CHEMOTAXONOMIC IMPLICATIONS OF THE VENOM CHEMISTRY OF SOME Monomorium "antarcticum" POPULATIONS

TAPPEY H. JONES,¹ SUSAN M. STAHL¥,² A. WARWICK DON,³ and MURRAY S. BLUM⁴

¹Laboratory of Chemistry
National Heart, Lung, and Blood Institute
Bethesda, Maryland 20892

²Department of Chemistry
College of William and Mary
Williamsburg, Virginia 23185

³Department of Zoology
University of Otago
P.O. Box 56, Dunedin, New Zealand

⁴Department of Entomology
University of Georgia
Athens, Georgia 30602

(Received February 2, 1987; accepted October 15, 1987)

Abstract—A comparative analysis of the venom alkaloids produced by ants in the genus Monomorium (=Chelaner) collected on North Island and South Island, New Zealand, has been undertaken. All of the ants produce trans-2,5-dialkylpyrrolidines along with 3,5-dialkylpyrrolizidines. The structures and stereochemistry of the novel alkaloids trans-2-butyl-5-(8-nonenyl)pyrrolidine, (5E,8Z)-3,5-di(5-hexenyl)pyrrolizidine, and (5Z,8E)-3-methyl-5-(8-nonenyl)pyrrolizidine were established by unambiguous synthesis. The geographic distribution and the chemotaxonomic significance of the alkaloids produced by these ants are discussed.

Key Words—Ants, Monomorium, Hymenoptera, Formicidae, 2,5-dialkylpyrrolidines, 3,5-dialkylpyrrolizidines, ant venom alkaloids, chemotaxonomy.
INTRODUCTION

A large variety of saturated nitrogen heterocycles has been identified in the venoms of ant species in the myrmicine genera *Monomorium* and *Solenopsis* (Jones et al., 1982b). 2,6-Dialkylpiperidines and 2,5-dialkylpyrrolidines are most commonly found, and (5Z,9Z)-3-alkyl-5-methylindolizidines have also been reported from both genera (Ritter and Persoons, 1975; Jones et al., 1984). On the other hand, except for the occurrence of (5Z,8E)-3-heptyl-5-methylpyrrolizidine in a *Solenopsis* sp. (Jones et al., 1980b), the 3,5-dialkylpyrrolizidine system has not been detected in the alkaloids produced by any other formicid species.

Recently we isolated and identified (5E,8Z)-3-(8-nonenyl)-5-(E,1-propenyl)pyrrolizidine (5) as the major alkaloidal component in the venom of *Monomorium (=Chelaner) antarcticum* (Jones et al., 1986; Bolton, 1987). In order to determine whether these results were typical of other *Monomorium* populations, we have analyzed the alkaloidal extracts of single-nest collections from 28 locations on North and South Island, New Zealand (Figure 1). The results show that there are major differences in the alkaloids produced by different populations. A variety of pyrrolidines and pyrrolizidines have been detected, and the structures and stereochemistry of one novel pyrrolidine and two novel pyrrolizidines from these ants have been established. These results further indicate that the venom alkaloids of these ants may provide useful taxonomic characters.

METHODS AND MATERIALS

**Chemical Analyses.** Gas chromatographic analyses were performed on a Gow-Mac model 750P using a 2-m × 2-mm-ID glass column packed with 5% SP-1000 on 100-120 mesh Supelcoport. This instrument was programmed from 40°C to 200°C at 10°C/min as soon as the solvent had eluted. Retention times and temperatures were found to be reproducible within one degree on a given day. Preparative gas chromatography was performed on a Varian model 920 using a 2-m × 5-mm-ID aluminum column packed with either 10% SP-2100 or 10% SP-1000 on 100-120 mesh Supelcoport. Infrared spectra were obtained from neat liquid films with a Perkin-Elmer 1320 grating infrared spectrophotometer. [1H]NMR spectra were obtained from CDCl₃ solutions at 80 MHz using a Varian FT-80 spectrometer and at 360 MHz using a Nicolet 360-MHz spectrometer. Chemical shifts (δ) are reported downfield from tetramethylsilane in parts per million (ppm). Mass spectra were obtained using an LKB-9000 GC-MS at an ionizing voltage of 70 eV and fitted with a 2-m × 2-mm-ID glass column packed with 1% SP-1000. High-resolution mass spectra were obtained