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REVISED STRUCTURES OF PRATORININE AND PRATORIMINE

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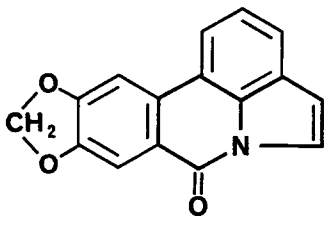
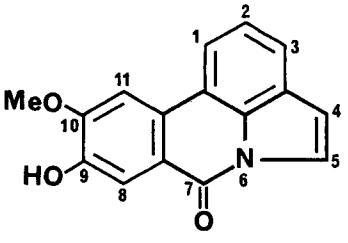
Summary: Two phenanthridone alkaloids isolated from the bulbs of Crinum bulbispermum L. have been shown to be identical with pratorinine and pratorimine. The structure proposed earlier for pratorinine has been revised to **3** *on the basis of an X-ray structure analysis and the structure of pratorimine has been shown to be* **2**.

From the 95% ethanol extract of the bulbs of *Crinum bulbispermum* L. (Amaryllidaceae) cultivated in Egypt, we have isolated by extensive column and vacuum liquid chromatography[1] hippadine (**1**)[2], and two related alkaloids **A**, m.p. 224-225°, and **B**, m.p. 265-267°. Both **A** and **B** were found to be isomers having the molecular formula $C_{16}H_{11}NO_3$, M^+ m/z 265. These alkaloids have properties closely resembling pratorinine[3] and pratorimine[4] isolated from *Crinum pratense* and *C. latifolium*, respectively.



1



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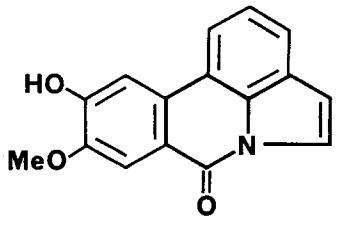

3

Pratorinine was reported to have m.p. 265-267°[5] and was assigned the structure **2** on the basis of the ^1H n.m.r. upfield shift of H-8 (ca 0.4 ppm) on addition of NaOD-D_2O. The isomeric alkaloid pratorimine, m.p. 263-265°, was formulated as **3** mainly on the basis of ^1H n.m.r. chemical shifts of the various aromatic protons and an upfield shift (0.12 ppm) exhibited by H-11 by the addition of NaOD-D_2O.[6] A comparison of the i.r. (KBr) spectra of our alkaloid **A** and pratorinine[7] showed them to be identical. To confirm the structure of A by an X-ray analysis, long, colorless needles were prepared by crystallization from methanol. The space group was determined to be the monoclinic $P2_1/n$ with a = 7.162 (2), b = 14.516 (2), c = 11.600 (2)Å, β = 98.01 (2)°, and z = 4. Data collection ensued utilizing an Enraf-Nonius CAD4 diffractometer with CuKα radiation (λ = 1.5418Å), an ω-2θ scan technique and a variable scan speed. Data were collected to a maximum 2θ of 150° with a scan width of (1.0 + 0.140 tan θ)°. Of the 2455 unique reflexions measured, 1826 reflexions with $I \geq 3\sigma(I)$ were used in the least squares refinement after application of Lorentz and polarization corrections.

The structure of the alkaloid was solved by multisolution methods using the program MULTAN. From 350 reflexions (minimum E of 1.39) a single phase set was produced. Full matrix least squares refinement converged at R = 0.057, Rw = 0.067 for 1826 reflexions.[8] The quantity minimized in refinement was $w(\Delta F)^2$ where $w = 1/\sigma\ (F)^2$. A difference Fourier revealed all hydrogens, which were refined isotropically. The ORTEP plot (Figure 1) shows a slight puckering, the dihedral angle between the indolic fragment and the plane of the benzoyl unit being 2.7°.[9] The structure of pratorinine should therefore be revised to **3**.

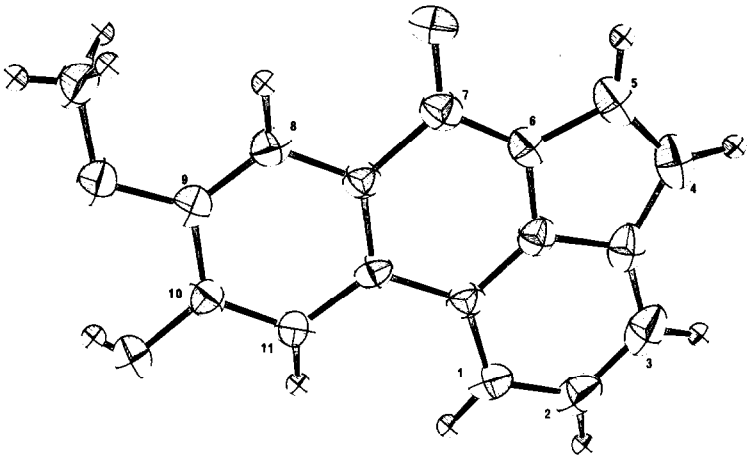

Figure 1. ORTEP drawing of pratorinine

As pratorimine was shown to be identical with alkaloid **B** by i.r. spectral comparison, its structure must be revised to **2**.

REFERENCES

1. S.W. Pelletier, B.S. Joshi and H.K. Desai, "Techniques for Isolation of Alkaloids" in *Advances in Medicinal Plant Research*, Editors: A.J. Vlietinck and R.A. Dommisse, Wissenschaftliche Verlagsgesellschaft mbH, Stuttgart, 1985, pp. 153-196.
2. A.A. Ali, M.K. Mesbah and A.W. Frahm, *Planta medica*, **43**, 407 (1981).
3. S. Ghosal, P.H. Rao, D.K. Jaiswal, Y. Kumar and A.W. Frahm, *Phytochemistry*, **20**, 2003 (1981).
4. S. Ghosal, K.S. Saini and A.W. Frahm, *Photochemistry*, **22**, 2305 (1983).
5. In a letter (to BSJ, March 28, 1985), Dr. Frahm has stated that pratorinine has a m.p. of 225° and the earlier reported m.p. 265-267° is incorrect. We thank Dr. Frahm for the i.r. spectra of pratorinine and pratorimine.
6. The chemical shifts reported for H-8 and H-11 for **1,2** and **3** in references 2, 3, 4 are not consistent.
7. The spectra were identical except for two peaks which were not well resolved in pratorinine.
8. Bond distances and angles, fractional coordinates and thermal parameters and a list of structure factors are deposited with the Cambridge Crystallographic Data Centre.
9. The greatest standard deviation from the calculated least squares plane is 0.004Å.

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