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ARISTOTELINONE AND SERRATOLINE: NEW INDOLE ALKALOIDS FROM *ARISTOTELIA SERRATA* W.R.B. OLIVER

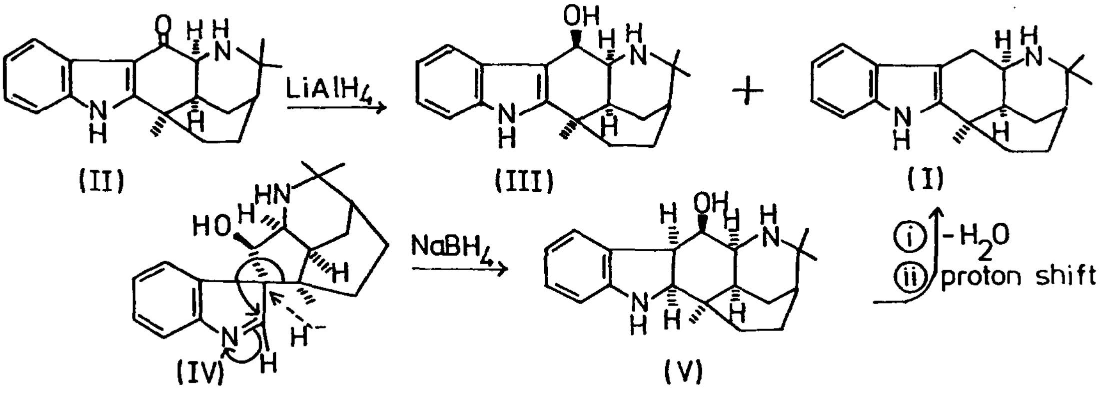
I. Ralph C. Bick**, Mohammad A. Hai*, Nigel W. Preston* and Rex T. Gallagher†
*Chemistry Department, University of Tasmania, Hobart, Australia
†Applied Biochemistry Division, D.S.I.R., Palmerston North, New Zealand

Summary: Aristotelinone and serratoline, two new *Aristotelia* alkaloids, are shown to have indole and indolenine structures respectively from their spectra and reduction products.

The structure and absolute configuration of aristoteline (I), the main alkaloid of the New Zealand plant *A. serrata* (and of the South American *A. chilensis*[2]) was established by X-ray crystallography[1]. A minor alkaloid of *A. serrata*, aristotelinone, was isolated by standard means and crystallised from methanol in fine needles, changing around 255° into longer needles which remained unaltered up to 320°, $[\alpha]_D^{19}$ + 122.7° (MeOH + $CHCl_3$ 1:1). From its molecular formula $C_{20}H_{24}N_2O$, aristotelinone had two less hydrogen atoms than (I), plus an oxygen; its ^{13}C nmr spectrum was largely similar to that of aristoteline, except for a signal due to a carbonyl group, which from the ir and uv spectra was attached to the 3-position of an indole nucleus[3]. This deduction was in accord with the absence of allylic proton signals in the ^1H nmr spectrum, which otherwise resembled that of (I); in both spectra the 2 and 3 positions of indole appeared to be substituted, and this was confirmed by a -ve Ehrlich test.

On LAH reduction of aristotelinone, the crystalline major product proved identical with (I): the structure and stereochemistry of aristotelinone are thus established as (II). Two minor reduction products were evidently the corresponding epimeric secondary alcohols from their spectra and molecular formulae. One of them crystallised, and showed signals in its ^1H nmr spectrum due to protons adjacent to the hydroxyl (δ 3.70), and to the aliphatic nitrogen (δ 2.50), which were weakly coupled (J = 3.1 Hz), and since the latter proton must be axial as in aristoteline (I), the hydroxyl group is also axial as in (III).

Another minor alkaloid from *A. serrata* crystallised as rhombs from methanol, mp 157-160°, with $[\alpha]_D^{19}$ - 68.25° ($CHCl_3$). This base, serratoline, was isomeric with the dihydro-reduction products of aristotelinone, and like them gave a -ve Ehrlich test and had an hydroxyl group from its ir and ^1H nmr spectra. The ms of all three bases were very similar, and the ^1H nmr spectra of serratoline and (III) showed a particular resemblance: the aliphatic regions were virtually identical, with only slight differences in chemical shifts and coupling constants of certain signals. There were also close similarities in the aromatic region, but the spectrum of (III) had a broad signal at δ 7.88 due to the proton on the indolic nitrogen; this was absent in the serratoline spectrum, which had instead an extra singlet at δ 7.30. The uv spectra of the two bases, however, were different: that of serratoline showed it was an indolenine (λ_{max} 262 nm). Structure (IV) suggested by these data was consistent with the reactions of serratoline, which was unaffected by heating with alkali, and did not rearrange to an indoxyl as would be expected if it had a 3-hydroxy group; on the other hand, it was smoothly reduced by borohydride to a single product with the uv spectrum of an indoline, which on acid-catalysed dehydration readily gave (I). The stereochemistry around the spiro carbon of (IV) is uncertain, but it is probable that on reduction, hydride addition takes place from the less hindered under side, leading to (V) which could readily dehydrate and rearrange to (I).



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