as the roots of *Aconitum falconeri* Stapf. Since then no detailed work on these alkaloids or this plant has appeared. We wish to report here the isolation and identification of three C₁₉-diterpenoid alkaloids from the roots of *Aconitum falconeri* Stapf. These three alkaloids are identified as veratroylpseudoaconine (1), pseudoaconitine (2) and indaconitine (3) by a successful application of ¹H and ¹³C NMR spectroscopy. During our investigation of the roots of *A. falconeri*, we did not encounter any atisine-type alkaloid or bishatisine.



- 1 R = H, R' = veratroyl
- 2 R = Ac, R' = veratroyl
- 3 R = Ac, R' = benzoyl
- 4 R = R' = H

The alkaloid A, one of the major constituents of the methanolic extracts of the roots of *A. falconeri*, was isolated by a combination of pH gradient, thin layer and column chromatographic techniques. Alkaloid A, C₃₄H₄₉NO₁₁, mp 211-213°, [α]_D²² + 36.8° (C ~ 1.0 ab.

EtOH) shows broad absorption at 3420 (hydroxyl groups), 1708 (ester group), 1610 (an aromatic ring) cm⁻¹ in its IR spectrum. The ¹H NMR spectrum of alkaloid A shows absorption for an N-CH₂-CH₃ group (3H, t, J = 7 Hz) centered at δ 1.11, four aliphatic methoxyl groups (3H s at δ 3.26, 3.29, 3.32, 3.44) and two aromatic methoxyls as a part of a veratroyl group (6H s at δ 3.92). The spectrum also exhibits a one-proton d at δ 5.1 (J 4.5 Hz), attributable to a proton attached to a carbon (C-14) carrying an aromatic ester group, and signals for a 3,4-dimethoxybenzoyl (veratroyl) group [δ 6.86, 1H, d, J 4.5 Hz (C-5 proton of veratroyl), δ 7.61, 1H, and δ 7.68, 1H (C-2 and C-6 protons of the veratroyl group)]. The ¹³C NMR spectrum [2] of alkaloid A also indicates the presence of a veratroyl group, four aliphatic methoxyl groups, an N-ethyl group and one secondary and two tertiary hydroxyl groups, and other signals characteristic of a C₁₉-diterpenoid alkaloid skeleton [3]. The ¹³C and ¹H NMR spectra of alkaloid A show some similarity with those of the known alkaloids pseudoaconitine [4](2) and indaconitine [5](3). The basic hydrolysis of alkaloid A yielded veratric acid and a crystalline parent amino alcohol, which was identical with pseudoaconine (4). On the basis of the above evidence, we have identified alkaloid A as veratroylpseudoaconine (1). Comparison of alkaloid A with an authentic sample of veratroylpseudoaconine, prepared by heating pseudoaconitine [4] with 0.1 N H₂SO₄ in a sealed tube, showed identity. The structure of alkaloid A as 1 was also established independently by ¹³C NMR analysis [6].

In addition to alkaloid A, we have isolated two very minor constituents, alkaloids B and C, from the roots of *A. falconeri*. Alkaloid B, C₃₆H₅₁NO₁₂, mp 205-207°, contains an N-ethyl group, hydroxyl groups, six methoxyl