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BIOGENESIS OF ARISTOTELIA ALKALOIDS

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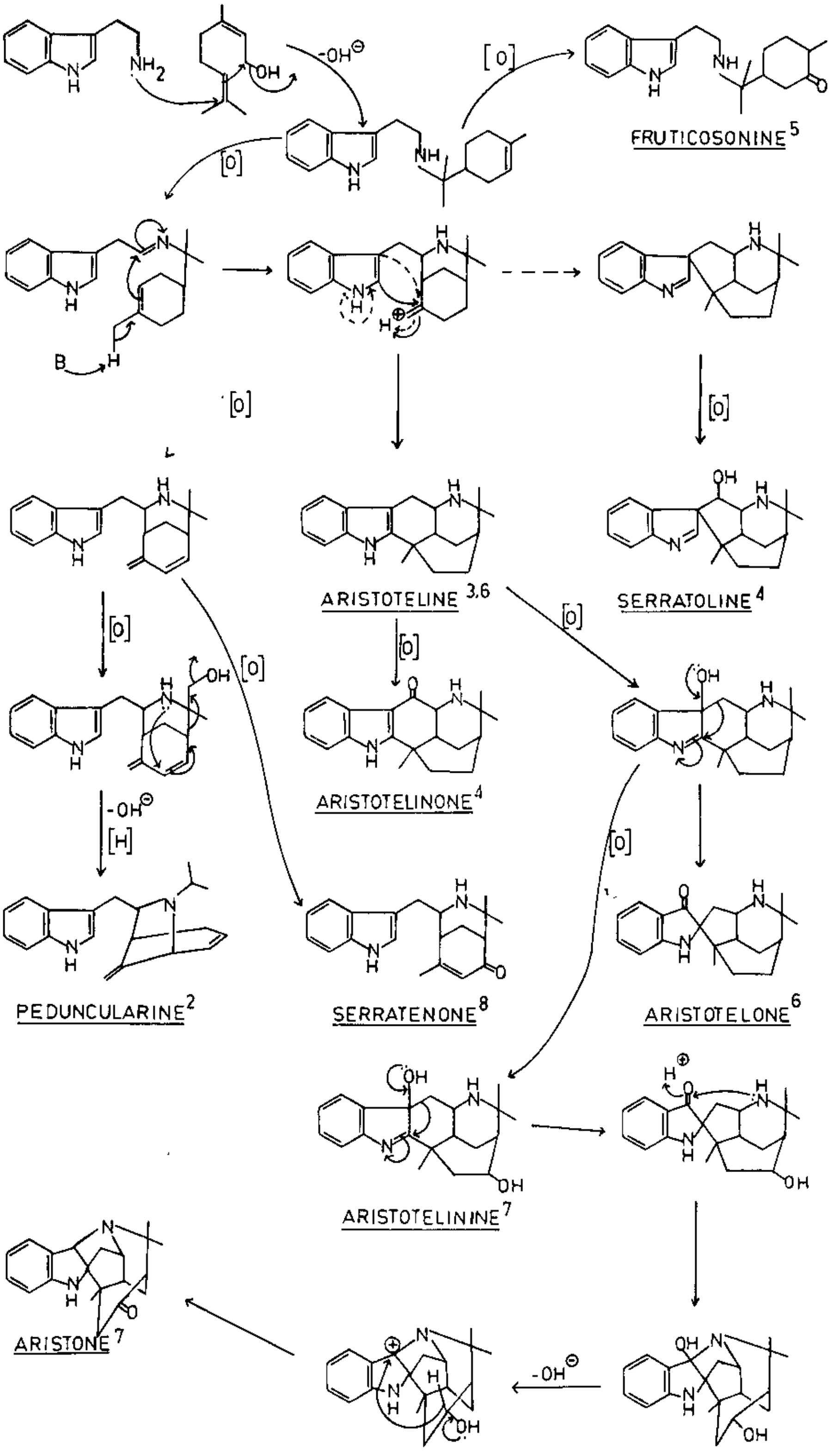
Abstract A possible biosynthetic scheme for the Aristotelia alkaloids is presented.

The Aristotelia spp. belong to the family Elaeocarpaceae and occur in countries bordering the South Pacific: A. peduncularis[1,2] is endemic in Tasmania, A. serrata[3,4] and A. fruticosa[5] in New Zealand, and A. chilensis[6,7] in South America. About twenty-five alkaloids have so far been isolated[1-8] from these plants, some of unknown or incompletely known structures.

Apart from the Aristotelias, of which there are one or two other species less well defined botanically, certain Elaeocarpus spp. from New Guinea belonging to the same family contain a range of indolizidine and related alkaloids[9], including one with an indole residue. The alkaloids so far reported from the Aristotelias all have 20 carbon atoms and two nitrogens, and contain an indole or some closely related nucleus; furthermore, they all have geminal dimethyls, plus an extra methyl group except one example which has a vinylidine group instead: these features strongly suggest that the Aristotelia alkaloids originate in a tryptamine and a monoterpenoid unit. A large range of well-known indole alkaloids have a similar origin, starting ultimately from geraniol as the terpenoid unit, but this undergoes profound structural changes to secologanin before being linked to the tryptamine[10].

The Aristotelia alkaloids on the other hand appear to owe their origin to a linkage between tryptamine and an unarranged terpenoid unit such as geraniol, followed by a variety of molecular rearrangements as in the biosynthesis of other indole alkaloids[10]. The following scheme, which at present lacks experimental support but may serve as a working hypothesis for labelling experiments, suggests a possible biogenetic pathway for all the Aristotelia alkaloids so far reported. The transformations involved in the scheme, such as oxidation at an α-position to nitrogen, or formation of a new N-C bond through nucleophilic attack by a nitrogen, are well-known and all have analogies in alkaloid biogenesis. The scheme presents a feasible pathway to peduncularine[1,2], which is unique amongst naturally-occurring alkaloids in having an N-isopropyl group. The plausible route from aristoteline to the A. chilensis alkaloids aristotelinine, aristotelone and aristone, was proposed by Bittner et al.[7]


-OH⊖
[O]
[O]
FRUTICOSONINE 5
B
[O]
[O]
ARISTOTELINE 3,6
SERRATOLINE 4
[O]
[O]
[O]
[O]
ARISTOTELINONE 4
-OH⊖
[H]
[O]
PEDUNCULARINE 2
SERRATENONE 8
ARISTOTELONE 6
ARISTOTELININE 7
ARISTONE 7
-OH⊖

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