1640, 1350, 1171, 730 cm^{-1}; ^{1}H NMR (300 MHz) 0.87 (t, 3 H, J = 6.4 Hz, CH_2CH_3), 1.15–1.44 (m, 14 H, $(CH_2)_7$), 2.03 (m, 2 H, n-$C_8H_{17}CH_2CH{=}CH$), 2.52 (m, 2 H, CH_2CH_2OMs), 2.80 (m, 4 H, 2 $=CCH_2C=$), 2.97 (s, 3 H, SO_3CH_3), 4.21 (t, 2 H, J = 6.4 Hz, CH_2CH_2OMs), 5.36 (m, 5 H) and 5.54 (m, 1 H) (olefinic protons).

(*Z*,*Z*,*Z*)-Bromo-3,6,9-Nonadecatriene (18): EI MS, *m/e* (relative intensity) 342 (2.3) and 340 (2.1) ($M^+ + 1$), 206 (11), 188 (34), 186 (37), 121 (10), 109 (10), 107 (15), 105 (15), 96 (11), 95 (23), 94 (13), 93 (32), 91 (28), 83 (14), 82 (19), 81 (38), 80 (50), 79 (100), 78 (13), 77 (19), 68 (11), 67 (71), 66 (10), 57 (18), 55 (37), 54 (13), 53 (13), 43 (34), 41 (65), 39 (13); CI MS, *m/e* (relative intensity) 343 (41), and 341 (89) ($M^+ + 1$), 342 (24), 340 (18), 339 (43), 262 (20), 261 (100), 257 (13), 245 (11), 243 (20), 241 (10), 231 (15), 229 (28), 227 (16), 219 (18), 217 (34), 215 (39), 213 (13), 207 (11), 206 (21), 203 (49), 202 (10), 201 (61), 199 (10), 193 (22), 191 (18), 189 (57), 188 (46), 187 (56), 186 (42), 179 (30), 177 (10), 175 (30), 173 (26), 165 (20), 163 (23), 161 (10), 151 (25), 149 (39), 139 (10), 137 (41), 136 (11), 135 (84), 125 (19), 123 (48), 122 (10), 121 (74), 119 (10), 111 (47), 109 (72), 107 (30), 105 (10), 97 (64), 95 (80), 93 (30), 91 (10), 85 (17), 83 (59), 81 (56), 80 (13), 79 (28), 71 (22), 69 (20), 67 (37); IR (film) 3010, 1661, 1658, 1650, 1211, 723, 690, 646 cm^{-1}; ^{1}H NMR (300 MHz) 0.86 (t, 3 H, J = 6.7 Hz, CH_2CH_3), 1.18–1.40 (m, 14 H, $(CH_2)_7$), 2.04 (m, 2 H, n-$C_8H_{17}CH_2CH{=}CH$), 2.65 (m, 2 H, $CH{=}CHCH_2CH_2Br$), 2.80 (m, 4 H, 2 $=CCH_2C=$), 3.36 (t, 2 H, J = 7.1 Hz, CH_2CH_2Br), 5.34 (m, 5 H), 5.50 (m, 1 H) (olefinic).

(*Z*,*Z*,*Z*)-1,3,6,9-Nonadecatetraene (3): CI MS, *m/e* (relative intensity) 261 (100, $M^+ + 1$), 260 (50), 259 (54), 219 (26), 217 (15), 206 (20), 205 (11), 179 (13), 177 (12), 165 (11), 163 (21), 161 (16), 151 (12), 149 (43), 147 (18), 137 (13), 136 (11), 135 (87), 133 (23), 125 (11), 123 (28), 122 (10), 121 (100), 119 (35), 111 (27), 109 (51), 108 (10), 107 (94), 106 (17), 105 (19), 97 (47), 95 (63), 94 (18), 93 (89), 92 (19), 91 (32), 85 (31), 83 (53), 81 (94), 80 (32), 79 (61), 71 (37), 69 (23), 67 (76); EI MS, *m/e* (relative intensity) 260 (10, M^+), 206 (13), 133 (13), 107 (10), 106 (31), 105 (26), 95 (14), 94 (24), 93 (63), 92 (46), 91 (77), 83 (11), 82 (13), 81 (26), 80 (87), 79 (100), 78 (32), 77 (34), 71 (11), 68 (10), 67 (55), 66 (19), 65 (12), 57 (27), 55 (39), 54 (12), 53 (12), 43 (41), 41 (71), 39 (18); IR (film) 3016, 1658, 1651, 1642, 1469, 995, 906, 723 cm^{-1}; ^{1}H NMR (300 MHz) 0.87 (t, 3 H, J = 6.7 Hz, CH_3CH_2), 1.21–1.39 (m, 14 H, $(CH_2)_7$), 2.05 (m, 2 H, n-$C_8H_{17}CH_2CH{=}$), 2.84 (m, 2 H) and 2.96 (m, 2 H) (2 $=CCH_2C=$), 5.19 (m, 2 H), 5.38 (m, 5 H), 6.01 (m, 1 H), 6.65 (m, 1 H) (olefinic).

Acknowledgment. The partial support of this research by research grants from the National Science Foundation (INT-8117801), the National Institutes of Health (AI-12020), and the Schering-Plough Corp. is acknowledged with pleasure.

Registry No. 2, 85612-05-1; **3**, 82970-94-3; **4**, 40365-61-5; **5**, 65050-36-4; **7**, 51309-22-9; **7** mesylate, 85612-06-2; **8**, 40924-12-7; **10**, 85612-07-3; **11**, 85612-08-4; **12**, 85612-09-5; **13**, 85612-10-8; **14**, 85565-88-4; **15**, 85612-11-9; **16**, 85612-12-0; **17**, 85612-13-1; **18**, 85612-14-2; $BrCH_2C{\equiv}CH$, 106-96-7.

Notes

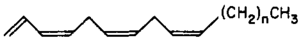
Synthesis of a Sex Attractant Pheromone from a Geometrid Moth, *Operophtera brumata* (the Winter Moth)

Subhash C. Jain,[1] Wendell L. Roelofs, and
Jerrold Meinwald*

Department of Chemistry, Cornell University, Ithaca,
New York 14853, and Department of Entomology,
New York State Agricultural Experimental Station,
Geneva, New York 14456

Received August 20, 1982

We have recently characterized the first sex attractant from a female geometrid moth (*Operophtera brumata*, the winter moth) as (*Z*,*Z*,*Z*)-1,3,6,9-nonadecatetraene (**1A**).[2]

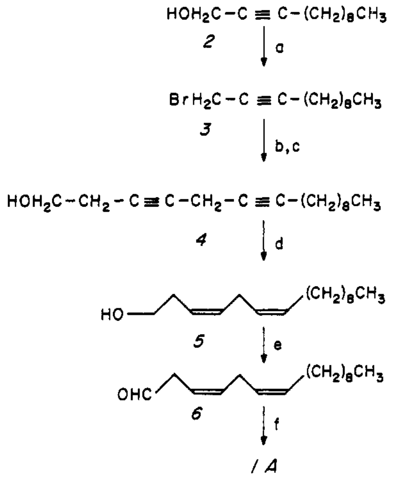


1A: n = 8

1B: n = 10

One key to the determination of the structure of this C-19 tetraene was the striking resemblance of its mass spectrum to that of a homologous C-21 tetraene, (*Z*,*Z*,*Z*)-1,3,6,9-heneicosatetraene (**1B**), which serves as one of several female pheromones produced by the arctiid moth *Utetheisa ornatrix*.[3]

Scheme I. Synthesis of (*Z*,*Z*,*Z*)-1,3,6,9-Nonadecatetraene[a]



[a] (a) PBr_3; (b) $HC{\equiv}CCH_2CH_2OTHP$; (c) CH_3OH,H^+; (d) P-2 Ni, H_2; (e) CrO_3, pyridine; (f) $Ph_3P{=}CHCH{=}CH_2$.

Because females of *O. brumata* yield less than 1 ng of this pheromone per individual, it proved impractical to collect more than a few micrograms of the pure natural product. Consequently, the synthesis of the postulated structure proved crucial not only in confirming the structure and stereochemistry of the pheromone but also in providing material for electroantennogram (EAG) studies and for field bioassays.[2] We here report the details of the synthesis outlined in our preliminary paper.[2,4] The synthetic scheme, summarized in Scheme I, parallels that

---

[1] K. M. College, University of Delhi, Delhi-110007, India.

[2] Roelofs, W. L.; Hill, A. S.; Linn, C. E.; Meinwald, J.; Jain, S. C.; Herbert, H. J.; Smith, R. F. *Science (Washington, D.C.)* **1982**, *217*, 657.

[3] Jain, S. C.; Dussourd, D.; Conner, W. E.; Eisner, T.; Guerrero, A.; Meinwald, J. *J. Org. Chem.*, previous paper in this issue.

[4] An alternative synthesis of **1A** and **1B**, which introduces all three *Z* double bonds simultaneously, is described by: Huang, W.; Pulaski, S. P.; Meinwald, J. *J. Org. Chem*, previous paper in this issue.

0022-3263/83/1948-2274$01.50/0

used for our earlier synthesis of **1B**.[3]

Dodec-2-ynol (**2**) was conveniently prepared by alkylation of propargyl alcohol with *n*-nonyl bromide. Phosphorus tribromide reacted with **2** in pyridine to give the corresponding 1-bromododec-2-yne (**3**). Coupling of **3** with the Grignard derivative of 1-(2-tetrahydropyranyloxy)-but-3-yne gave the expected diynol, **4**, after deprotection. Partial hydrogenation of **4** over P-2 nickel catalyst in ethanol gave the (Z,Z)-dienol **5**. Oxidation of **5** with chromium trioxide–pyridine complex yielded the labile aldehyde **6**, which was subjected to a Wittig reaction with allyltriphenylphosphorane without prior purification. The resulting hydrocarbon product was purified on silver nitrate impregnated silica gel to give **1A** in 27% yield. The infrared spectrum of this material is devoid of characteristic trans double bond absorption in the 970-cm^{-1} region, and on this basis a *Z,Z,Z* configuration is assigned to the tetraene. This product was indistinguishable from the natural pheromone by GC/MS, and it proved as active as the female secretion in EAG reponses and in field tests.[3]

Experimental Section

Melting points were obtained in sealed capillary tubes by using a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra were obtained on a Perkin-Elmer 299B spectrophotometer. Proton magnetic resonance spectra were recorded on Brucker WM-300 (300 MHz) spectrometer with chloroform as the reference. Mass spectra were taken on an AEI MS 902/CIS-2 mass spectrometer, while GC/MS analyses (EI and CI) was carried out by using a Finnigan 3300 GC/MS instrument coupled to a System Industries "System 150" data system. Ultraviolet spectra were recorded on either a Cary 14 or a Hewlett-Packard 8450 AUV/vis spectrophotometer. GLC analyses were carried out by using a Varian Aerograph Series 2100 instrument equipped with a Shimadzu C-RIA Chromatopac recorder. TLC separations were carried out by using Polygram SIL G/UV$_{254}$ precoated plastic plates (40 × 80 mm; 0.25-mm silica gel with fluorescent indicator). The components were located by spraying with 2% ethanolic phosphomolybdic acid solution and warming with a hot-air gun.

Dodec-2-ynol (2) was obtained in 95% yield from 1-bromononane by using an experimental procedure analogous to that described for tetradec-2-ynol.[5] The product was crystallized from aqueous alcohol (mp 30–31 °C) and appeared homogeneous upon TLC (8:2 hexane/ether) and GLC (10% XF-1150 at 170 °C and 3% OV-17 at 140 °C): IR (CCl_4) ν_{max} 3620, 2924, 2852, 2286, 2223, 1466, 1380, 1138, 1010 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.22 (2 H, t, J = 2.2 Hz, CH_2OH), 2.17 (2 H, m, $CH_2C{\equiv}C$), 1.42 (2 H, m, $CH_2CH_2C{\equiv}C$), 1.24 (12 H, s, $(CH_2)_6$), 0.85 (3 H, t, J = 6.7 Hz, CH_3); EI MS, m/z (relative intensity) 135 (13), 121 (18), 111 (34), 109 (15), 108 (11), 107 (19), 97 (13), 96 (13), 95 (47), 94 (25), 93 (57), 91 (11), 84 (13), 83 (44), 82 (29), 81 (74), 80 (18), 79 (57), 77 (14), 70 (73), 69 (30), 68 (22), 67 (85), 57 (29), 56 (21), 55 (92), 54 (21), 53 (21), 52 (10), 43 (85), 42 (22), 41 (99), 39 (41).

1-Bromododec-2-yne (3). Dodec-2-ynol (**2**), on treatment with phosphorus tribromide in ahydrous pyridine, gave 1-bromododec-2-yne in 60% yield as a colorless oil, after purification by column chromatography on silica gel.[3] The product appeared homogeneous on TLC (hexane) and GLC (10% XF-1150 and 3% OV-17 at 150 °C): IR (film) ν_{max} 2923, 2852, 2232, 1463, 1210, 665 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.90 (2 H, t, J = 2.4 Hz, CH_2Br), 2.20 (2 H, m, $CH_2C{\equiv}C$), 1.48 (2 H, m, $CH_2CH_2C{\equiv}C$), 1.24 (12 H, s, $(CH_2)_6$), 0.85 (3 H, t, J = 6.5 Hz, CH_3); EI MS, m/z (relative intensity) 109 (25), 95 (83), 93 (19), 91 (10), 83 (15), 82 (10), 81 (69), 80 (11), 79 (35), 77 (16), 70 (11), 69 (44), 68 (11), 67 (80), 66 (15), 65 (15), 56 (13), 55 (10), 54 (56), 53 (16), 52 (39), 51 (27), 50 (23), 41 (100), 40 (22), 39 (21), 38 (66), 36 (51); CI MS, m/z (relative intensity) 245 (MH^+, 1), 175 (12), 165 (25), 163 (14), 123 (22), 109 (56), 97 (14), 95 (100), 83 (27), 81 (33), 69 (13).

Hexadeca-3,6-diynol (4). The Grignard derivative of 1-(2-tetrahydropyranyloxy)but-3-yne was coupled with **3**, by using a procedure similar to that described in our previous report,[3] to give 1-(2-tetrahydropyranyloxy)hexadeca-3,6-diyne which on hydrolysis with *p*-toluenesulfonic acid in methanol gave **4** in 58% yield (from 1-bromododec-2-yne) after purification by column chromatography on silica gel. Diynol **4** appeared homogeneous by TLC (6:4, hexane/ether) and GLC (3% OV-17, 150–250 °C, 12 °C/min): IR (CCl_4) ν_{max} 3220, 2922, 2850, 1462, 1410, 1318, 1050 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.68 (2 H, t, J = 6.1 Hz, CH_2OH), 3.12 (2 H, t, J = 2.4 Hz $C{\equiv}CCH_2C{\equiv}C$), 2.43 (2 H, m, $C{\equiv}CCH_2CH_2OH$), 2.13 (2 H, m, $CH_2C{\equiv}C$), 1.45 (2 H, m, $CH_2CH_2C{\equiv}C$), 1.25 (12 H, s, $(CH_2)_6$), 0.86 (3 H, t, J = 6.6 Hz, CH_3); EI MS, m/z (relative intensity) 234 (M^+, 4), 164 (17), 163 (12), 149 (14), 136 (14), 135 (14), 133 (12), 123 (32), 122 (17), 121 (40), 120 (10), 119 (17), 117, (21), 108 (13), 107 (36), 106 (11), 105 (37), 103 (12), 97 (13), 95 (36), 94 (26), 93 (39), 92 (27), 91 (100), 82 (15), 81 (50), 80 (22), 79 (98), 78 (27), 77 (46), 71 (25), 69 (29), 68 (11), 67 (50), 66 (21), 65 (30), 64 (10), 56 (11), 54 (51), 52 (25), 51 (16), 50 (43), 41 (85), 40 (24), 39 (25), 38 (77), 36 (52).

(*Z,Z*)-Hexadeca-3,6-dienol (5). The diynol **4** was partially hydrogenated by using P-2 Ni catalyst[6] as described previously for the reduction of octadeca-3,6-diynol.[3] Dienol **5** was obtained as a colorless oil in 88% yield after purification by column chromatography. It appeared homogeneous on TLC (1:1 hexane/ether) and GLC (10% XF-1150 at 170 °C and 3% OV-17, 150–220 °C, 12 °C/min): IR (film) ν_{max} 3325, 3010, 2920, 2850, 1470, 1050 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.52 (1 H, m) and 5.34 (3 H, m) (olefinic protons), 3.64 (2 H, t, J = 6.4 Hz, CH_2OH), 2.80 (2 H, t, J = 6.8 Hz, $CH{=}CHCH_2CH{=}CH$), 2.34 (2 H, m, $CH{=}CHCH_2CH_2OH$), 2.03 (2 H, m, $CH_2CH{=}CH$), 1.24 (14 H, s, $(CH_2)_7$), 0.86 (3 H, t, J = 6.8 Hz, CH_3); EI MS, m/z (relative intensity) 238 (M^+, 9), 220 (3), 121 (17), 112 (11), 110 (11), 109 (20), 108 (10), 107 (25), 98 (23), 97 (19), 96 (32), 95 (43), 94 (39), 93 (56), 91 (21), 84 (15), 83 (32), 82 (53), 81 (65), 80 (52), 79 (100), 77 (20), 71 (10), 70 (16), 69 (37), 68 (57), 67 (99), 66 (13), 57 (27), 56 (12), 55 (79), 54 (29), 53 (18), 43 (55), 41 (94), 39 (21).

(*Z,Z*)-Hexadeca-3,6-dienal (6). Dienol **5** on oxidation with dipyridine chromium(VI) oxide in CH_2Cl_2 gave the corresonding aldehyde **6** in 83% yield:[3] IR (film) ν_{max} 3002, 2916, 2845, 2712, 1728, 1690, 1463 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.65 (1 H, t, CHO), 5.37 (4 H, m, olefinic protons), 3.20 (2 H, m, $CH{=}CHCH_2CHO$), 2.77 (2 H, t, J = 7 Hz, $CH{=}CHCH_2CH{=}CH$), 2.01 (2 H, m, $CH_2CH{=}CH$), 1.24 (14 H, s, $(CH_2)_7$), 0.86 (3 H, t, J = 6.6 Hz, CH_3). This aldehyde was used directly for the Wittig reaction without purification.

(*Z,Z,Z*)-1,3,6,9-Nonadecatetraene (1A). The desired tetraene was obtained in 27% yield from **6** by using the Wittig reaction conditions described earlier for the synthesis of C-21 tetraene.[3] After chromatographic purification, the product appeared homogeneous by TLC (hexane) and GLC (10% XF-1150 at 160 °C, 3% OV-17, 120–250 °C, 10 °C/min, and 3% OV-1 at 170 °C): IR (film) ν_{max} 3014, 2926, 2856, 1467, 1436, 995, 904 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.65 (1 H, m), 6.0 (1 H, t, J = 10.9 Hz), 5.36 (5 H, m), 5.19 (1 H, d, J = 16.6 Hz), 5.10 (1 H, d, J = 9.9 Hz) (olefinic protons), 2.95 (2 H, t, J = 6.1 Hz, $=CHCH_2CH{=}CHCH{=}CH_2$), 2.80 (2 H, t, J = 5.9 Hz, $=CHCH_2CH{=}$), 2.03 (2 H, m, $CH_2CH{=}$), 1.25 (14 H, s, $(CH_2)_7$), 0.86 (3 H, t, J = 6.8 Hz, CH_3); EI MS, m/z (relative intensity) 262 (M^+), 119 (19), 106 (24), 105 (23), 95 (11), 94 (19), 93 (34), 92 (39), 91 (80), 82 (12), 81 (23), 80 (86), 79 (100), 78 (38), 77 (33), 71 (12), 69 (15), 67 (50), 66 (24), 65 (15), 56 (19), 54 (33), 53 (11), 52 (11), 41 (47), 38 (64), and 36 (24). This product was indistinguishable from the female winter moth secretion on the basis of GC/MS comparison and bioassays.[2]

Acknowledgment. We are grateful to the Indian Ministry of Education for the award of a National Scholarship to S.C.J. Additional support was provided by research grants from the Schering-Plough Corp. and the National Institutes of Health (AI-12020).

Registry No. **1A**, 82970-94-3; **2**, 69064-46-6; **3**, 85565-88-4; **4**, 85565-89-5; **4** (THP ether), 85565-90-8; **5**, 84653-91-8; **6**, 85565-91-9; $HC{\equiv}CCH_2CH_2OTHP$, 40365-61-5; $Ph_3P{=}CHCH{=}CH_2$, 15935-94-1.

---

(5) Ames, D. E.; Cornell, A. N.; Goodburn, T. G. *J. Chem. Soc.* **1963**, 5890.

(6) Brown, C. A.; Ahuja, V. K. *J. Org. Chem.* **1973**, *38*, 2226; *J. Chem. Soc., Chem. Commun.* **1973**, 553.