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THE C_{19}-DITERPENOID ALKALOIDS FROM *ACONITUM FALCONERI*

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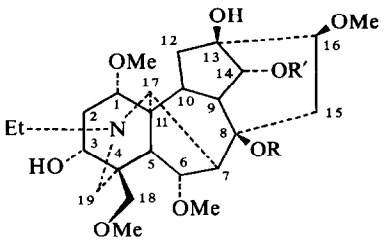
In 1966, Singh *et al.* [1] made a preliminary study of two new diterpenoid alkaloids designated as bishatisine and bishaconitine from the indigenous crude drug known as Bish, Bikh or Mitha telia. This drug was identified as the roots of *Aconitum falconeri* Stapf. Since then no detailed work on these alkaloids or this plant has appeared. We wish to report here the isolation and identification of three C_{19}-diterpenoid alkaloids from the roots of *Aconitum falconeri* Stapf. These three alkaloids are identified as veratroylpseudaconine (**1**), pseudaconitine (**2**) and indaconitine (**3**) by a successful application of ^1H and ^{13}C 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, $C_{34}H_{49}NO_{11}$, mp 211–213°, $[\alpha]^{22}$ + 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-CH_2-CH_3 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 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-dimethyoxylbenzoyl (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 ^{13}C 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 C_{19}-diterpenoid alkaloid skeleton [3]. The ^{13}C and ^1H NMR spectra of alkaloid A show some similarity with those of the known alkaloids pseudaconitine [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 pseudaconine (**4**). On the basis of the above evidence, we have identified alkaloid A as veratroylpseudaconine (**1**). Comparison of alkaloid A with an authentic sample of veratroylpseudaconine, prepared by heating pseudaconitine [4] with 0.1 N H_2SO_4 in a sealed tube, showed identity. The structure of alkaloid A as **1** was also established independently by ^{13}C 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*. Alkaoid B, $C_{36}H_{51}NO_{12}$, mp 205–207°, contains an *N*-ethyl group, hydroxyl groups, six methoxyl

groups of which two are aromatic, an acetyl group and an aryl ester carbonyl group as indicated by its IR and ^{1}H NMR spectra. On alkaline hydrolysis alkaloid B gives veratric acid, acetic acid, and the corresponding amino alcohol, pseudaconine (**4**). The IR and ^{1}H NMR spectra of alkaloid B were similar to those reported for pseudaconitine [3](**2**). The identity of this alkaloid as pseudaconitine was confirmed by a direct comparison with an authentic sample. Alkaloid C, shows spectral characteristics similar to those of alkaloid B, except for the presence of a benzoate group instead of a veratroyl group and was therefore identified as indaconitine [5](**3**). The identity of alkaloid C was also confirmed by comparison with an authentic sample. The structures of alkaloids B and C as **2** and **3**, respectively, were also established independently by ^{13}C NMR analysis [2].

Veratroylpseudaconine was isolated for the first time as a very minor constituent of *Aconitum ferox* by Indian workers [7]. It is interesting to note that veratroylpseudaconine is one of the major constituents of *A. falconeri* while pseudaconitine occurs as a very minor alkaloid.

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