10 mmol), 2-methyl-2-ethyl-1,3-dioxolane (40 mL), ethylene glycol (1.6 mL), and few crystals of *p*-toluenesulfonic acid was stirred at room temperature for 3 h. Triethylamine (0.15 mL) was added, followed by benzene (20 mL) and water (20 mL). The organic layer was separated, dried, and concentrated to give **9**, as an oil, in a virtually quantitative yield (2.41 g, 95%): ^{1}H NMR ($CDCl_3$) δ 1.26 (t, 3 H, J = 7 Hz), 3.9 (s, 4 H), 4.2 (q, 2 H, J = 7 Hz); IR (film) 1725, 1650, 1615 cm^{-1}. Anal. Calcd for $C_{13}H_{18}O_5$: C, 61.40; H, 7.14. Found: C, 61.22; H, 7.30.

Registry No. 4. 694-98-4; 5, 74877-19-3; 5 methyl ester, 74877-20-6; 6, 74877-21-7; 6 methyl ester, 51388-62-6; 7, 74877-22-8; 8, 74877-23-9; 9, 74923-22-1; *endo*-5-norbornen-2-ol, 694-97-3; *exo*-5-norbornen-2-ol, 2890-98-4; magnesium monoethyl malonate, 37517-78-5.

(5*Z*,8*E*)-3-Heptyl-5-methylpyrrolizidine from a Thief Ant

Tappey H. Jones* and Murray S. Blum

Department of Entomology, University of Georgia, Athens, Georgia 30602

Henry M. Fales

Laboratory of Chemistry, National Heart, Lung, and Blood Institute, Bethesda, Maryland 20014

Catherine R. Thompson

Department of Entomology, University of Florida, Gainseville, Florida 32611

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Alkyl-substituted piperidines,[1] pyrrolidines,[2] and an indolizidine[3] have been reported as venomous constituents from ant species in the related genera *Monomorium* and *Solenopsis*. In this note, we describe the occurrence, identification, and synthesis of (5*Z*,8*E*)-3-heptyl-5-methylpyrrolizidine (**1**) from the cryptic thief ant *Solenopsis sp.* near *tennesseensis*.[4]

The ants were collected in the Ocala National Forest near Ocala, Florida, and immediately placed in methylene chloride. Analysis of the methylene chloride extracts by GC/MS showed one major component whose mass spectrum showed a molecular ion at m/z 223 and other significant peaks at m/z 208 and 124. These fragments result from the loss of CH_3 and C_7H_{15}, respectively. These losses can occur from carbons adjacent to nitrogen, and, assuming one nitrogen atom, the compound must have two units of unsaturation and a molecular formula of $C_{15}H_{29}N$. Vigorous hydrogenation conditions had no effect on the mass spectrum of the natural product, indicating a bicyclic structure containing seven carbons and one nitrogen. The existence of pyrrolidines in related species[2] suggested that this substance might contain a 3,5-disubstituted pyrrolizidine ring system.

The overall carbon–nitrogen skeleton of 3-heptyl-5-methylpyrrolizidine (**1**) was confirmed by synthesis

Scheme I

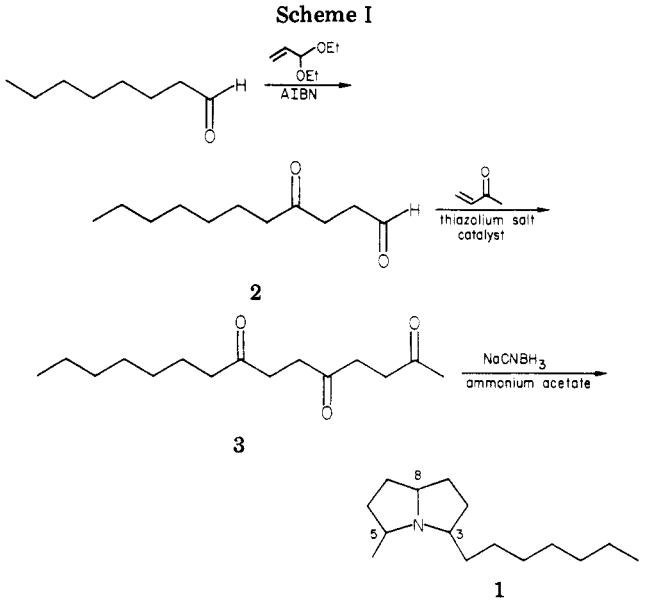
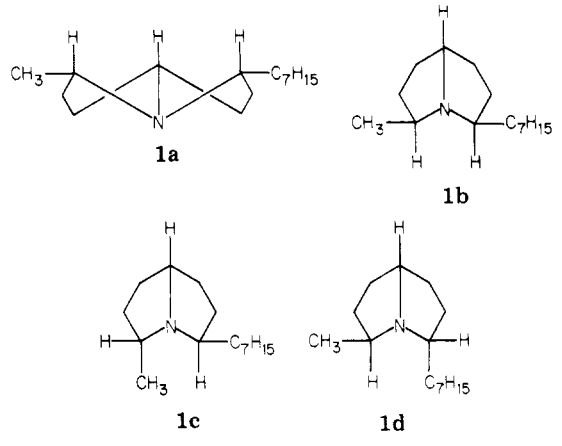


Chart I



(Scheme I). Treatment of a mixture of octanal and acrolein diethyl acetal with azobis(isobutyronitrile) (AIBN) followed by hydrolysis yielded 4–oxoundecanal (**2**), which, when condensed with methyl vinyl ketone in the presence of triethylamine and 5-(2-hydroxyethyl)-4-methyl-3-benzylthiazolium chloride,[5] gave the known 2,5,8-pentadecatrione (**3**).[6] Reductive amination[7] of the triketone **3** with sodium cyanoborohydride and ammonium acetate[2] formed pyrrolizidine **1** in good yield.

Gas chromatographic analysis (SP-1000) of synthetic **1** showed four isomers (**1a–d**) present in a 2:14:2.2:1 ratio. These compounds had essentially identical mass spectra which matched the mass spectrum of the natural material. Pure samples of each isomer were obtained by preparative GLC (SP-1000).

The stereochemistry of the pyrrolizidine ring junction of the isomers of **1** can be determined from their infrared and nuclear magnetic resonance spectra. Only (5*Z*,8*Z*)-3-heptyl-5-methylpyrrolizidine (**1a**)[8] shows strong Bohlmann bands in its infrared spectrum in the region 2600–2800 cm^{-1}, identical with those reported for

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(2) T. H. Jones, J. B. Franko, M. S. Blum, and H. M. Fales, *Tetrahedron Lett.*, 789 (1980).
(3) F. J. Ritter, I. E. M. Rotgens, E. Talman, P. E. J. Verweil, and F. Stein, *Experientia*, **29**, 530 (1973). For recent synthetic work see T. L. Macdonald, *J. Org. Chem.*, **45**, 193 (1980).
(4) This undescribed, hypogeic ant is referred to as *Solenopsis* (*Diplorhoptrum*) Species E in the collection of W. F. Buren, Department of Entomology, University of Florida, Gainesville, FL. Because of the novelty of the venom alkaloid from this ant, the name *Solenopsis* (*D.*) *xenovenenum* has been proposed for this species (C. R. Thompson, Ph.D. Dissertation, Aug 1980, University of Florida).
(5) H. Stetter and H. Kuhlmann, *Tetrahedron Lett.*, 4505 (1974).
(6) H. Stetter, W. Basse, H. Kuhlmann, A. Landsheidt, and W. Schlenker, *Chem. Ber.*, **110**, 1007 (1977).
(7) R. F. Borch and B. C. Ho, *J. Org. Chem*, **42**, 1225 (1977).
(8) This nomenclature system is used to describe the configurational isomers of 3-butyl-5-methylindolizidine from the Pharaoh ant, *Monomorium pharaonis*. P. E. Sonnett, D. A. Netzel, and R. Mendoza, *J. Heterocycl. Chem.*, **16**, 1041 (1979).

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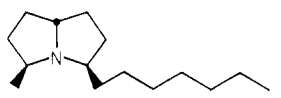
(5Z,8Z)-3,5-dimethylpyrrolizidine,[9] attributed to α-hydrogens oriented trans antiperiplanar to the nitrogen lone pair.[10] In addition, the ^{1}H NMR spectrum of **1a** has no signals further downfield than δ 2.72, while the spectra of isomers **1b–d** display single-proton multiplets at δ 3.66, 3.66, and 3.69, respectively, for their C_8 protons. These values are characteristic for cis-fused pyrrolizidines where the bridgehead proton is cis to the nitrogen lone pair.[11] Finally, in the ^{13}C NMR spectra of alkyl-substituted pyrrolizidines, the C_8 signal appears furthest downfield. In isomer **1a**, this signal is at 72.33 ppm, similar to the chemical shifts reported for C_8 of other trans-fused pyrrolizidines; in isomers **1b–d**, the C_8 signals appear at 66.29, 66.23, and 66.79 ppm, respectively, consistent with chemical shifts reported for C_8 of cis-fused pyrrolizidines.[12] Thus **1a** is the trans-fused (5Z,8Z)-3,5-disubstituted isomer, forced to assume this conformation because of steric hindrance between the heptyl and methyl groups at C_3 and C_5 in the alternative cis conformation. Isomers **1b–d** are free to assume the less strained cis-fused conformations shown in Chart I.

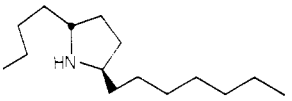
The nuclear magnetic resonance data for isomers **1b–d** also reveal the stereochemistry of their substitution patterns. The ^{1}H NMR spectrum of each of these isomers has three downfield signals for protons on carbons adjacent to nitrogen (Table I). In addition to the C_8-H signal already mentioned, isomer **1b** has the furthest upfield signals for the other two C_α hydrogens, indicating that they are on the opposite side of the ring system from the nitrogen lone pair.[11] In **1c** and **1d**, at least one of the C_α H signals is further downfield, indicative of a hydrogen on the same side of the ring system as the nitrogen lone pair.[11] Thus **1b** is the (5Z,8E)-3-heptyl-5-methylpyrrolizidine. In decoupling experiments, irradiation of the C_5 methyl doublets indicates which signals are attributable to the C_5 α-hydrogens. Since the C_5-H of **1c** is further downfield than the C_5-H of **1d**, it should be on the same side of the ring system as the nitrogen lone pair,[11] which leads to the assignment of (5E,8E)-3-heptyl-5-methylpyrrolizidine to isomer **1c** and of (5E,8Z)-3-heptyl-5-methylpyrrolizidine to isomer **1d**, as shown in Chart I.

Examination of the ^{13}C NMR spectra of isomers **1a–d** corroborates these assignments. In each, the terminal methyl of the *n*-heptyl group appears at approximately 14.4 ppm, and there are two other signals above 25 ppm. One of these is likely to be the penultimate methylene of the *n*-heptyl group, and the other is the C_5 methyl group. In **1a**, **1b**, and **1d**, these two signals are close together at approximately 23 ppm,[13] indicating that the C_5 methyl is deshielded by the nitrogen lone pair. In isomer **1c**, one of these two signals appears at 17.66 ppm, which might be expected from a shielded methyl group on the opposite side of the ring system from the nitrogen lone pair and forced into the cavity between the rings of the cis-fused system.

The naturally occurring pyrrolizidine has a gas chromatographic retention time identical with that of the major synthetic isomer **1b** by direct comparison and co-injection and is (5Z,8E)-3-heptyl-5-methylpyrrolizidine, which, considering each ring as a separate pyrrolidine, is all trans substituted. This is the first report of a 3,5-dialkylpyrrolizidine from a natural source. It is noteworthy that all of the 2,5-dialkylpyrrolidines that have been found in the venoms of the related ant genera *Monomorium* and *Solenopsis* are also trans disubstituted about the ring.[2,14] In addition, the close structural relationship between the ant alkaloid 2-butyl-5-heptylpyrrolidine (**4**)[15,16] and (5Z,8E)-3-heptyl-5-methylpyrrolizidine suggests a common biosynthetic precursor, or less likely, perhaps, **4** is the precursor of **1b**. We assume that, as is the case for the ant-derived pyrrolidines and piperidines, the pyrrolizidine **1b** is a venomous constituent.



1b



4

Experimental Section

All boiling points and melting points are uncorrected. Infrared spectra were obtained from neat liquid films with a Perkin-Elmer 297 grating infrared spectrophotometer. ^{1}H NMR spectra were obtained at 60 MHz, using a Varian T-60 or a JEOL FX-60 spectrometer, and at 100 MHz, using a Varian XL-100 spectrometer. ^{13}C NMR spectra were obtained at 15 MHz, using a JEOL FX-60 spectrometer. Mass spectra were obtained by using a LKB 2091 GC/MS fitted with a column packed with 10% SP-1000 on Supelcoport. Combustion analyses were performed by Atlantic Microlabs, Atlanta, GA.

***Solenopsis sp.* near *tennesseensis* (Species E).**[4] Examination of the methylene chloride extracts of approximately thirty specimens by GC/MS showed one major alkaloid component; mass spectrum, *m/z* (relative intensity) 223 (4), 222 (2), 208 (8), 194 (3), 180 (3), 166 (2), 152 (2), 139 (1), 138 (2), 136 (2), 125 (10), 124 (100), 110 (9), 98 (1), 97 (1), 84 (2), 82 (1), 81 (5), 69 (3), 68 (2), 67 (2), 56 (3), 55 (7), 54 (1), 43 (4), 41 (8). There were trace amounts of higher molecular weight alkaloids which also had a base peak at *m/z* 124, but there was insufficient material to observe the parent ions of these compounds.

Attempted Hydrogenation of the Extract. A portion of the extract was treated with approximately 10 mg of platinum black, and a gentle stream of hydrogen was passed through the mixture for 10 min. Reexamination by GC/MS revealed that the mixture was completely unchanged.

4-Oxoundecanal (2). A solution containing 1 g of 2,2-azobis(2-methylpropionitrile) (AIBN) in 3 mL of freshly distilled octanal was added to a stirred solution containing 4.6 mL (0.03 M) of acrolein diethyl acetal in 15.6 mL (0.1 M) of freshly distilled octanal. The resulting mixture was heated to 80 °C for 40 h, while additional 0.25-g portions of AIBN were added every 6–8 h. After vacuum distillation, the fraction boiling at 115–135 °C (0.4 mmHg) was stirred with 50 mL of 5% HCl for 1 h. Subsequent extraction with ether, drying of the ether extracts (anhydrous K_2CO_3), and distillation gave 1.7 g of pure keto aldehyde (31% yield): bp 85–95 °C (0.3 mmHg); IR 2822, 2710, 1715 cm^{-1}; ^{1}H NMR (60 MHz) δ 9.77 (1, s, CHO), 2.68 (4, s, $COCH_2CH_2CO$), 2.45 (2, t, J = 7.0 Hz, CH_2CO), 1.3 (10, br s, $(CH_2)_5$), 0.91 (3, br t, CH_3).

Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 71.49; H, 10.92.

2,5,8-Pentadecatrione (3). Triethylamine (1.1 mL, 8 mmol) was added to a solution containing 1.5 g (8 mmol) of keto aldehyde **2**, 0.56 g of methyl vinyl ketone, and 0.2 g (0.8 mmol) of 5-(2-hydroxyethyl)-4-methyl-3-benzylthiazolium chloride. The mixture was refluxed for 12 h under a nitrogen atmosphere, cooled, and filtered through Florisil. The solvents were removed in vacuo, and the residue was recrystallized from ether to give 1.6 g of triketone **3** (79% yield): mp 77 °C (lit.[6] mp 77 °C); ^{1}H NMR (60 MHz) δ 2.62 (4, s, $COCH_2CH_2CO$), 2.40 (2, t, J = 7.0 Hz, CH_2CO),

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(14) T. H. Jones, M. S. Blum, and H. M. Fales, *Tetrahedron Lett.*, 1031 (1979).
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Table I. Selected 100-MHz ^{1}H NMR Chemical Shifts for Individual Cis-Fused Stereoisomers 1b–d

compd	assigned stereochemistry	ppm from Me_4Si C_3-H	C_5-H	C_8-H
1b	(5*Z*,8*E*)-3-heptyl	2.78	2.66	3.66
c	(5*E*,8*E*)-3-heptyl	2.95	3.29	3.66
d	(5*E*,8*Z*)-3-heptyl	3.08	3.02	3.69

2.12 (3, s, $COCH_3$), 1.26 (10, br s, $(CH_2)_5$), 0.93 (3, br t, CH_3). This spectrum matches the data reported in the literature.[6]

3-Heptyl-5-methylpyrrolizidine (1). A solution containing 0.5 g of triketone **3** (2 mmol), 170 mg of ammonium acetate, 60 mg of potassium hydroxide, and 200 mg of sodium cyanoborohydride in 10 mL of methanol was stirred under a nitrogen atmosphere for 12 h. A slight excess of sodium borohydride was then added and the mixture was stirred for 1 h, carefully acidified with 5% HCl, and washed with ether. The aqueous solution was made basic with potassium hydroxide and extracted with ether (3 × 30 mL). The ether extracts were dried (anhydrous K_2CO_3), and the solvent was removed in vacuo to give 0.35 g (80% yield) of pyrrolizidine **1**. GLC analysis (2 m × 2 mm column packed with 10% SP-1000 on Gas Chrom Q) showed four components, **1a**, **1b**, **1c**, and **1d** in the ratio 2:14:2.2:1, which had retention times of 5.5, 7, 12.5, and 16 min, respectively, at an oven temperature of 155 °C (He carrier gas, flow rate 60 mL/min). The four components had almost identical mass spectra: mass spectrum, *m/z* (relative intensity) 223 (4), 222 (2), 208 (8), 194 (2), 180 (2), 166 (1), 152 (2), 139 (1), 138 (1), 136 (1), 125 (11), 124 (100), 110 (10), 98 (2), 97 (1), 84 (2), 82 (2), 81 (6), 69 (4), 68 (3), 67 (2), 56 (2), 55 (5), 54 (2), 43 (3), 41 (6).

Anal. Calcd for $C_{15}H_{29}N$: C, 80.65; H, 13.09; N, 6.27. Found: C, 80.63; H, 13.08; N, 6.25.

The four isomers, eluting in the order **1a**, **1b**, **1c**, and **1d**, were separated by preparative GLC (2 m × 5 mm column packed with 10% SP-1000 on Gas Chrom Q), and IR, ^{1}H NMR, and ^{13}C NMR spectra were obtained for each.

1a: IR 2780, 2700, 2640 (w), 1460, 1385, 1335, 1280, 1200, 1165, 720 cm^{-1}; ^{1}H NMR (60 MHz) δ 2.72 (1, m), 2.31 (2, m), 1.8–1.2 (20, br m), 1.21 (3, d), 0.92 (3, br t); ^{13}C NMR (C_6D_6) δ 72.33, 60.64, 55.58, 38.83, 35.97 (2 C), 32.34, 30.58, 29.93, 26.75 (2 C), 26.49, 23.18, 22.01, 14.41.

1b: IR 2790 (w), 2690 (w), 1460, 1370, 1355, 1180, 1130, 1105, 720 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 3.66 (1, m), 2.78 (1, m), 2.66 (1, m), 1.8 (4, m), 1.6–1.3 (16, m), 1.12 (3, d, *J* = 6.2 Hz), 0.88 (3, br t) (irradiation of the multiplet at δ 2.66 collapsed the doublet at δ 1.12 to a singlet, and irradiation of the doublet at δ 1.12 simplified the multiplet at δ 2.66); ^{13}C NMR (C_6D_6) δ 66.29, 64.99, 61.81, 37.46, 35.13, 32.59, 32.40 (2 C), 32.20, 30.45, 29.93, 27.33, 23.11, 22.59, 14.35.

1c: IR 1460, 1380, 1365, 1160, 1130, 720 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 3.66 (1, m), 3.29 (1, m), 2.95 (1, m), 2.2–1.8 (4, m), 1.6–1.3 (16, m), 1.16 (3, d, *J* = 6.5 Hz), 0.88 (3, br t) (irradiation of the signal at δ 3.29 collapsed the doublet at δ 1.16 to a singlet); ^{13}C NMR (C_6D_6) δ 66.23, 57.59, 57.07, 38.83, 34.41, 34.15, 33.44, 32.34, 31.17, 30.58, 29.93, 27.33, 23.11, 17.66, 14.35.

1d: IR 1460, 1370, 1175, 1148, 1130, 1098, 720 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 3.69 (1, m), 3.08 (1, m), 3.02 (1, m), 2.1–1.8 (4, m), 1.6–1.3 (16, m), 1.14 (3, d, *J* = 6.5 Hz), 0.90 (3, br t) (irradiation of the signal at δ 3.02 collapsed the doublet at δ 1.14 to a singlet); ^{13}C NMR (C_6D_6) δ 66.29, 63.63, 52.85, 38.76, 35.45, 32.27 (2 C), 31.94, 31.68, 30.32, 29.80, 28.83, 23.96, 23.12, 14.35.

Isomer **1b** had identical GLC retention times by direct comparison and co-injection under isothermal conditions with the major component of the methylene chloride extract of *S. sp.* near *tennesseensis* (species E).

Acknowledgment. We thank W. F. Buren for species identification and Dr. R. J. Highet and Mr. E. A. Sokoloski for obtaining the nuclear magnetic resonance spectra of the isomers.

Registry No. **1a**, 74986-28-0; **1b**, 75023-37-9; **1c**, 75023-38-0; **1d**, 75023-39-1; **2**, 71525-51-4; **3**, 62619-73-2; acrolein diethyl acetal, 3054-95-3; octanal, 124-13-0; methyl vinyl ketone, 78-94-4.

^{2}H NMR Analysis of the Diastereomeric 2-Adamantanols-*4-d*

J. Eric Nordlander* and Jerome E. Haky

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

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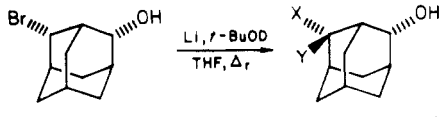
The conformational inflexibility, symmetry, and relative stability of the adamantane nucleus has made various derivatives attractive substrates for structural and mechanistic studies.[1] Stereochemical analysis of reactions of 2-substituted adamantanes, however, requires the presence of a second substituent for configurational reference. Whiting has incorporated a 5-methyl label for this purpose[2] and le Noble a 5-phenyl group.[3] Schleyer has made use of an intrinsic 1-methyl substituent.[4]

We have undertaken a group of mechanistic investigations based on ^{2}H NMR analysis of the diastereomeric 2-adamantanols-*4-d*. The isotopic label avoids the risk of steric effects likely with larger substituents[2,3] and provides for the study of related acid addition reactions. We describe here our synthetic entry into this system and establishment of a secure configurational analysis.

Cuddy, Grant, and McKervey[5] have ascertained the bromohydrin from protoadamantene and *N*-bromosuccinimide in aqueous dimethyl sulfoxide to be 4(a)-bromo-2(a)-adamantanol (**1**). We debrominated[6] purified **1** with lithium and *tert*-butyl alcohol-*d*[7] in boiling tetrahydrofuran to produce 2-adamantanol whose 15.4-MHz ^{2}H NMR spectrum in the presence of $Pr(fod)_3$ indicated the composition 83% 2(a)-adamantanol-*4(a)-d* (**2**) and 17% of the 4(e)-*d* isomer **3**. The induced (upfield) shift for the major product was markedly greater than that for the minor component, allowing epimeric assignments to be made on the basis of published pseudo-contact analyses of Eu-dispersed proton spectra of 2-adamantanol[8] and the



1 2, X = D; Y = H (83%) 3, X = H; Y = D (17%)

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