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3-HEXYL-5-METHYLINDOLIZIDINE ISOMERS FROM THIEF ANTS, *Solenopsis (Diplorhoptrum)* SPECIES

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Abstract—The venom alkaloids from the workers of nine collections of *Solenopsis (Diplorhoptrum)* from California contain either (5*E*,9*E*)-3-hexyl-5-methylindolizidine (**1c**) or (5*Z*,9*E*)-3-hexyl-5-methylindolizidine (**1d**) along with *cis*-2-methyl-6-nonylpiperidine. The structures of these compounds were determined from their mass spectra and by comparison of their GC-FTIR spectra with those of a synthetic mixture. In view of the facts that a third diastereomer of 3-hexyl-5-methylindolizidine had been reported in previous collections of *Solenopsis (Diplorhoptrum)* queens from Puerto Rico, and that indolizidines along with other ant venom alkaloids are sequestered by amphibians, the determination of species in this difficult group of ants is significant. In particular, the chemotaxonomic value of the stereochemistry of these venom alkaloids is discussed.

Key Words—Venom, alkaloids, *Solenopsis (Diplorhoptrum)*, indolizidine, chemotaxonomy.

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INTRODUCTION

The 3,5-dialkylindolizidines are one of the earliest reported classes of saturated heterocycles identified in the venoms of ant species in the myrmicine genera *Monomorium* and *Solenopsis* (Ritter et al., 1973; Jones et al., 1984, 1990, 1996). In *Solenopsis* these compounds are found in the "subgenus" *Diplorhoptrum*, a large, worldwide group (Bolton, 1987). Although *Diplorhoptrum* has been elevated to the status of genus (Baroni-Urbani, 1968), it is usually treated as a synonym of *Solenopsis* (Ettershank, 1966). Herein we use *Diplorhoptrum* as a matter of convenience without implying that it is a valid taxonomic entity.

The numerous species of so-called thief ants belonging to *Diplorhoptrum* present many vexing problems for the systematist. There are about 100 names applied to various taxa in the New World, mostly in South America. In the Old World there are almost as many more. Most of these have been superficially described from limited material and, almost invariably, in a nonrevisionary context.

Creighton (1950) recognized about a dozen presumed valid taxa in North America and presented a key for their separation. His key is, unfortunately, largely unworkable, principally due to the unsuspected existence of a number of then undescribed species. This deficiency has been partially rectified by the subsequent recognition and description of a number of these additional species (MacKay and Vinson, 1989; Thompson, 1989; Thompson and Johnson, 1989).

In particular, the vexatious problem of the identity of *S. molesta* Say remains to be resolved. The species level taxonomy of this group is presently unresolved and is likely to remain so until the identity of *S. molesta* is firmly established. This species was originally described by the pioneer American naturalist Thomas Say (1836) from specimens collected at his home in Indiana; none of these original specimens are known to exist in any collection, hence the uncertainty as to the correct identity of this ant. Say's original description (1836) of *S. molesta* is sufficiently vague that it may be applied to any *Diplorhoptrum* in the United States. Since no original material is known to exist, there is no certainty as to which species Say had before him. Our interpretation is that exemplified by Creighton's characterization; even that interpretation is probably polytypic. The venom chemistry of *Diplorhoptrum* shows promise as an aid in the resolution of some of the difficulties of this group.

Indolizidines are also a major heterocyclic class found in the skins of dendrobatid frogs; for example, three isomers of 3-butyl-5-methylindolizidine have been found in an Argentine toad (Garraffo, et al., 1993). There is growing support for the hypothesis that alkaloid-containing amphibians sequester such compounds from their diet (Jones et al., 1996, and references therein), which contains a high proportion of small ants. The ant–frog connection adds to the

importance of the taxonomy of this ant group because it is possible that not all *Diplorhoptrum* may be a source for frog-sequestered compounds. It is not known whether the frogs can discriminate against species that may not be suitable.

There are four possible diastereomers of any 3-alkyl-5-methylindolizidine, and within a particular myrmicine species the structure and stereochemistry of the alkaloids present has not been observed to vary. Previously, in those *Solenopsis (Diplorhoptrum)* species where indolizidines have been found, the natural compounds were the all-*cis* 5*Z*,9*Z* isomer with no trace of the other isomers present; (5*Z*,9*Z*)-3-hexyl-5-methylindolizidine (**1a**) has been detected in collections from Florida and Puerto Rico (Jones et al., 1984, 1996). This report describes the identification of two of the remaining three diastereomers of **1** from the extracts of *Solenopsis (Diplorhoptrum)* species (*S. molesta* group) collected in North America. The implications of different indolizidine diastereomers in separate collections of these ants are presented.

METHODS AND MATERIALS

Chemical Analyses

A Hewlett-Packard model 5890 gas chromatograph equipped with a Rtx-5 30-m × 0.32-mm column was used in gas chromatographic analysis. Vapor-phase FTIR spectra were obtained from a Hewlett-Packard model 5965B detector interfaced with a Hewlett-Packard 5890 gas chromatograph fitted with a 30-m × 0.25-mm Rtx-5 Amine column. FTIR spectra of neat liquids were obtained with a Perkin-Elmer 1600 series FTIR instrument. Mass spectra were obtained in the EI mode from a Shimadzu QP-5000 GC/MS equipped with a Rtx-5, 30-m × 0.32-mm column. For high-resolution mass spectrometry (HR-MS) we used a Jeol SX102 instrument equipped with a 15-m × 0.20-mm HP-5 column. Boiling points were uncorrected.

Ants

Solenopsis (Diplorhoptrum) specimens were collected at the sites indicated in Table 1 and immediately placed in small vials of methylene chloride. Voucher specimens of all samples were deposited in the collection of the Los Angeles County Museum of Natural History, Los Angeles, California. The mass spectra and the gas chromatographic retention times of the alkaloids detected in the ants were identical to those of authentic samples. The GC-FTIR spectra of the indolizidines found in collections 1–5 were identical to those of the synthetic isomers prepared below. In collections 3 and 5 the major component had a mass spectrum and gas chromatographic retention time identical to an authentic sample of *cis*-2-methyl-6-nonylpiperidine (Jones et al., 1996).

TABLE 1. 3-HEXYL-5-METHYLINDOLIZIDINES IN *Solenopsis* (*Diplorhoptrum*) SPECIES

Collection	Alkaloids				Comments
	1a	1b	1c	1d	
1 Desert Center, CA			×		
2 Long Beach, CA			×		*cis*-2-methyl-6-nonylpiperidine (t)[a]
3 Alta Loma, CA	t		×		*cis*-2-methyl-6-nonylpiperidine
4 Lake Solano, CA				×	*cis*-2-methyl-6-nonylpiperidine (t)
5 Orange Co., CA	t			×	*cis*-2-methyl-6-nonylpiperidine
6 Irwindale, CA, 1	t			×	*cis*-2-methyl-6-nonylpiperidine
7 Irwindale, CA, 2	t			×	*cis*-2-methyl-6-nonylpiperidine
8 Irwindale, CA, 3	t			×	*cis*-2-methyl-6-nonylpiperidine
9 Marathon Key, FL	×				(Jones et al., 1984)
10 Mona Island, PR	×				Queens (Jones et al., 1996)
11 Cabo Rojo, PR	×				Queens (Jones et al., 1996)
12 Cabo Rojo, PR	×				Queens
13 Cabo Rojo, PR	×				Alate queens

[a]t = trace detected.

Synthesis of **1a–1d**.

2-Hexyl-2-[2-(6-methylpyridyl)-ethyl]-1,3-dioxolane ***(4)***. A solution of 6.0 g (25.8 mmol) of alcohol **2** (Jones et al., 1984) in 20 ml of methylene chloride was added to 13.7 g of pyridinium dichromate in 40 ml of methylene chloride. Fifteen drops of pyridine and six drops of trifluoroacetic acid were added and the solution was stirred overnight. The mixture was diluted with ether and filtered through a florisil column, and the solvent was removed *in vacuo*, providing 4.7 g of 2-methyl-6-(3-oxononyl)pyridine (**3**) as a viscous liquid. IR (neat) 3067, 1713, 1592, 1578, 1156, 1127 cm^{-1}; MS, *m/z* (rel %) 232 (M^+-1, 1), 218 (1), 176 (11), 163 (5), 149 (5), 148 (67), 121 (15), 120 (100), 107 (9). A solution containing 20 ml of ethylene glycol and 5.6 g (24 mmol) of ketone **3** in 100 ml of benzene was acidified by dropwise addition of concentrated HCl and a small crystal of *p*-toluene sulfonic acid. The mixture was refluxed 4hr with a Dean-Stark trap and, after cooling, was neutralized with aqueous $NaHCO_3$. The aqueous layer was extracted with 3 × 40 ml of diethyl ether, the ether layer was dried over K_2CO_3, and the solvent was removed *in vacuo*. The resulting residue, after dilution with a 1:1 hexane–ether solution was filtered through a Florisil column, and the solvent was removed *in vacuo* to give 5.2 g (19 mmol, 78%) of liquid. IR (neat) 3063, 1592, 1579, 1456, 1156, 1136, 1086, 1049 cm^{-1}; MS, *m/z* (rel %) 276 (M^+-1, 1) 192 (95), 157 (100), 148 (7), 120 (18), 107 (8). HR-MS, calcd for $C_{17}H_{27}NO_2$: 277.2042; observed, 277.2047.

*2-Hexyl-2-[2-(6-methylpiperidyl)-ethyl]-1.3-dioxolane (**5a** and **5b**).* A: Sodium-in-Ethanol Reduction. A solution containing 2.0 g (7.2 mmol) of dioxolane **4** in 70 ml of absolute ethanol was stirred and heated to reflux under a drying tube and ca. 15 g of sodium metal was added in small pieces. After 2 hr the mixture was allowed to cool and was quenched by slowly adding water. The aqueous layer was extracted with 3 × 25 ml of ether. The ether layer was washed with brine and dried over K_2CO_3 and the solvent was removed *in vacuo*, producing 1.9 g (6.7 mmol, 93%) of a liquid. GC-MS analysis of the residue showed the presence of two components in a 5:2 ratio with identical mass spectra. MS, *m/z* (rel %) 282 (M^+-1, 1), 268 (1), 198 (20), 157 (17), 98 (100). The GC-FTIR spectrum of the first eluting isomer (**5a**) had bands at 2803 and 2716 cm^{-1} not present in the second isomer. HR-MS, calcd for $C_{17}H_{33}NO_2$: 283.2511; observed, 283.2520; calcd for $C_{17}H_{32}NO_2$: 282.2433; observed, 282.2448.

B: Catalytic Hydrogenation. A solution of 1.018 g of dioxolane **4** and 0.365 g of 5% Rh-on-alumina catalyst in 50 ml of ethyl acetate was hydrogenated at 3 atm for 4 hr. After filtration, the solvent was removed *in vacuo*. GC-MS analysis of the residue showed the presence of one component with a mass spectrum and retention time identical to that of **5a**.

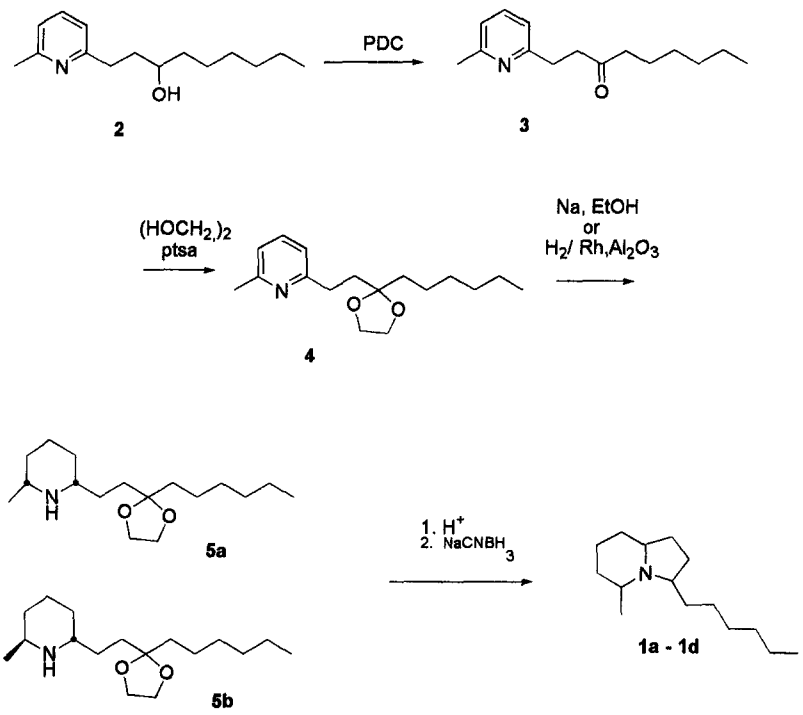
*3-Hexyl-5-methylindolizidine (**1a**, **1b**, **1c**,* and *1d).* A solution containing 1.1 g of the mixture of **5a** and **5b**, 35 ml of THF, 4 ml of water, and 4 ml of concentrated HCl was stirred for 3 hr. The solution was made basic with aqueous NaOH, and the aqueous layer was extracted with 3 × 25 ml of ether. The solvent was removed from the combined ether extracts and the residue was treated with $NaCNBH_3$ as previously described (Jones et al., 1984). The solution was acidified with dilute hydrochloric acid and made basic again with aqueous NaOH. The usual work-up provided 0.7 g (3 mmol, 77%) of a colorless liquid. GC-MS analysis showed four eluting peaks (**1a–1d**) in a 3:2:2:1 ratio with identical mass spectra. MS, *m/z* (rel %) 223 (M^+, 1) 208 (6), 139 (10), 138 (100), 41 (14). HR-MS, calcd for $C_{15}H_{29}N$: 223.2300; observed for first eluting peak, 223.2286; observed for second eluting peak, 223.2297; observed for third eluting peak, 223.2296; observed for fourth eluting peak, 223.2274. A sample of **5a**, from the hydrogenation of **4**, was treated in a similar fashion to provide **1a** and **1c** in 2:1 ratio.

RESULTS AND DISCUSSION

Preliminary GC-MS examination of the extracts of the *Solenopsis* (*Diplorhoptrum*) species in collections 1–8 (Table 1) revealed the presence of 3-hexyl-5-methyl indolizidine (**1**) from its mass spectrum [*m/z* 223 (M^+, 1), 222(1), 139(8), 138(100)]; however, the FTIR spectra of the indolizidines in these collections clearly indicated that they were not the all-*cis* 5*Z*,9*Z* diastereomer

(**1a**) that had been previously described from ants in this genus (Jones et al., 1984, 1996). In previous work the FTIR spectrum showed a broad range of Bohlmann bands, decreasing in intensity from 2800 to 2500 cm^{-1}. In collections 1–3, a single absorption at 2793 cm^{-1} was observed while in collections 4–8 no Bohlmann bands were observed for the hexylmethylindolizidine.

In order to establish the stereochemistry of the indolizidines in these collections, a nonselective synthesis of the four possible isomers was carried out (Scheme 1). The pyridine alcohol (**2**) was successfully oxidized to the ketone (**3**) with pyridinium dichromate. Following ketalization, the pyridine ring was reduced either with sodium-in-ethanol or by hydrogenation over a rhodium catalyst. The former gave a 5:2 mixture of the *cis* and *trans* piperidines **5a** and **5b**, while the latter provided only the *cis* piperidine **5a** (MacConnell et al., 1971). These assignments were confirmed by the FTIR spectra where the spectrum of the *cis*-**5a** showed Bohlmann bands at 2803 and 2716 cm^{-1} that were not present in the spectrum of *trans*-**5b** (Garraffo et al., 1994). The 3-hexyl-5-



SCHEME. 1. Synthesis of the isomeric 3-hexyl-5-methylindolizidines **1a–1d**.

methylindolizidines **1** were formed by reductive amination following removal of the ketal protecting group. Thus, the mixture of **5a** and **5b** provided **1a–1d** in a 3:2:2:1 ratio, while reductive amination of pure **5a** gave only **1a** and **1c**.

Although the isomeric indolizidines **1a–1d** have nearly identical mass spectra, these syntheses along with the FTIR spectra of the four diastereomers (Figure 1) permitted the assignment of stereochemistry for each isomer (Figure 2). In previous studies of 3,5-disubstituted indolizidines, Bohlmann band patterns have been used to assign stereochemistry (Sonnet and Oliver, 1975; Garraffo et al., 1993). The first eluting isomer had been previously prepared stereospecifically (Jones et al., 1984), and its FTIR spectrum matched that of an authentic sample of (5*Z*,9*Z*)-**1a**. The third eluting isomer must be (5*E*,9*E*)-**1c** since it is also formed in the reductive amination of pure *cis*-**5a**.

The second and fourth eluting isomers are those with a *trans*-substituted six-membered ring. In the former, (5*E*,9*Z*)-**1b**, the presence of strong Bohlmann bands indicates the presence of *trans*-antiparallel C–H bonds, and this isomer has been shown to have an axial methyl group configuration (Sonnet et al., 1979; Jones et al., 1984). The last eluting isomer, (5*Z*,9*E*)-**1d**, shows no Bohlmann bands in its FTIR spectrum as a consequence of adapting a *cis*-fused ring system (Figure 2) to relieve the steric crowding that would result from the 1,3-diaxial configuration of the hexyl and methyl groups in a *trans*-fused indolizidine (Sonnet et al., 1979).

The (5*E*,9*E*)-**1c** and (5*Z*,9*E*)-**1d** indolizidines found in collections 1–8 had FTIR spectra and GC retention times that matched those of the synthetic isomers. Their stereochemistry contrasts with the (5*Z*,9*Z*)-**1a** found in collections 9–13, including previous investigations (Table 1) and with the 5*Z*,9*Z* 3-ethyl and 3-butyl indolizidine analogs found in *Solenopsis conjurata* and *Monomorium pharaonis* (Jones et al., 1984; Ritter and Persoons, 1975). Additionally, collections 3 and 5 contained more of the monocyclic homolog, *cis*-2-methyl-6-nonylpiperidine, than indolizidine **1c** or **1d**. The stereochemistry of this piperidine was established by direct comparison with an authentic sample.

The 5*Z*,9*Z* isomer **1a** had previously been found as a caste-specific compound in queens of a *Solenopsis* (*Diplorhoptrum*) species (Jones et al., 1984, 1996). A reinvestigation of a collection from Cabo Rojo, Puerto Rico, has confirmed this and demonstrated its presence in queens and alate queens from the same nest (Table 1). Within a group such as *Diplorhoptrum*, superficially similar species may produce different venom alkaloids or alkaloids in varying combinations. Thus it was shown that the queens of two similar species (collections 10 and 11) both produce indolizidine **1a**. However, their respective workers were sufficiently different chemically that they clearly belong to different taxa despite their morphological similarities: workers of 10 produce an unsaturated piperidine while those of 11 produce two indolizidine 223AB

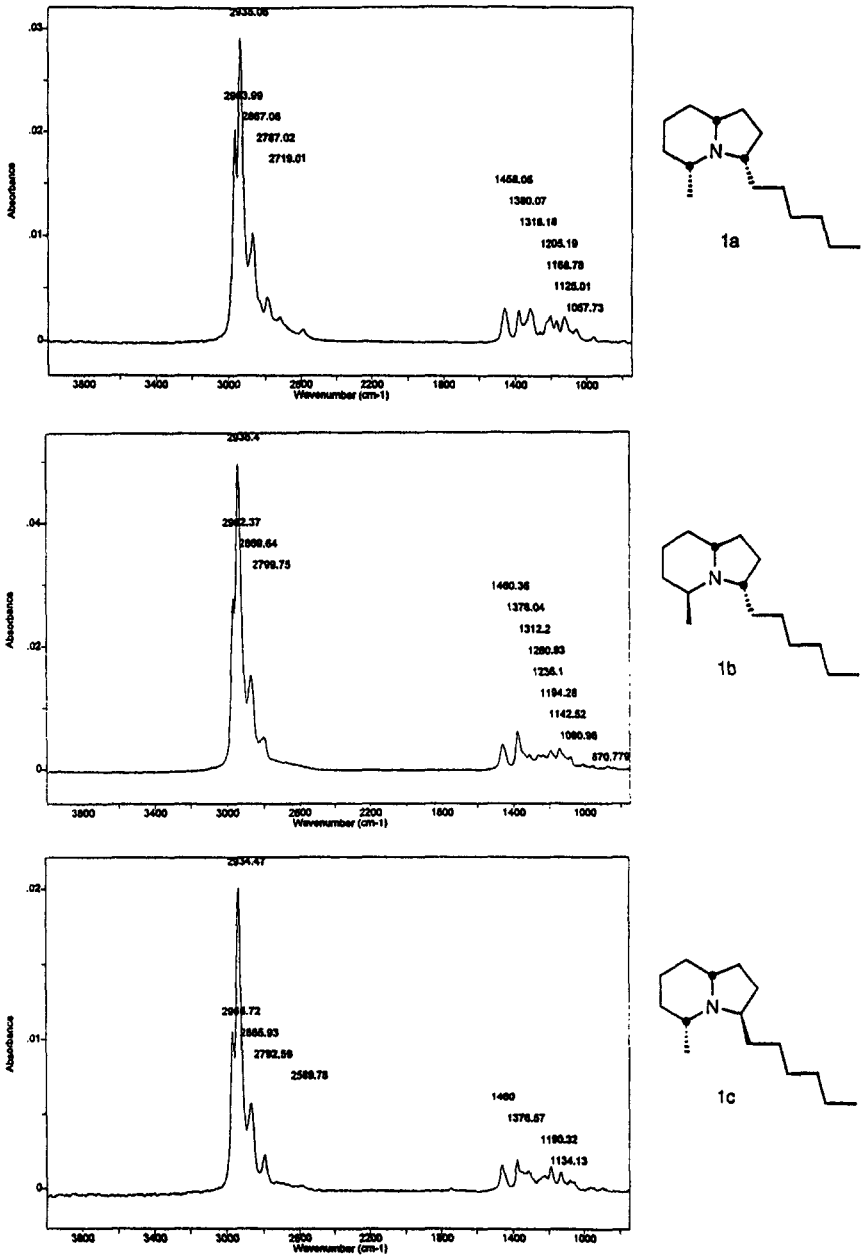


FIG. 1. Vapor-phase FTIR spectra of the indolizidine isomers **1a–1d**.

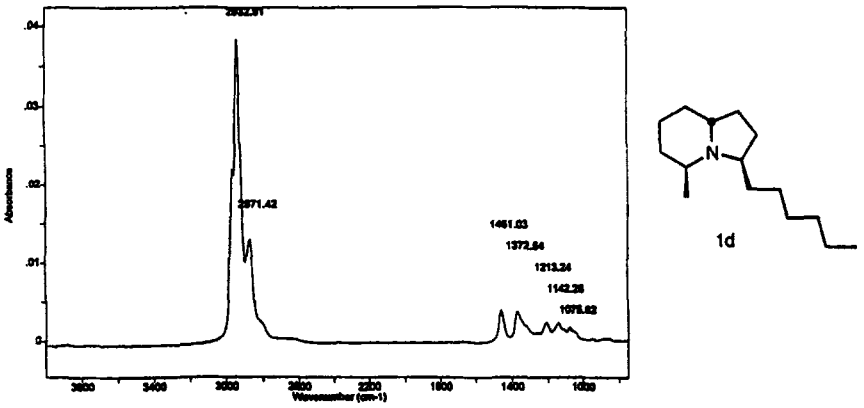


FIG. 1. Continued.

diastereomers (Jones et al., 1996). These *Solenopsis* (*Diplorhoptrum*) containing indolizidine **1a** are clearly different species and castes from those containing indolizidines **1c** or **1d**.

These results showing the occurrence of three of the four diastereomers of 3-hexyl-5-methylindolizidine (**1**) in *Solenopsis* (*Diplorhoptrum*) species naturally raise the question of whether venom alkaloid stereochemistry can play a

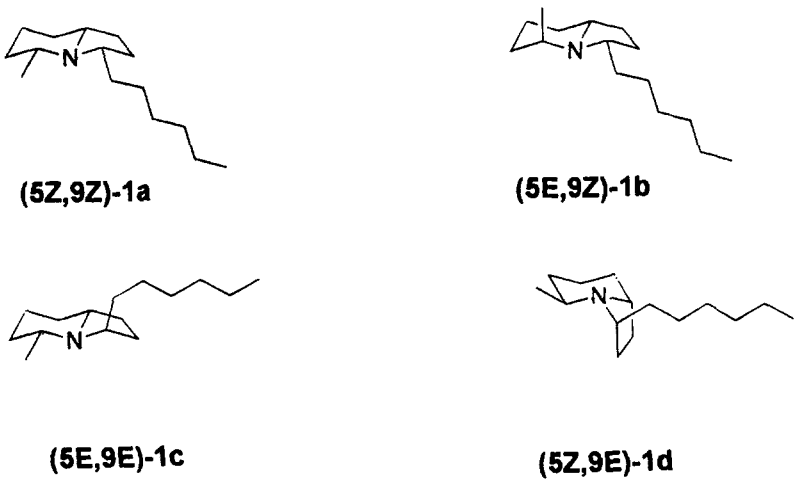


FIG. 2. Four possible diastereomers of 3-hexyl-5-methylindolizidine **1**.

significant role in the taxonomic characterization of these ants. It has been shown that the venoms of *Solenopsis* (*Solenopsis*) species (fire ants) are characterized by 2-alkyl-6-methylpiperidines, compounds that occur as *cis* and *trans* diastereomers, and particular species produce different mixtures of these compounds (Brand et al., 1972). Even when hybrids between species occur, and their venom compositions reflect both species, the ratios of *cis*/*trans* stereoisomers remain unchanged (Vander Meer and Lofgren, 1988). The *Solenopsis* piperidine alkaloids arise from a polyacetate chain, with the ring stereochemistry being established in the final reduction of a piperideine intermediate (Leclercq et al., 1996). If this step is enzymatically controlled, as is likely given the stereospecificity observed in these and other natural ant venom alkaloids, then the stereochemistry of these compounds should be considered to be a valid taxonomic character.

The specimens from California (Table 1) were described as a variety (*validiuscula*) of *S. molesta* by Emery (1895). However, since the venom of collections 1–3 contains **1c** while collections 4–8 contain **1d**, collections 1–3 are probably not conspecific with collections 4–8 even though both fall within the concept of *S. molesta validiuscula* as explicated by Creighton (Creighton, 1950). Which, if either, of the California forms is actually *validiuscula* is unclear, as is the identity of *S. molesta*; we predict that neither is a form of the eastern species.

In the future, the evidence provided by analysis and identification of venom alkaloids may allow the sorting of samples into putative taxonomic units. With such sorted samples available, it may be possible for a systematist to discern features of external morphology such as would resolve some of the current difficulties with the systematics in this taxonomically challenging complex.

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