# NOVEL PYRROLIDINES IN THE VENOM OF THE ANT MONOMORIUM INDICUM

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ABSTRACT.—New 2,5-dialkylpyrrolidines found in the venom of *Monomorium indicum* include *trans*-2-butyl-5-(4-pentenyl)pyrrolidine [1], *trans*-2-butyl-5-(6-heptenyl)pyrrolidine [4], *trans*-5-(5-hexenyl)-2-(4-pentenyl)pyrrolidine [6], *trans*-5-(6-heptenyl)-2-(5-hexenyl)pyrrolidine [8], and *trans*-5-heptyl-2-hexylpyrrolidine [16], whose structures were confirmed by synthesis. The concomitance of five previously reported *trans*-2,5-dialkyl-pyrrolidines along with small amounts of the cis isomers and N-methyl analogues makes the venom of M. *indicum* the most qualitatively diverse blend of alkaloids reported from an ant to date. The toxicities to termites of four of these alkaloids were determined.

Characteristic components of the alkaloidal venoms of ants in the genus *Monomorium* are 2,5-dialkylpyrrolidines, which have also been detected in some species of *Solenopsis* (*Diplorhoptrum*) (1). Common structural features of the natural pyrrolidines are their odd-numbered carbon skeletons and the predominance of the trans configuration of the ring substituents. These characteristics are easily elucidated by ms in the first case and by gc comparison with synthetic cis/trans mixtures in the second (2,3). Terminal double bonds on the alkyl side chains are a third feature that occurs frequently in pyrrolidines from *Monomorium* species. The position of these olefins has traditionally been assigned by derivitization and gc comparison with synthetic material (4,5).

In the present paper we report on the elucidation of the venom alkaloids produced by workers of *Monomorium indicum* Forel (Formicidae), a large monomorphic species belonging to the *Salomonis* group (6). No analyses of the venoms of any species in this large Afrotropical group have been previously reported. *Salomonis* group members are reported to be scavengers and predators of small arthropods (6).

## RESULTS

Initial examination of the  $CH_2Cl_2$  extracts of whole ant workers or extracts of venom secretion collected in Bangalore, India, provided the chromatogram shown in Figure 1. Because the mass spectra of several of the components indicated the presence of more than one unit of unsaturation, as well as the presence of more than one compound, the mixture was hydrogenated over  $PtO_2$ . This provided a greatly simplified mixture in which three gc peaks accounted for 90% of the alkaloids detected. These three peaks were identified as *trans*-2-butyl-5-pentylpyrrolidine [13], a mixture of *trans*-2-butyl-5-heptylpyrrolidine [2] and *trans*-2-hexyl-5-pentylpyrrolidine [3], and *trans*-5-heptyl-2-hexylpyrrolidine [16] from their mass spectra and comparison with authentic samples.

Because of the complexity of the pyrrolidine mixture in *M. indicum*, assignment of the double bond positions in these compounds did not lend itself to the usual derivitization methods; <sup>1</sup>H- and <sup>13</sup>C-nmr spectra of the crude extracts were obtained and clearly showed the resonances unique to terminal double bonds (4, 10). In the <sup>1</sup>H spectra, these consist of a sharp doublet of doublet of triplets (J = 10, 18, and 6 Hz) at 5.8 ppm for



 $R^1 = n - C_4 H_9$ ,  $R^2 = CH_2 CH_2 CH_2 CH_2 CH_2$ 1  $R^{1} = n - C_{4}H_{9}, R^{2} = n - C_{7}H_{15}$ 2  $R^1 = n - C_6 H_{13}, R^2 = n - C_5 H_{11}$ 3 4  $R^1 = n - C_5 H_{11}$ ,  $R^2 = C H_2 C H_$ 5  $R^1 = CH_2CH_2CH_2CH = CH_2, R^2 = CH_2CH_2CH_2CH_2CH_2CH = CH_2$ 6  $R^1 = CH_2CH_2CH_2CH_2CH = CH_2$ ,  $R^2 = n - C_7H_{15}$ 7 8 9 N-Methyl-1 10 farnesene 11 cis-13 12 cis-1 **13**  $R^{1}=n-C_{4}, H_{9}, R^{2}=n-C_{5}H_{11}$  **14**  $R^{1}=CH_{2}CH_{2}CH=CH_{2}, R^{2}=CH_{2}CH_{2}CH_{2}CH=CH_{2}$  (?) 15 N-Methyl-2 **16**  $R^1 = n - C_6 H_{13}, R^2 = n - C_7 H_{15}$ 

the methine olefinic proton and a pair of broad doublets near 5.0 ppm (J = 10 and 18 Hz) for the olefinic methylene protons. In the <sup>13</sup>C spectrum, the corresponding resonances at 139 ppm and 116.5 ppm for terminal double bonds were also observed. Additionally, the presence of some nonterminal double bonds was indicated by a resonance in the <sup>1</sup>H spectrum at 5.35 ppm with less intensity than the terminal olefinic methine resonance at 5.8 ppm. Although they were very weak, indistinct resonances in the 130 ppm region of the <sup>13</sup>C spectrum were observed. Treatment of a small amount of the mixture with ethereal CH<sub>2</sub>N<sub>2</sub> followed by gc-ms analysis revealed the presence in the whole ant extract of oleic and linoleic acids as their methyl esters in quantities equivalent to those of the two major pyrrolidines 7 and 8. These amounts of unsaturated fatty acids account for the nonterminal olefinic signals observed in the nmr spectra of the crude extract.

The overall carbon-nitrogen skeletons of the 2,5-dialkylpyrrolidines could be assigned from their mass spectra which are characterized by clear  $[M]^+$  and  $[M-1]^+$  ions as well as intense even mass ions resulting from the  $\alpha$ -cleavage of the alkyl side chains (2). With the determination that the side chain unsaturation in the alkaloids was terminal, the structures of all the pyrrolidines in *M. indicum* could be assigned from the gcms data obtained from the crude extract. Comparison with synthetic material was then necessary to assign the stereochemistry of the natural alkaloids.

Samples of pyrrolidines 2, 3, 5, 7, and 13 were available from previous studies (1,10), and direct comparison confirmed their structures. Samples of the novel pyrrolidines 1, 4, 6, and 8 were prepared by reductive amination of the corresponding 1,4-diketones, which were obtained from the appropriate aldehydes and vinyl ketones by means of the Stetter reaction (3,7,10,12). A sample of 16 was obtained by hydrogenation of 7 over PtO<sub>2</sub> in EtOH. The cis and trans pyrrolidine stereoisomers separate on polar gc columns, with the cis isomer eluting first (2,3), so that the stereochemistry of the natural pyrrolidines could be assigned by comparison with the synthetic cis/trans mixtures. In this way, the small peak containing 11 and 12 was shown to contain the cis isomers of 13 and 1, respectively.

In a survey of the venom alkaloids from North American *Monomorium* species, *N*-methyl pyrrolidines were found as minor concomitants (4). In the same way, in *M. indicum*, peaks 9 and 15 can be assigned as *N*-methyl-1 and *N*-methyl-2, respectively, from their characteristic mass spectra and their early elution relative to the correspond-

ing NH compounds (4). It is quite likely that small amounts of the N-methyl analogues of all the major pyrrolidine components are produced by workers of *M. indicum*, as small peaks eluting before the corresponding NH compounds with mass spectra indicative of *N*-methyl-**13**, *N*-methyl-**2**, *N*-methyl-**3**, and *N*-methyl-**16** were detected in the hydrogenation mixture.

The insecticidal activities of pyrrolidines 1, 6, and 8 were roughly comparable, whereas that of 7 was significantly less. The toxicities of the cis/trans mixtures of the two alkaloids, in  $\mu g/g$  termite, were: 1 = 570, 6 = 600, 7 = 1380, and 8 = 400. For comparison the activities of two commercial insecticides, nicotine and Methomyl, were determined to be 500  $\mu g/g$  and 250  $\mu g/g$ , respectively. The toxicities of these dialkyl-pyrrolidines are similar to those of the alkaloids identified in the venom of an Australian species of *Monomorium* (5).

### DISCUSSION

The pyrrolidines found in M. indicum fall into three structural categories having tridecane, pentadecane, or heptadecane carbon skeletons with the more highly unsaturated compounds predominating in each case. The tridecane alkaloids are all butyl-pentylpyrrolidines and the heptadecane alkaloids are all heptyl-hexylpyrrolidines. On the other hand, the pentadecane alkaloids appear as butyl-heptylpyrrolidines and hexyl-pentylpyrrolidines in nearly equal amounts but with the greater degree of unsaturation predominating in the latter. The butyl-heptylpyrrolidines are present only as the saturated and mono-unsaturated compounds, while the hexyl-pentylpyrrolidines appear in the saturated, mono-unsaturated, and di-unsaturated forms, with the last, 6, predominating. The tridecane alkaloids are present mainly as the mono-unsaturated 1 with small amounts of the saturated 13 and presumably the di-unsaturated 14 (from its mass spectrum) present. In the heptadecane class the saturated alkaloid 16 is a minor component and the mono-unsaturated 7 and the di-unsaturated 8 predominate.

While *trans*-2,5-dialkylpyrrolidines are the characteristic alkaloids found in the genus *Monomorium*, this is the first report of the pyrrolidines 1, 4, 6, 8, and 16, of which the first four are major components of the pyrrolidine mixture from *M. indicum*. Pyrrolidines 2 and 3 have been found in *Solenopsis (Diplorboptrum)* species (1). Pyrrolidines 5, 7, and 13 have been reported from *Monomorium pharaonis* (monomorines III, IV, and II, respectively) (8,9), and 2, 7, and 13 have also been found in some New Zealand *Monomorium* species (10).

It is noteworthy that the venom of M. *indicum* contains eight different 2,5-dialkylpyrrolidines as major components. In contrast, an overview of previous studies reveals that *Solenopsis punctaticeps*, a South African thief ant with a venom considerably more diverse than other pyrrolidine-producing ants, has only three pyrrolidines and the corresponding 1-pyrrolines in its venom (1,13). The mixture of 2,5-dialkylpyrrolidines in the venom of M. *indicum* is clearly more complex than any reported from other Myrmicine species that produce these alkaloids.

The toxicities of the *M. indicum* pyrrolidines to termite workers compare favorably to some commercial insecticides and indicate that this blend of venom constituents may be utilized to immobilize arthropod prey. It is not unlikely that the predatory propensity of *M. indicum* and its relatives may be correlated with the utilization of insecticidally active venoms.

## EXPERIMENTAL

CHEMICAL ANALYSES.—Gc analyses were carried out using a Shimadzu GC-9A equipped with a 30 m  $\times$  0.5 mm i.d. open FFAP column (1  $\mu$ m film thickness). The temperature for the analyses was programmed from 60 to 210° at 5°/min, and the carrier gas flow rate was 15 ml/min. On a given day, retention

temperatures were reproducible to 1°. <sup>1</sup>H- and <sup>13</sup>C-nmr spectra were obtained from CDCl<sub>3</sub> solutions using a Varian XL-200 spectrometer. Electron impact mass spectra were obtained using a LKB-9000 gc/ms equipped with a 2 m  $\times$  2 mm i.d. glass column packed with 5% SP-1000 on 100–120 mesh supelcoport. High resolution mass spectra were obtained using a VG 7070F in the ei mode at an ionizing voltage of 70 eV.

ANALYSIS OF M. INDICUM.—Four collections of 50-100 individuals were placed in vials of CH2Cl2. Specimens of these ants have been deposited in the collection of the Los Angeles County Museum of Natural History, Los Angeles, California. A representative gas chromatogram of the concentrated extract is shown in Figure 1; the chromatograms of the extracts from all four collections were nearly identical. The mass spectra and retention temperatures of compounds 1, 6, 7, 8, and 16 were identical with those of synthetic compounds. Peak mixture 2,3 had the following ions in its mass spectrum: m/z (rel. int.) [M]<sup>+</sup> 225 (2), 224 (3), 169 (10), 168 (74), 155 (1), 154 (10), 141 (2), 140 (11), 127 (11), 126 (100), 83 (7), 82 (7), 69 (10), 68 (9), 67 (7), 55 (13), 44 (5), 43 (6), and 41 (11) and had a retention temperature identical with those of authentic samples of 2 and 3. Peak mixture 4,5 had the following ions in its mass spectrum: m/z(rel. int.) [M]<sup>+</sup> 223 (4), 222 (3), 167 (12), 166 (85), 153 (4), 152 (31), 141 (3), 140 (30), 127 (10), 126 (100), 82 (12), 81 (11), 70 (5), 69 (10), 68 (13), 67 (15), 55 (24), 44 (8), 43 (8), and 41 (19) and had a retention temperature identical with those of authentic samples of 4 and 5. The remaining compounds had the following characteristic ions in their mass spectra: 9 m/z 209, 152, 140; 11, 12 m/z 197, 195, 140, 138, 126; 13 m/z 197, 140, 126; 14 m/z 193, 138, 124; 15 m/z 239, 182, 140. The mass spectrum of compound 10 had characteristic ions at m/2 204, 121, 119, 105, and 93, and was identical to that reported for farnesene (11). The <sup>1</sup>H-nmr spectrum of the crude extract had important resonances at  $\delta$  5.8 (d of d of t,



FIGURE 1. Gas chromatogram of the extract of Monomorium indicum (30 m×0.5 mm i.d. open FFAP column/1 μm film thickness; temperature program = 5°/ min). The compounds identified in each peak are indicated.

J = 18, 10, and 6 Hz), 5.0 (br d, J = 18 Hz), and 4.9 (br d, J = 10 Hz) in the  $\delta$  4.5–6.0 ppm region. In addition, there was a broad singlet at  $\delta$  5.35–5.38 ppm. The ratio of this signal to the one at 5.8 ppm was 1:1. The <sup>13</sup>C-nmr spectrum of this sample had characteristic multiplets at 138.5–139 ppm and at 114.5 ppm. In addition, there were weak signals at 128–130 ppm of less than 20% the intensity of the signal at 114.5 ppm. A small sample of the extract was treated with a few drops of ethereal CH<sub>2</sub>N<sub>2</sub>. Analysis by gcms revealed the presence of two additional components eluting after the pattern of peaks shown in Figure 1. The mass spectrum of the first of these had characteristic ions at m/z 296, 265, 264, 222, 180, 87, and 74 and was identical to that reported for methyl oleate. The mass spectrum of the second of these had characteristic ions at m/z 294, 264, 263, 262, 150, 110, 109, 81, 67, and 59 and was identical to that reported for methyl linoleate (11).

A gentle stream of H<sub>2</sub> was bubbled through a mixture containing 10 mg of PtO<sub>2</sub> in 0.25 ml of the *M.* indicum extract for 10 min. Analysis by gc-ms revealed the presence of three peaks in a 1:3:2 ratio constituting 90% of the mixture. The mass spectrum of the first of these had characteristic ions at m/z 197, 196, 140, and 126 and was identical to that of 2-butyl-5-pentylpyrrolidine [**13**]. The mass spectrum of the second of these had characteristic ions at m/z 225, 224, 168, 154, 140, and 126 and was identical to that of a mixture of 2-butyl-5-heptylpyrrolidine [**2**] and 2-hexyl-5-pentylpyrrolidine [**3**]. The mass spectrum of the third peak had characteristic ions at m/z 253, 252, 168, and 154 and was identical to that of 5-heptyl-2-hexylpyrrolidine [**16**]. The trans stereochemistry was confirmed by gc comparison to authentic samples. In addition, small peaks (less than 1%) with the following mass spectra characteristic of *N*-methyl-**13**, a mixture of *N*-methyl-**2** and *N*-methyl-**3**, and *N*-methyl-**16** were detected: m/z [**M**]<sup>+</sup> 211, 210 (1), 154 (100), 140 (90); m/z [**M**]<sup>+</sup> 239, 228 (1), 182 (75), 168 (85), 154 (90), 140 (100); m/z [**M**]<sup>+</sup> 267, 266 (1), 182 (90), 168 (100), respectively.

SYNTHESES.—The 1,4-diketone precursors for pyrrolidines 1, 4, 6, and 8 were prepared on a 5-10 mmol scale by the usual method (3,7,10) from the appropriate vinyl ketone and aldehyde which were obtained by pyridinium chlorochromate oxidation of the corresponding alcohols. The 1,4-diketones were purified by Kugelrohr distillation and had the following spectral data.

*1-Tridecen-6*, 9-*dione.*—From 5-hexenal and 1-hepten-3-one: <sup>1</sup>H nmr  $\delta$  5.73 (1H, d of d of t, J = 10, 18, 6 Hz), 5.0 (1H, br d, J = 18 Hz), 4.95 (1H, br d, J = 10 Hz), 2.64 (4H, s), 2.43 (4H, pair of t, J = 7.5 Hz), 2.02 (2H, m), 1.5–1.7 (4H, m), 1.30 (2H, m), 0.87 (3H, t, J = 7.0 Hz); <sup>13</sup>C nmr  $\delta$  209.65, 209.36, 137.90, 115.11, 42.47, 41.85, 36.01, 35.94, 32.99, 25.87, 22.74, 22.24, 13.77; ms *m*/z (rel. int.) [M]<sup>+</sup> 210 (5), 169 (5), 168 (6), 156 (50), 141 (55), 140 (20), 135 (15), 127 (39), 125 (35), 114 (42), 113 (53), 111 (35), 110 (18), 97 (26), 93 (31), 85 (100), 71 (65), 69 (55), 57 (95), 55 (66), 41 (99).

*1-Pentadecen-8,11-dione.*—From 7-octenal and 1-hepten-3-one: <sup>1</sup>H nmr  $\delta$  5.78 (1H, d of d of t, J = 10, 18, 6 Hz), 5.0 (1H, br d, J = 18 Hz), 4.92 (1H, br d, J = 10 Hz), 2.66 (4H, s), 2.44 (4H, t, J = 7.6 Hz), 2.04 (2H, m), 1.6–1.2 (10H, m), 0.89 (3H, t, J = 7.0 Hz); <sup>13</sup>C nmr  $\delta$  209.71, 209.62, 138.80, 114.30, 42.71, 42.51, 35.95 (2C), 33.51, 28.60, 25.89, 23.59, 22.26, 13.79; ms *m/z* (rel. inr.) [M]<sup>+</sup> 238 (1), 209 (2), 197 (3), 181 (5), 169 (9), 168 (10), 156 (39), 153 (12), 141 (49), 127 (19), 125 (11), 121 (10), 114 (24), 113 (25), 111 (16), 107 (10), 85 (57), 71 (25), 57 (45), 55 (100), 43 (15), 41 (30).

1,14-Pentadecadien-6,9-dione.—From 6-heptenal and 1,7-octadien-3-one: <sup>1</sup>H nmr  $\delta$  5.8 (2H, d of d of r, J = 18, 10, 6 Hz), 5.06 (2H, br d, J = 18 Hz), 4.96 (2H, br d, J = 10 Hz), 2.68 (4H, s), 2.47 (4H, br t), 2.07 (4H, m), 1.78–1.3 (6H, m); <sup>13</sup>C nmr  $\delta$  209.49, 209.41, 138.46, 137.94, 115.18, 114.60, 42.61, 41.91, 36.06, 35.99, 33.47, 33.03, 28.39, 23.24, 22.78; ms m/z (rel. int.) [M]<sup>+</sup> 236 (2), 195 (3), 182 (5), 181 (6), 168 (5), 167 (3), 154 (16), 140 (22), 139 (17), 136 (12), 135 (10), 125 (24), 122 (15), 114 (14), 111 (48), 100 (13), 107 (20), 83 (42), 71 (34), 69 (44), 55 (100), 43 (15), 41 (70).

1,16-Heptadecadien-7,10-dione.—From 7-octenal and 1,8-nonadien-3-one: <sup>1</sup>H nmr  $\delta$  5.8 (2H, d of d of t, J = 18, 10, 6 Hz), 5.0 (2H, t, J = 8 Hz), 4.95 (2H, br d, J = 10 Hz), 2.68 (4H, s), 2.46 (2H, t, J = 8 Hz), 2.47 (2H, t, J = 8 Hz), 4.95 (2H, br d, J = 10 Hz), 2.68 (4H, s), 2.46 (2H, t, J = 8 Hz), 2.47 (2H, t, J = 8 Hz), 4.95 (2H, br d, J = 10 Hz), 2.68 (4H, s), 2.46 (2H, t, J = 8 Hz), 2.47 (2H, t, J = 8 Hz), 2.06 (4H, m), 1.7–1.25 (10H, m); <sup>13</sup>C nmr  $\delta$  209.64, 209.54, 138.83, 138.46, 114.59, 114.32, 42.74, 42.61, 35.97, 33.52, 33.46, 28.61 (2C), 28.37, 23.60, 23.23; ms m/z (rel. int.) [M]<sup>+</sup> 264 (1), 209 (5), 195 (3), 182 (5), 181 (6), 168 (10), 167 (40), 154 (15), 153 (10), 139 (15), 136 (12), 125 (10), 121 (15), 114 (8), 111 (35), 107 (20), 83 (30), 71 (20), 69 (15), 67 (21), 55 (100), 43 (15), 41 (40).

The pyrrolidines 1, 4, 6, and 8 were prepared as cis/trans diastereometic mixtures by reductive amination of the appropriate diketone with sodium cyanoborohydride and  $NH_4OAc$  in the usual manner (12). These pyrrolidines had the following mass spectral data.

2-Butyl-5-(4-pentenyl)pyrrolidine [1].—Ms m/z (rel. int.) [M]<sup>+</sup> 195 (3), 194 (1), 166 (2), 152 (10), 139 (15), 138 (95), 127 (12), 126 (100), 95 (12), 83 (10), 82 (15), 68 (10), 67 (14), 56 (12), 44 (8), 41 (22); hrms m/z [M]<sup>+</sup> 195.1993 (calcd for C<sub>13</sub>H<sub>25</sub>N, 195.1987).

2-Butyl-5-(6-beptenyl)pyrrolidine [4].—Ms m/z (rel. int.) [M]<sup>+</sup> 223 (3), 222 (2), 182 (1), 167 (14), 166 (95), 127 (10), 126 (100), 83 (5), 82 (7), 81 (8), 70 (4), 69 (5), 68 (9), 67 (10), 56 (8), 55 (13), 44 (5), 41 (11); hrms m/z [M]<sup>+</sup> 223.2294 (calcd for C<sub>15</sub>H<sub>29</sub>N, 223.2300).

5-(Hexenyl)-2-(4-pentenyl)pyrrolidine [6].—Ms m/z (rel. int.) [M]<sup>+</sup> 221 (5), 220 (1), 178 (10), 153 (10), 152 (85), 139 (10), 138 (100), 95 (9), 82 (8), 67 (17), 56 (9), 55 (12), 44 (3), 43 (3), 41 (16); hrms m/z [M]<sup>+</sup> 221.2141 (calcd for C<sub>15</sub>H<sub>27</sub>N, 221.2143).

2-(6-Heptenyl)-5-(5-bexenyl)pyrrolidine [8].—Ms m/z (rel. int.) [M]<sup>+</sup> 249 (4), 248 (2), 208 (3), 167 (4), 166 (95), 153 (14), 152 (100), 82 (9), 81 (10), 70 (4), 69 (5), 68 (8), 67 (15), 56 (9), 55 (12), 44 (3), 43 (3), 41 (13); hrms m/z [M]<sup>+</sup> 249.2472 (calcd for  $C_{17}H_{31}N$ , 249.2457).

5-Heptyl-2-bexylpyrrolidine [16].—A slow stream of H<sub>2</sub> was passed through a mixture containing 50 mg of 5-heptyl-2-(5-hexen-1-yl) pyrrolidine [7] and 10 mg of PtO<sub>2</sub> in 0.5 ml of EtOH for 15 min. Analysis by gc-ms revealed the presence of only two isomeric products: ms m/z (rel. int.) [M]<sup>+</sup> 253 (2), 252 (4), 169 (12), 168 (95), 155 (12), 154 (100), 114 (8), 82 (15), 70 (5), 69 (15), 70 (5), 69 (15), 68 (10), 67 (7), 56 (8), 55 (16), 44 (5), 53 (12), 51 (15); hrms m/z [M – H]<sup>+</sup> 252.2689 (calcd for C<sub>17</sub>H<sub>34</sub>N, 252.2691).

TOXICITY DETERMINATIONS.—The insecticidal activities of cis/trans mixtures of 1, 6, 7, and 8 were determined against termite workers of *Reticuletermes alavipes* as previously described (5).

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### LITERATURE CITED

- 1. T.H. Jones, M.S. Blum, and H.M. Fales, Tetrahedron, 38, 1949 (1982).
- 2. D.J. Pedder, H.M. Fales, T. Jaouni, M. Blum, J. MacConnell, and R.M. Crewe, Tetrahedron, 32, 2275 (1976).
- 3. T.H. Jones, M.S. Blum, and H.M. Fales, Tetrahedron Lett., 1031 (1979).
- T.H. Jones, M.S. Blum, R.W. Howard, C.R. McDaniel, H.M. Fales, M.D. DuBois, and J. Torres, J. Chem. Ecol., 8, 285 (1982).
- 5. T.H. Jones, M.S. Blum, A.N. Andersen, H.M. Fales, and P. Escoubas, J. Chem. Ecol., 14, 35 (1988).
- 6. B. Bolton, Bull. Br. Mus. (Nat. Hist.) Entomol., 54, 263 (1987).
- 7. H. Stetter and H. Kuhlmann, Tetrahedron Lett., 4505 (1974).
- F.J. Ritter, I.E.M. Rotgans, E. Verkuil, and C.J. Persoons, in: "Pheromones and Defensive Secretions in Social Insects, A. Symposium of the International Union for the Study of Social Insects." Ed. by Ch. Noirot, P.E. Howse, and G. Le'Masne, Université de Dijon, Dijon, 1975, p. 99.
- 9. F.J. Ritter and C.J. Persoons, Neth. J. Zool., 25, 261 (1975).
- 10. T.H. Jones, S.M. Stahly, A.W. Don, and M.S. Blum, J. Chem. Ecol., 14, 2197 (1988).
- 11. S.R. Heller and G.W.A. Milne, Eds., "EPA/NIH Mass Spectral Data Base," U.S. Department of Commerce, NSRDS-NBS63, Washington, D.C., 1982.
- 12. T.H. Jones, J.B. Franko, M.S. Blum, and H.M. Fales, Tetrabedron Lett., 21, 789 (1980).
- 13. D.J. Pedder, H.M. Fales, T. Jaouni, M. Blum, J. MacConnell, and R.M. Crewe, *Tetrahedron*, **32**, 2275 (1976).

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