Biogenesis of *Elaeocarpus* and *Peripentadenia* alkaloids

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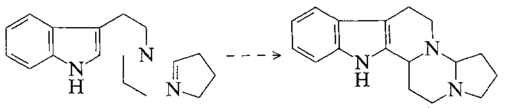
Summary. A pathway for the biogenesis of alkaloids of *Elaeocarpus* and *Peripentadenia* spp. (Elaeocarpaceae) is put forward, which involves methionine as the source of the central C3 unit in the structures of all these bases except mearsine, for which acetate units appear to furnish all the carbon atoms in its structure.

Key words. Biogenesis; *Elaeocarpus* alkaloids; *Peripentadenia* alkaloids.

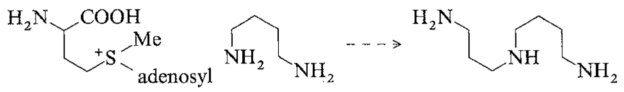
The pioneer work on alkaloids of *Elaeocarpus* spp., which belong to the plant family Elaeocarpaceae and grow in remote areas of New Guinea and north Queensland, was carried out by Johns and Lamberton[3], who determined their structures and suggested that the majority were biosynthesized from a pyrroline derived from a unit of ornithine, and a polyketide chain formed from acetate units. The only exception appeared to be the unique indole alkaloid elaeocarpidine (**1**), which they considered to be derived from tryptamine, ornithine, and a C3 unit:



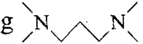
1 Elaeocarpidine

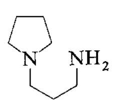
It appears highly probable to us that all the other *Elaeocarpus* alkaloids contain the same C3 unit in addition to a polyketide chain, an idea first proposed by Onaka[4], who did not, however, specify the origin of this unit. We suggest that it is derived from methionine, and that most of the alkaloids of the closely related genus *Peripentadenia*, from far north Queensland, also include a similar C3 unit in their structures.

Methionine, in the form of its S-adenosyl derivative, is well-known to be involved in N-methylation during the biosynthesis of many alkaloids, but instead of the methyl, it is possible under some circumstances for the propylamine group to be transferred to another nitrogen from the decarboxylated methionine residue, for instance, to putrescine, to form the alkaloid spermidine (**2**)[5]:



2 Spermidine

Most of the *Peripentadenia* alkaloids have the same grouping  in their structures[6,7] as in (**2**), and we consider this diamino group to be produced in a similar way from a methionine unit and a pyrrolidine formed from ornithine. The diamine (**3**) so formed could then provide a key intermediate in the biosynthesis of all the *Peripentadenia* alkaloids except mearsine (**10**):



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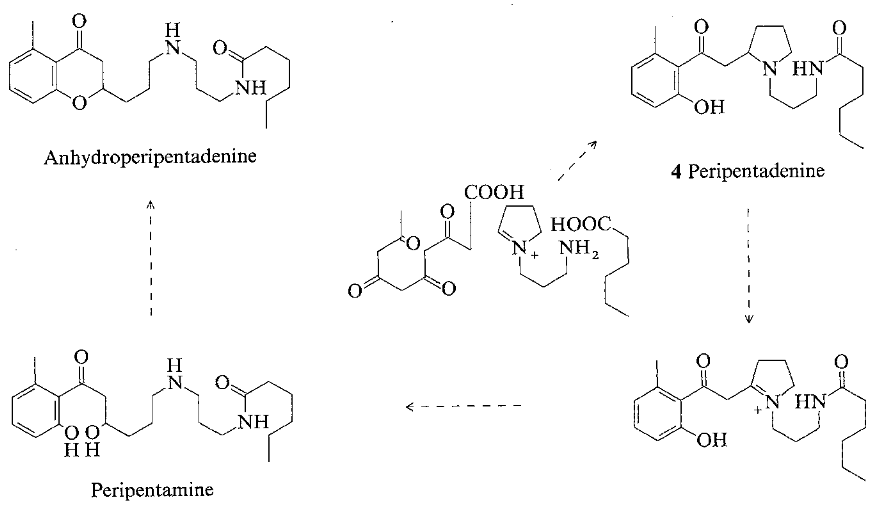
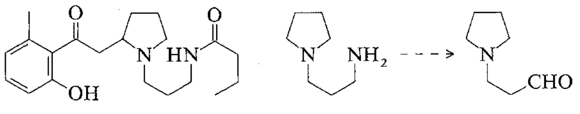


Anhydroperipentadenine

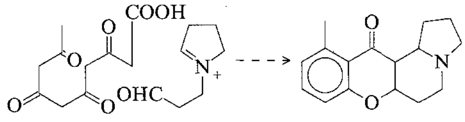
4 Peripentadenine

Peripentamine

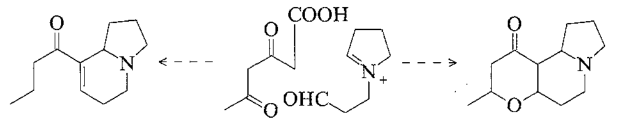
Dinorperipentadenine (**5**)[7] is a homologue of (**4**) with a shorter side-chain, which is evidently formed in a similar way to (**4**) from butanoic instead of hexanoic acid.


5 Dinorperipentadenine **3** **6**

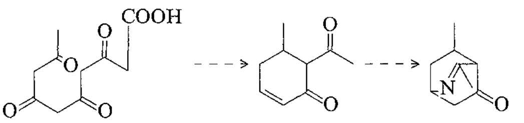
The diamine (**3**) could be metabolized by oxidative deamination into the aminoaldehyde (**6**), which could then serve as a building block for the biogenesis of elaeocarpidine (**1**), elaeocarpine (**7**) and other C16 *Elaeocarpus* alkaloids[4]:


7 Elaeocarpine

The C12-type bases such as elaeokanines A (**8**) and D (**9**) could be derived in a similar way from a shorter polyketide chain:


8 Elaeokanine A **9** Elaeokanine D

The *Peripentadenia* alkaloid mearsine (**10**)[8] is exceptional inasmuch as acetate units appear to form the only source of carbon atoms in its structure:


10 Mearsine

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(+)-α-Pinene in the defensive secretion of *Nasutitermes princeps* (Isoptera, Termitidae)

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Summary. The frontal secretion of *Nasutitermes princeps* consists of 89 % diterpenes and 11 % monoterpenes. In the samples studied, (+)-α-pinene, whose optical purity reaches 99.5 %, accounts for more than 80 % of the monoterpenic content.

Key words. (+)-α-Pinene; *Nasutitermes princeps*; defensive secretion.

One of the most obvious characteristics of the genus *Nasutitermes* (Isoptera, Termitidae, Nasutitermitinae) is the existence of a highly specialized defensive caste. Their defensive mechanism consists of the ejection of a gluey frontal secretion onto predators or competitors which are thereby quickly incapacitated. The secretion consists mainly of a mixture of membrane-derived diterpenes dissolved in monoterpenes[4–7].

Besides being a solvent for the diterpenes, the monoterpenes have a role as alarm pheromones, which has been demonstrated in some termites[8–11], and are also irritant[10] and toxic[12–14]. Diterpenes are responsible for secretion viscosity, and as solutes may reduce monoterpene evaporation[4].

The nature of the monoterpenoid components has been studied in some Nasutitermitinae species reviewed by