

Primary Tetradecenyl Amines from the Ant *Monomorium floricola*

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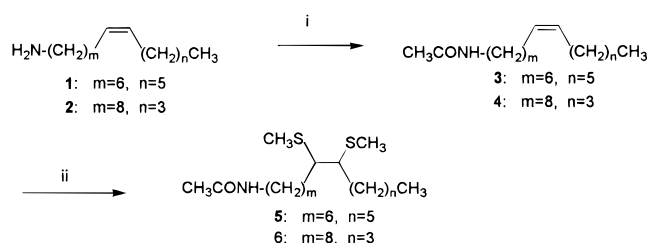
In contrast to other ants in the genus *Monomorium* that produce cyclic amines, extracts of *Monomorium floricola* contain (Z)-7-tetradecenylamine (**1**) and (Z)-9-tetradecenylamine (**2**). The structures of these compounds were established from their spectral data and by comparison with synthetic **2**.

In an earlier report, the venom alkaloids from a number of North American and Caribbean *Monomorium* species were described.¹ The venoms of most of these ants contain 19-carbon 2,5-dialkylpyrrolidines and the corresponding 1-pyrrolines having both a six-carbon and a nine-carbon side chain. This contrasts with other *Monomorium* species, where the venom alkaloids may be mixtures of various odd-numbered carbon compounds.^{2–5} At that time, the absence of the 19-carbon pyrrolidines in two collections of *Monomorium floricola* from Puerto Rico was also reported. A third collection had a trace of one of the pyrrolidine alkaloids, but this may have been the result of some contamination from another collection. In this report we describe the reinvestigation of the extracts of *M. floricola*.

A member of the Old World *minutum* group, *Monomorium floricola* Jerdon (Formicidae) is only distantly related to the native New World species reported on earlier.¹ This is a common tropicopolitan "tramp" species, apparently originally native to tropical Asia.⁶ The large multiple-queened colonies are located in preexisting cavities in trees and shrubs, such as hollow stems, termite galleries, and old beetle borings.

The CH₂Cl₂ extracts from the queens and workers of four collections of *M. floricola* contained two major volatile components, **1** and **2**. The EIMS of both compounds showed molecular ions at *m/z* 211, which were confirmed by their CIMS. HRMS established a formula of C₁₄H₂₉N for the *m/z* 211 ion in both **1** and **2**. These compounds must then have one ring or double bond. Additionally, two exchangeable hydrogens were detected in each compound in deuterium exchange experiments. Absorptions at 3012 and 1623 cm^{–1} in the GC/FTIR spectra of these compounds revealed the presence of an internal Z carbon-carbon double bond, and the *E* geometry could also be ruled out by the

Scheme 1^a



^a Key: (i) Ac₂O; (ii) DMDS, I₂.

absence of a sharp band at 968–964 cm^{–1}. Acetylation of the mixture produced a pair of unsaturated acetamides, **3** and **4** (Scheme 1), evident from their parent ions at *m/z* 253 and their characteristic molecular fragments at *m/z* 60 and 73, establishing the primary amine function in **1** and **2**.

The positions of the double bonds in **1** and **2** were suggested by their EIMS. Allylic cleavage on the amine side of the double bond produced the significant (60%) ion at *m/z* 86 in the EIMS of amine **1**, and the presence in the EIMS of amine **2** of an ion at *m/z* 114 (15%), not present in that of amine **1**, suggested double bonds at C-7 and C-9 in **1** and **2**, respectively. These assignments were confirmed from the mass spectra of the dimethyldisulfide adducts **5** and **6** of the acetamides **3** and **4**.⁷ In the mass spectrum of **5**, cleavage between two vicinal thiomethyl groups gave an intense ion at *m/z* 202 (99%) corresponding to [M – CH₃(CH₂)₅CHSCH₃]⁺, accompanied by an ion at *m/z* 145 [CH₃(CH₂)₅CHSCH₃]⁺, while the mass spectrum of **6** showed analogous ions at *m/z* 230 (100%) and 117 for the loss of [CH₃(CH₂)₃CHSCH₃]⁺.

(Z)-7-Tetradecenylamine (**1**) and (Z)-9-tetradecenylamine (**2**) have not been reported as natural products, although **2** has been prepared as a synthetic intermediate.^{8,9} The gas chromatographic retention times, EIMS, and GC/FTIR of natural **2** were identical to those of an authentic sample of **2** prepared from myristoleic acid by LiAlH₄ reduction of the amide.

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Acyclic amines have been reported in ants of certain *Mesoponera* species, but in those cases, they were all secondary amines or their *N*-acyl derivatives, the carbon chains were odd-numbered, and many contained branched alkyl groups as isoamyl.¹⁰

Experimental Section

General Experimental Procedures. FTIR spectra were obtained using a Hewlett-Packard Model 5965B detector interfaces with a Hewlett-Packard 5890 gas chromatograph equipped with an HP-5 column. MS were obtained in the EI mode using a Shimadzu QP-5000 GC/MS equipped with a Rtx-5, 30-m $\times$ 0.25-mm i.d. column, or a Finnigan ion trap Model 800 equipped with a 30-m $\times$ 0.32-mm i.d. HP-5 column. The latter instrument with NH₃ or ND₃ reagent gases was used for CIMS and for the determination of exchangeable hydrogens, respectively.

Ants. Four collections of *Monomorium floricola* from Guaynabo, Puerto Rico, were made in July, October, and November 1995. The ants were placed in vials containing CH₂Cl₂ immediately upon collection. Voucher specimens of all collections were deposited in the collection of the Los Angeles County Museum of Natural History, Los Angeles, California. Each collection represented a different colony, and workers and queens of each colony were collected separately. There were 50–100 workers and 5–20 queens in each collection.

Analytical Data for 1 and 2. Initial GC/MS analysis of the *M. floricola* extracts revealed the presence of compounds **1** and **2** in a 3:2 ratio, respectively, comprising nearly 95% of the detectable components in the extracts of both workers and queens.

Compound 1: MS *m/z* 211 (3 [M]⁺), 168 (5), 140 (9), 126 (20), 112 (15), 96 (14), 95 (13), 86 (54), 82 (20), 81 (30), 73 (9), 57 (12), 56 (100), 55 (53), 54 (22), 53 (11), 45 (25), 44 (14), 43 (47), 41 (98).

Compound 2: MS *m/z* 211 (5 [M]⁺), 168 (10), 154 (30), 140 (5), 114 (14), 100 (7), 97 (6), 96 (9), 95 (14), 86 (11), 82 (13), 81 (21), 72 (9), 69 (20), 67 (27), 56 (38), 55 (78), 54 (21), 44 (46), 43 (31), 41 (100).

For both compounds: CIMS (NH₃), *m/z* 212 and CI (ND₃), *m/z* 215; HRMS *m/z*, calcd for C₁₄H₂₉N, 211.2300; obsvd, 211.2310 (collection A), 211.2305 (collection B), error, +4.7, +2.2 ppm, respectively); the GC/FTIR spectra of these compounds showed significant absorptions at 3012, 2933, 2865, 1623, 1460, 1381, 1355, 1313, 1074, and 771 cm⁻¹.

The solvent was removed from a portion of the extract, and the residue was warmed (80 °C) with an excess of Ac₂O for 20 min. After the solvent was removed *in vacuo*, GC/MS analysis revealed the presence of two isomeric acetamides, **3** and **4**.

Compound 3: MS *m/z* 253 (5 [M]⁺), 168 (4), 154 (4), 140 (4), 110 (3), 109 (4), 100 (18), 96 (15), 95 (14), 87 (21), 86 (36), 82 (14), 81 (22), 73 (62), 72 (51), 69 (15), 68 (12), 67 (27), 60 (100), 56 (25), 55 (44), 44 (38), 43 (92), 41 (79).

Compound 4: MS *m/z* 253 (6 [M]⁺), 182 (4), 168 (4), 154 (5), 140 (4), 126 (3), 114 (16), 109 (8), 100 (22), 96 (15), 95 (16), 87 (23), 86 (38), 82 (12), 81 (18), 73 (80),

72 (59), 69 (17), 68 (10), 67 (25), 60 (100), 56 (21), 55 (73), 54 (17), 44 (40), 43 (96), and 41 (93); HRMS *m/z*, calcd for C₁₄H₃₁NO, 253.2406; obsvd, 253.2409 (error, +1.2 ppm). This mixture of amides was treated with an excess of dimethyldisulfide and a trace of iodine for 18 h. After the usual workshop, GC/MS analysis revealed the presence of two dimethyldisulfide adducts, **5** and **6**.

Compound 5: MS *m/z* 347 (3 [M]⁺), 300 (5), 252 (6), 203 (12), 202 (99), 160 (66), 156 (32), 154 (31), 145 (28), 112 (22), 109 (5), 97 (22), 95 (44), 87 (16), 81 (19), 79 (10), 73 (14), 72 (33), 69 (21), 67 (33), 61 (83), 60 (40), 56 (15), 55 (100), 45 (18), 43 (72), 41 (45).

Compound 6: MS *m/z* 347 (3 [M]⁺), 300 (2), 299 (6), 252 (7), 232 (8), 231 (14), 230 (100), 188 (18), 184 (12), 182 (11), 140 (10), 123 (15), 117 (27), 95 (13), 87 (17), 81 (33), 73 (14), 72 (32), 69 (52), 67 (34), 61 (90), 60 (46), 56 (10), 55 (53), 45 (13), 44 (15), 43 (59), 41 (5).

(Z)-9-Tetradecenylamine (2). A solution of myristoleic acid (40 mg) (0.18 mmol) (Aldrich Chemical Co.) and oxalyl chloride (50 mg) in 2 mL of C₆H₆ was stirred for 30 min at 60 °C. The solvent was removed *in vacuo*, and the residue was taken up in Et₂O (5 mL) and stirred for 4 h with conc NH₄OH (1 mL). The Et₂O was dried and the solvent removed to provide 35 mg of a solid: MS *m/z* 225 (2 [M]⁺), 208 (1), 182 (3), 168 (3), 154 (5), 140 (6), 126 (10), 112 (10), 98 (15), 86 (14), 72 (65), 60 (22), 59 (100), 55 (30), 44 (35), 43 (30), 41 (50); HRMS *m/z* calcd for C₁₄H₂₇NO, 225.2093, obsvd 225.2101 (error, +3.8 ppm). A solution of 30 mg of this amide in 2 mL of Et₂O was stirred with an excess of LiAlH₄ overnight. The usual basic workup (H₂O, 10% NaOH, H₂O) provided an oil whose gas chromatographic retention time, mass spectrum, and GC/FTIR spectrum were identical to those of **2**; HRMS *m/z* calcd for C₁₄H₂₉N, 211.2300; obsvd 211.2294 (error, -2.7 ppm).

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References and Notes

- Jones, T. H.; Blum, M. S.; Howard, R. W.; McDaniel, C. A.; Fales, H. M.; DuBois, M. D.; Torres, J. *J. Chem. Ecol.* **1982**, *8*, 285–300.
- Jones, T. H.; Blum, M. S.; Fales, H. M. *Tetrahedron* **1982**, *38*, 1949–1958.
- Jones, T. H.; Stahly, S. M.; Don, A. W.; Blum, M. S. *J. Chem. Ecol.* **1988**, *14*, 2197–2212.
- Jones, T. H.; Laddago, A.; Don, A. W.; Blum, M. S. *J. Nat. Prod.* **1990**, *53*, 375–381.
- Jones, T. H.; Blum, M. S.; Robertson, H. G. *J. Nat. Prod.* **1990**, *53*, 429–435.
- Wilson, E. O.; Taylor, R. W. *Pac. Inst. Monogr.* **1967**, *14*, 1–109.
- Buser, H.-R.; Arn, H.; Guerin, P.; Rawsher, S. *Anal. Chem.* **1983**, *55*, 818–822.
- Janusz, J. M.; Buckwalter, B. L.; Young, P. A.; LaHann, T. R.; Farmer, R. W.; Kasting, G. B.; Loomans, M. E.; Kerckaert, G. A.; Maddin, C. S.; Berman, E. F.; Bohne, R. L.; Cupps, T. L.; Milstein, J. R. *J. Med. Chem.* **1993**, *36*, 2595–2604.
- Kabara, J. J.; Conley, A. J.; Truant, J. P. *Antimicrob. Agents Chemother.* **1972**, *2*, 492–498.
- Fales, H. M.; Blum, M. S.; Bain, Z.; Jones, T. H.; Don, A. W. *J. Chem. Ecol.* **1984**, *10*, 651–665.

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