POISON GLAND PRODUCTS OF *SOLENOPSIS* AND *MONOMORIUM* SPECIES[1]

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ABSTRACT

2-Alkyl-6-methylpiperidines have been identified in the venoms of workers of five species of ants in the genus *Solenopsis*. *S. (Euophthalma) globularia pacifica* Wheeler produces *cis*- and *trans*-2-nonyl-6-methylpiperidine whereas *S. (Diplorhoptrum) steinheili* Forel and *S. (Diplorhoptrum)* sp. PR synthesize N-methyl-2-nonyl-6-methylpiperidine as well. Workers of *S. (Solenopsis) geminata rufa* (Jerdon) produce *cis*- and *trans*-2-undecyl-6-methylpiperidine as do workers of *S. (Solenopsis) maniosa* Wheeler. Phenol and salicylaldehyde have been identified in extracts of workers of *Monomorium (Parholcomyrmex) destructor* (Jerdon) in contrast to 2,5-dialkylpyrrolidines that are considered to be characteristic natural products of this genus.

Key Words: *Solenopsis, Monomorium,* ant venoms, dialkylpiperidines, salicylaldehyde.

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INTRODUCTION

The venoms of ants in the genera *Solenopsis* and *Monomorium* have proven to be a rich source of alkaloids (Jones et al. 1982), all of which have been demonstrated to be novel natural products. A host of 2,6-dialkylpiperidines and 2,5-dialkylpyrrolidines have been identified as poison gland products of species in these two genera (Jones and Blum 1983) in addition to several new indolizidines (Ritter et al. 1975; Jones et al. 1984) and pyrrolizidines (Jones et al. 1980). The virtuosity of *Solenopsis* and *Monomorium* species as biosynthesizers of alkaloids in their poison glands is emphasized by the fact that more than 40 of these nitrogen heterocycles have been identified as venom products (Jones and Blum 1983).

In the present report, the chemistry of the poison gland products of five species of *Solenopsis* in three subgenera is described. In addition, analyses of the products synthesized by a *Monomorium* species are presented.

METHODS AND MATERIALS

Ants

Workers of *S. (Euophthalma) globularia pacifica* Wheeler were collected at Isla Santa Fe, Isla Isabela (Beagle Crater), and Isla Rabida, Galapagos Islands. *S.*

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(Diplorhoptrum) steinheili Forel workers were collected at Cayo Ratones, Culebrita, and Isla Palominos, Puerto Rico, and workers of *S. (Diplorhoptrum)* sp. PR were taken at Rio Grande, Puerto Rico. Both workers and soldiers of *S. (Solenopsis) geminata rufa* (Jerdon) were collected in Bangkok, Thailand.

S. (Solenopsis) maniosa Wheeler had been previously considered to be a subspecies of *S. xyloni*, but research by one of us (R.R.S.) suggests that it deserves specific status; its taxonomy will be described elsewhere. Workers from four populations were analyzed: a) Tucson, Arizona (dark phase divided into small and large workers), b) Riverside, California, c) Tucson, Arizona, and d) Senoita, Arizona. Populations b - d constitute the typical light phase.

Workers of *Monomorium (Parholcomyrmex) destructor* (Jerdon) were collected at Cajo de Muertes, Puerto Rico.

Specimens of all species described in this report have been deposited in the Los Angeles County Museum of Natural History.

Chemical Analyses

Ants were immediately placed in glass vials containing 1 - 2 ml of methylene chloride. For analyses, solutions of these pooled samples were reduced in volume to 0.2 ml with a slow stream of nitrogen. Workers from different populations were analyzed separately.

All mass spectra were obtained using an LKB 9000 gas chromatograph-mass spectrometer. Extracts of *Solenopsis* spp. were analyzed on columns of either 1% SP-1000 or 1% OV-17 on Supelcoport (Jones et al. 1982). Retention time comparisons were made using a Gow-Mac Model 750P gas chromatograph equipped with a 2 m $\times$ 2 mm glass column packed with 5% SP-1000 operated under isothermal conditions. Extracts of *M. destructor* were analyzed on a 30 m column of Carbowax 20M programmed from 50 - 230°C at a rate of 10°/min.

RESULTS AND DISCUSSION

Workers in all three populations of *S. (Euophthalma) globularia pacifica* produce *trans*-2-nonyl-6-methylpiperidine. The population from Isla Rabida is distinctive in containing *cis*-2-nonyl-6-methylpiperidine as well (4:1 *trans:cis).* In contrast, workers in a North American population of this species, *S. g. littoralis* Creighton (Florida, U.S.A.), produce 2-tridecyl-6-methylpiperidine as their sole poison gland product (Jones et al. 1982). *trans*-2-Nonyl-6-methylpiperidine has also been detected in workers of two species of *Diplorhoptrum* (Jones et al. 1982), as well as in the venom of queens of a species in the subgenus *Solenopsis* (MacConnell et. al. 1974).

The alkaloidal chemistry of all three populations of *S. (Diplorhoptrum) steinheili* was similar to that of *S. globularia pacifica* in being characterized by the presence of *trans*-2-nonyl-6-methylpiperidine. However, one population of *S. steinheili* was distinctive in also producing a trace of N-methyl-2-nonyl-6-methylpiperidine, as was the case for *S.* sp. PR. One other *Diplorhoptrum* species, *S. carolinensis,* also produces the same 2,6-dialkylpiperidine and its N-methylated homolog (Jones et al. 1982).

Workers and soldiers of *S. (Solenopsis) geminata rufa* produce only the *cis*- and *trans*-isomers of 2-undecyl-6-methylpiperidine, characteristic alkaloids of *S. (Solenopsis)* species. This subspecies, which is the only Old World member of the subgenus *Solenopsis*, possesses the same venom chemistry as members of New World populations (Brand et. al. 1972; MacConnell et al. 1976).

All populations of *S. (Solenopsis) maniosa* produce venoms dominated by the *cis*- and *trans*-isomers of 2-undecyl-6-methylpiperidine. Traces of *cis*- and *trans*-2-tridecyl-6-methylpiperidine, well-known compounds of *S. (Solenopsis)* species (Brand et al. 1972), occur as concomitants. No major quantitative or qualitative differences in alkaloidal chemistry characterized the light and dark phases as was the case for the large and small workers of the latter. This species was formerly considered to be a synonym of *S. xyloni* (Smith 1979), the venom of which is also dominated by the two isomers of 2-undecyl-6-methylpiperidine (Brand et al. 1972). However, whereas the *cis:trans* ratio of the stereoisomers in the venom of *S. xyloni* is about 6:1, in that of *S. maniosa* it is about 1.2:1. In addition, the venom of *S. xyloni* contains 2-undecyl-6-methyl-1-piperideine (Brand et al. 1972), an alkaloid that has not been detected as a poison gland product of any other species of *Solenopsis*. Significantly, another *S. (S.)* species, *S. aurea*, which was also previously considered to be a subspecies of *S. xyloni* (Creighton 1950), also produces a venom dominated by the isomers of 2-undecyl-6-methylpiperidine (Blum et al. 1973) in the absence of the 1-piperideine characteristic of the venom of *S. xyloni*.

Phenol is the major volatile compound present in extracts of *Monomorium destructor*, and this compound is accompanied by another aromatic constituent, salicylaldehyde. No alkaloidal compounds were detected, even in concentrated extracts of hundreds of workers, a surprising finding in view of the fact that 2,5-dialkylpyrrolidines have been identified as poison gland products of all other *Monomorium* species that have been analyzed (Jones and Blum 1983). *M. destructor* is the only species in the subgenus *Parholcomyrmex* (Emery 1922) analyzed to date, a fact whose significance can only be evaluated after analysis of the natural products produced by other species in this taxon. Neither phenol nor salicylaldehyde have been previously detected as exocrine products of ants, and for that matter, aromatic compounds have rarely been identified as glandular products of ant workers. The apparent absence of alkaloids in *M. destructor* further emphasizes the natural product surprises that have heretofore characterized the species in the genus *Monomorium*, and for that matter, *Solenopsis* as well.

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