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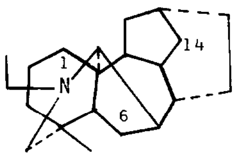
THE STRUCTURE OF DELPHINIFOLINE, A DITERPENOID ALKALOID FROM ACONITUM DELPHINIFOLIUM

V. Nambi Aiyar, Penelope W. Codding, K. Ann Kerr and M.H. Benn*
Chemistry Department, The University, Calgary, Alberta, Canada T2N 1N4
and Alan J. Jones
The National NMR Centre, Australian National University,
Canberra, ACT 2600, Australia

Summary: The structure of delphinifoline, a minor alkaloid of Aconitum delphinifolium DC, was established by spectroscopic methods, and X-ray crystallography.

During an investigation of the alkaloids of Aconitum delphinifolium DC, we isolated, by careful chromatography of the mixed bases on neutral alumina, very small amounts of an apparently previously undescribed base, which we have named delphinifoline.

Delphinifoline, homogenous by tlc analysis, had m.p. 218-220°. The MS revealed an apparent molecular ion at m/e 439.2555 (50), with fragment ions at 424.2365 (62) and 422.2537 (100) amu: corresponding to a $C_{23}H_{37}NO_7$ molecular composition (calcd. 439.2560), and losses of CH_3 (calcd. 424.2335), or OH (calcd. 422.2542). The IR spectrum (KBr pellet) included strong absorbtions at 3510, 3320, 1105, 1080 and 1050 cm^{-1}, indicating the presence of OH and ether functions, but was devoid of absorbtions in the carbonyl region. Prominent signals in the 200 MHz ^{1}H-NMR spectrum ($CDCl_3$ solution, internal TMS reference) at δ1.08 (3H, t, J = 7.4 Hz), 3.34 (3H, s), 3.36 (3H, s), 3.64 (1H, m), 4.22 (1H, dd, J = 4.5 Hz) and 4.56 ppm (1H, broad s) were attributed respectively to the methyl of an N-ethyl function, two methoxyl, and three C$\underline{\underline{H}}$OH groups. This suggested that delphinifoline belonged to the C_{19}-diterpenoid alkaloids, characterised[1] by the skeleton *1*. Assuming a conventional, lycoctonine-like, oxygenation-pattern, we than wrote *2* as a plausible structure for delphinifoline: ascribing the low-field ^{1}H-NMR signal at δ3.64 to H-1 (β)[2], at 4.22 to H-14 (β)[2], and 4.65 ppm to H-6 (α)[3]. A ^{13}C-NMR spectrum of delphinifoline



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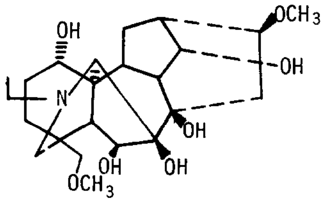

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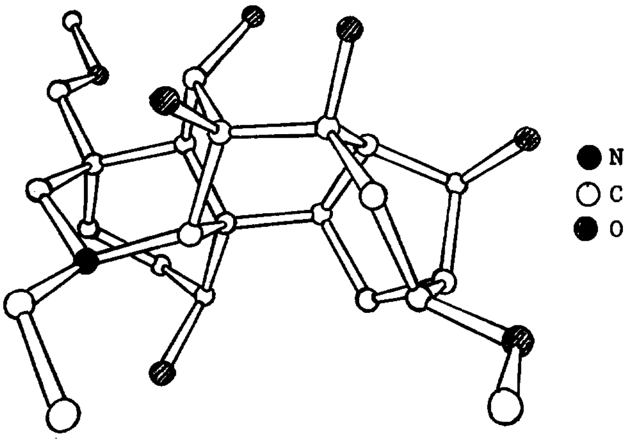
(in $CDCl_3$, with TMS as internal reference) was in accord with this structure although, with the amount of the alkaloid available to us, only signals attributable to 19 carbon atoms could be seen clearly. Lack of material also prevented us from making any meaningful measurements of the specific rotation, or attempting any chemical transformations. We therefore turned to a single-crystal X-ray crystallographic structure determination, which finally confirmed that delphinifoline was correctly represented as *2*, by yielding[4] the structure *3*.



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Delphinifoline is thus seen to be closely related to the well known[1] C_{19}-diterpenoid alkaloids delcosine, and delsoline (these being formally the 6-O-methyl, and 6,14-di-O-methyl derivatives of *2*).

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References:

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2. S.W. Pelletier, Z. Djamarti, S. Lajšić, and W.H. DeCamp, J. Amer. Chem. Soc., *98*, 2617 (1976).
3. A.S. Narzullaev, M.S. Yunusov, and S. Yu. Yunusov, Khim. Prirod. Soed., 497 (1973).
4. The R-factor was 0.040. Full details of this work will be published elsewhere.

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