2001-55

Caste Specific Alkaloid Chemistry of *Solenopsis maboya* and *S. torresi* (Hymenoptera: Formicidae)

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ABSTRACT

Examination of the alkaloids of *Solenopsis maboya* Snelling and comparison with those previously found in *S. torresi* Snelling, reveals a clear example of caste-specific alkaloid production in the queens and workers of each species .The queens of *Solenopsis maboya* contain a single piperidine while the workers produce a different piperidine along with two indolizidine isomers. In contrast, the queens of *S. torresi* contain a single indolizidine while the workers produce an unsaturated piperidine , In both species there is structural analogy between the bicyclic indolizidines and the monocyclic piperidines, and in *S. maboya* both classes of compounds even share six-membered ring stereochemistry.

INTRODUCTION

The venoms of *Solenopsis* (*Diplorhoptrum*) species have been known to contain saturated nitrogen heterocycles for over twenty years (Jones *et al.* 1982), Compared to other alkaloid producing ants this groups produces the greatest structural variety of these compounds, including piperidines, pyrrolidines, and pyrrolizidines (Jones *et al.* 1982) as well as indolizidines (Jones *et al.* 1984, Gorman *et al.* 1998), and more recently, quinolizidines and decahydroquinolines (Jones *et al.* 1999).

Our use here of the subgeneric name *Diplorhoptrum* is intended solely as a convenient designation for purposes of discussion. *Diplorhoptrum* has long been in the synonomy of *Solenopsis* in the broad sense (Ettershank 1966) and we specifically do not intend to formally resurrect that name.

Along with their structural variety, each of these classes of compounds, which may occur as more than one stereoisomer, are produced stereospecifically by the ants. It is the variety and stereospecificity of

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these alkaloids in *Solenopsis* (*Diplorhoptrum*) that have led to their consideration as taxonomic characters in this group (Gorman *et al.* 1998). Recently, the workers and queens of a related thief ant, *S. azteca*, have been shown to contain very different alkaloids (Spande *et al.* 1999). In this paper, we describe the caste-specific alkaloids of *Solenopsis maboya* and compare them with previously published results from *S. torresi*, both new species described in a separate paper in this issue of Sociobiology.

MATERIALS AND METHODS

Samples of both workers and queens of *S. maboya* were collected at Guaynabo (18°17'N, 66°07'W) Puerto Rico, on 14 February 1999 ,Workers and queens were separately preserved in 100% methanol for analysis, Gas chromatographic analyses and mass spectra were obtained using a Shimadzu QP-5000 GC/MS equipped with a 30m x 0.25mm i.d. RTX-5 column programmed from 60 to 250 °C at 10°C/min. The natural alkaloids were identified by direct GC/MS comparison with authentic synthetic samples.

RESULTS

Analysis of the extracts of the workers of *Solenopsis maboya* revealed the presence of three alkaloids ,In order of elution, the first two had identical EI mass spectra [*m/z* (rel. int.: 195 (M+, 0.5), 194 (1), 180 (5) 138 (100)] indicative of 3-butyl-5-methylindolizidine, one of the first alkaloids found in ants (Ritter, et al., 1973) ,The mass spectrum of the third alkaloid was identical to that of 2-methyl-6-nonylpiperidine [*m/z* (rel. int.: 225 (M+, 0.5), 210 (1), 98 (100)] (Jones *et al.* 1982) ,The two indolizidines were shown to be (5Z,9Z)-3-butyl-5-methylindolizidine (1) and its (5E,9E) stereoisomer (2) (Fig. 1) by direct comparison with a synthetic sample of the four possible isomers (Oliver and Sonnet, 1974). Similarly, the piperidine was shown to be *trans*-2-methyl-6-nonylpiperidine (**3**) (Fig. 1) by comparison with an authentic sample (Jones *et al.* 1982).

Analysis of the extracts of the queens of this species revealed the presence of a single alkaloid with a mass spectrum [*m/z* (rel. int.: 197 (M+, 0.5), 196 (1), 182 (3), 98 (100)] suggesting 2-heptyl-5-methylpiperidine ,This compound was shown to be *cis*-2-heptyl-5-methylpiperidine (4) (Fig. 1) by direct comparison with a synthetic sample of the two piperidine isomers (Sonnet and Oliver, 1975).

DISCUSSION

The occurrence of compounds 1-4 together in *S. maboya* is unique.

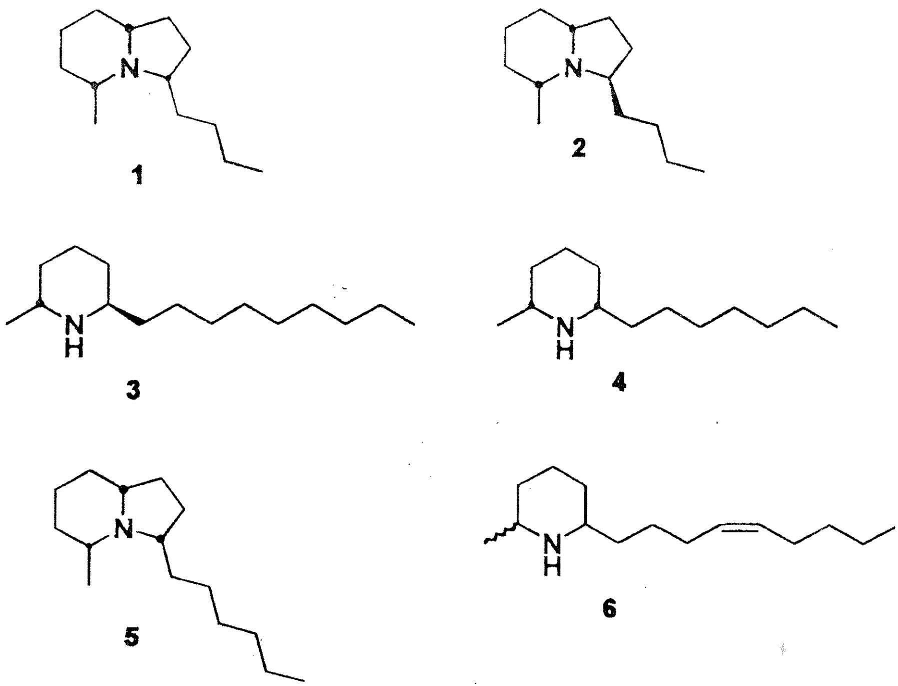

Fig. 1. Venom alkaloids from *Solenopsis maboya*. 1, 2, and 3 from workers; 4 from queens) and from *S. torresi* Snelling (5 from queens and 6 from workers

The all-*cis* indolizidine (1) in the workers of *S. maboya* was first discovered in *Monomorium pharaonis* (Ritter *et al.* 1973), where it was shown that these ants are capable of recognizing this particular stereoisomer (Edwards & Pinniger 1978), Indolizidine (2) has not been previously reported in ants, although 1 and 2 have been found together in poison-dart frogs, so that finding both indolizidine isomers in *S. maboya* fits the dietary hypothesis for the origin of the skin alkaloids of these amphibians (Jones *et al.* 1999) , The *trans* piperidine (3) has been reported as a venom component of both *Solenopsis* (*Solenopsis*) and *Solenopsis* (*Diplorhoptrum*) species (Jones *et al.* 1982), while *cis*-2-heptyl-5-methylpiperidine (4) has not been reported from natural sources , The presence of only *cis*-2-heptyl-5-methylpiperidine (4) in the queens of *S. maboya* is a clear example of the caste specificity of the alkaloids in *Solenopsis* (*Diplorhoptrum*) species,

It is of interest to compare the venom alkaloids of *S. maboya* with those previously reported from *S. torresi* (Jones *et al.* 1996), since both species are described together in the previous paper (Snelling 2001) ,In *S. torresi* the queens contain a single alkaloid, (5Z, 9Z)-3-hexyl-5-

methylindolizidine (5) (Figure 1), a bicyclic rather than a monocyclic compound as in the queens of *S. maboya*, On the other hand, the workers of *S. torresi* also contain a pair of monocyclic isomeric alkaloids, *cis* and *trans*-2-methyl-6-(Z,4-nonenyl)piperidine (6) (Fig. 1), in contrast with the pair of bicyclic indolizidines, 1 and 2, from *S. maboya* workers.

In *S. maboya*, 1 and 2 in the workers and 4 in the queens are all thirteen carbon alkaloids sharing the same (*cis*) six-membered ring stereochemistry, while in *S. torresi*, 5 and 6 are both fifteen carbon compounds where indolizidine 5 has the same six-membered ring stereochemistry as the minor (*cis*) isomer of 6 , These suggest a similar biosynthetic pathway for the cyclization of indolizidines in both species consistent with that suggested for the indolizidine found in the venom of the Costa Rican thief ant *S. conjurata* (Jones *et al.* 1984).

Such complete structural differences in the venom alkaloids produced by the queen and worker castes, as reported herein, have been found in *S.* (*Diplorhoptrum*) *azteca* (Spande *et al.* 1999) and in some other undescribed *Solenopsis* (*Diplorhoptrum*) species (Jones *et al.* 1996), and they suggest different roles for the alkaloids in each caste. At the same time, the diversity and unique distribution by caste of the alkaloids produced in *S. maboya* and *S. torresi* may serve as identifying characteristics in light of the very difficult taxonomy of this group of ants (Gorman *et al.* 1998; Snelling 2001).

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