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# MEARSINE, A UNIQUE ISOQUINUCLIDINE ALKALOID: X-RAY CRYSTAL STRUCTURE OF MEARSINE PICRATE

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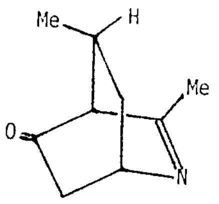
*Summary. X-ray crystallography shows that mearsine, a minor alkaloid of the north Queensland plant Peripentadenia mearsii, has the novel isoquinuclidine structure 1, which permits charge transfer to take place between a carbonyl and an azomethine group.*

Mearsine (1) is a minor alkaloid of the elaeocarpaceous plant Peripentadenia mearsii (C.T. White) L.S. Smith which grows in rain forests of north Queensland.[1] Its formula $C_9H_{13}NO$ was established by mass spectrometry and by microanalysis of its crystalline picrate, m.p. 212-213°; the base, m.p. 43-44°, $[\alpha]_D^{17}$ -34.5° (c, 0.495, $CH_2Cl_2$), was isolated by ptlc and purified by sublimation in vacuo. The n.m.r. spectra of mearsine show the presence of two methyl groups attached to an aliphatic methine and to a quaternary olefinic carbon respectively. The latter carbon resonates at 173.9 ppm in the $^{13}C$ spectrum, and appears to form part of an azomethine group since the proton signal of the methyl group attached to it is shifted from δ2.12 to δ3.35 on quaternisation of the nitrogen with methyl iodide. Further evidence for the presence of an azomethine group in 1 comes from an i.r. absorption at 1660 $cm^{-1}$, and from the fact that mearsine methiodide has one extra methyl group, whereas if 1 is first reduced with borohydride, two methyls are added on quaternisation. Treatment of mearsine with borohydride increases the molecular weight by four units, and reduces both the azomethine group and a carbonyl, whose presence in 1 is attested by its i.r. and $^{13}C$ n.m.r. absorptions at 1730 $cm^{-1}$ and δ208 respectively. The reduction product forms a diacetyl derivative, whereas mearsine is not acetylated under the same conditions.

From the n.m.r. spectra of 1, the remaining atoms are in two methylene and two methine groups; the latter must be at ring junctions, and adjacent to the carbonyl and azomethine groups since their protons resonate at δ3.15 and 4.52. They are not coupled to one another, but their signals are split by a set of protons resonating around δ2.0 that are further coupled to another high-field proton, and whose mutual couplings proved difficult to trace because of



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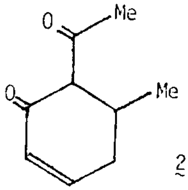

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overlapping. The u.v. spectrum, with maxima at 234 and 275 nm (log $\varepsilon_{max}$ 3.67 and 2.78), suggests that the carbonyl and azomethine groups are conjugated.

The structural features indicated by these data could not be satisfactorily fitted into the bicyclic system required by the formula. The structure was eventually established from single crystal data X-ray diffraction analysis of mearsine picrate (2412 unique data, R = 0.037)[†] which shows (Fig. 1) that the base has an isoquinuclidine skeleton in which the carbonyl and azomethine groups are in fact not conjugated, but are close enough for charge transfer to take place. The structure suggests that mearsine (**1**) is biosynthesised from acetate units *via* an intermediate such as **2**; the skeleton of **2** also appears in the partial structures of most of the other bases occurring in *P. mearsii*[1] and in the botanically related *Elaeocarpus* spp.[5]

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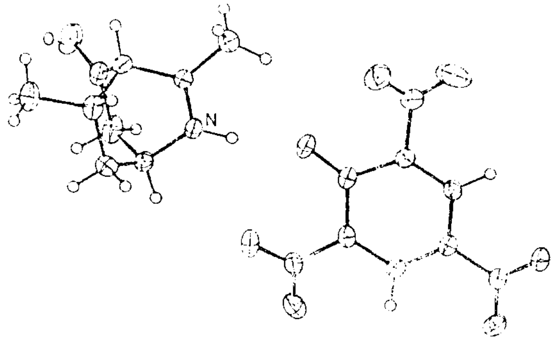

Fig. 1

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[†] The structure was solved with MULTAN[2] and refined by full-matrix least-squares analysis; the probability that Fig. 1 depicts absolute configuration is 99.5%.[3] The figure was drawn with ORTEP.[4] Crystal data and atomic coordinates are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW. Any request should be accompanied by a full literature citation for this communication.

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