of the alkenes, (tetraene, 2.47 ± 0.22 mV; triene, 1.52 ± 0.16 mV; diene, 1.34 ± 0.13 mV) were significantly ($p < 0.001$)[15] greater than that of the control (0.54 ± 0.07 mV). The higher activity of the tetraene relative to the other two alkenes is also significant ($p < 0.001$). An isomer of the natural diene, (*Z,Z*)-3,6-heneicosadiene,[16] assayed in similar tests (nine antennae from 4-day-old Gainesville and Poplarville males) proved significantly ($p < 0.001$) less active (0.42 ± 0.03 mV) than the natural diene (1.56 ± 0.11 mV) and only slightly more active ($p < 0.05$) than the control (0.33 ± 0.04 mV).

(15) Paired *t* tests were used in all statistical analyses of electroantennogram data.

(16) This diene was prepared by reaction of the Wittig reagent from (*Z*)-(3-hexenyl)triphenylphosphonium bromide with *n*-pentadecanal: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.330 (4 H, m, olefinic protons), 2.76 (2 H, t, J = 6.4 Hz, $=CHCH_2CH=$), 2.06 (4 H, m, $CH_2CH=CHCH_2CH=CHCH_2$), 1.24 (24 H, s, $(CH_2)_{12}$), 0.95 (3 H, t, J = 7.3 Hz, $CH_3CH_2CH=$), 0.86 (3 H, t, J = 6.8 Hz, CH_3). The EI MS showed a molecular ion at m/z (relative intensity) 292 (0.8) corresponding to the molecular formula $C_{21}H_{40}$. Other major ions appear at m/z (relative intensity) 110 (15), 109 (23), 97 (15), 96 (58), 95 (51), 83 (21), 82 (100), 81 (60), 80 (12), 79 (21), 69 (19), 68 (37), 67 (84), 57 (12), 55 (33), 54 (16), 43 (22), and 41 (26).

Field tests, comparable to those carried out previously with the triene,[1] have been done only in areas of low *Utetheisa* density. The results, preliminary so far, show the tetraene (100 μg/moth trap) to be active.

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Registry No. **2**, 85612-05-1; **3**, 85613-23-6; **4**, 51309-22-9; **5**, 40924-12-7; **6**, 40365-61-5; **7**, 18202-26-1; 7 THP ether, 85613-24-7; **8**, 65050-40-0; **9**, 65050-43-3; **10**, 544-35-4; **11**, 506-43-4; **12**, 56401-30-0; $(CH_3CH_2CH_2)_2CuLi$, 43093-17-0; prop-2-yn-1-ol, 107-19-7; 1-bromoundecane, 693-67-4; but-3-yn-1-ol, 927-74-2; allyltriphenylphosphonium bromide, 1560-54-9.

Synthesis of Highly Unsaturated Insect Pheromones: (*Z,Z,Z*)-1,3,6,9-Heneicosatetraene and (*Z,Z,Z*)-1,3,6,9-Nonadecatetraene

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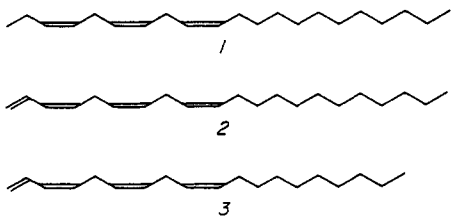
Convenient syntheses of (*Z,Z,Z*)-1,3,6,9-heneicosatetraene (**2**) and (*Z,Z,Z*)-1,3,6,9-nonadecatetraene (**3**), female sex pheromones of an arctiid moth and of a geometrid moth, are reported. For each of these compounds, the key step is the partial hydrogenation of a crystalline triynol (**10**, **15**) by using Lindlar catalyst to give the corresponding (*Z,Z,Z*)-trienol (**11**, **16**).

Our recent studies of chemical communication in the arctiid moth *Utetheisa ornatrix* have led to the characterization of a C-21 triene, (*Z,Z,Z*)-3,6,9-heneicosatriene (**1**) as the major constituent of this insect's female pheromone.[2] Subsequent research has revealed that different populations of this moth have different female pheromone compositions and that a minor component in our original pheromone samples is a major component in the pheromone from other populations of the same species.[3] This new compound proved to be a C-21 tetraene, much more labile than **1**. We have shown this tetraene to be (*Z,Z,Z*)-1,3,6,9-heneicosatetraene (**2**) on the basis of chemical, spectral, and synthetic evidence.[3]



In an independent, parallel study, the first pheromone from a geometrid moth, *Operophtera brumata* (the winter moth), was isolated and found to be a straight-chain C-19 tetraene with a mass spectrum strikingly similar to that of **2**.[4] Additional degradative and synthetic evidence supported the hypothesis that the winter moth's female pheromone is (*Z,Z,Z*)-1,3,6,9-nonadecatetraene (**3**), a lower homologue of the C-21 arctiid tetraene.[5]

While the stereospecific synthesis of **1** can be achieved simply by a three-carbon extension of the triply unsaturated eighteen-carbon chain provided by linolenic acid,[2] syntheses of **2** and **3** are somewhat more of a challenge, since no correspondingly constituted, naturally occurring tetraenic acid appears to be known. We were interested in finding a good synthetic route to these two pheromones for several reasons. *U. ornatrix* females show the remarkable behavior of releasing their pheromonal signal in a pulsed fashion.[2] It would be very useful to have pure, synthetic samples of each of the pheromone components for this moth in order to try to unravel the biological significance of this pulsing behavior. In the C-19 case, the winter moth is an important forest pest in Europe, Canada, and the U.S.A.; a synthetic pheromone should be useful in monitoring populations of this pest and might even permit the disruption of its mating. Finally, with the discovery of these two closely related tetraenes among members of the arctiid and geometrid moths, it can be anticipated that these compounds or closely related ones will be found as pheromones in other lepidopteran species

(1) Dr. Huang Wenkui, of the Department of Chemistry, Lanzhou University, Lanzhou, Gansu, The People's Republic of China, died in a tragic plane accident in the PRC on Dec 25, 1982.

(2) Conner, W. E.; Eisner, T.; Vander Meer, R. K.; Guerrero, A.; Ghiringhelli, D.; Meinwald, J. *Behav. Ecol. Sociobiol.* **1980**, *7*, 55.

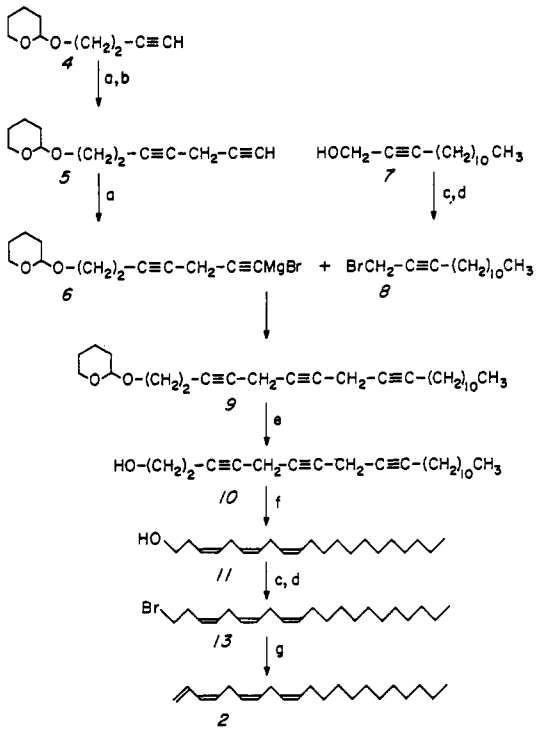
(3) Jain, S. C.; Dussourd, D.; Conner, W. E.; Eisner, T.; Guerrero, A.; Meinwald, J. *J. Org. Chem.*, preceding paper in this issue.

(4) Roelofs, W. L., private communication.

(5) 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.

0022-3263/83/1948-2270$01.50/0

Scheme I[a]



[a] (a) C_2H_5MgBr; (b) $BrCH_2C{\equiv}CH$, CuCl; (c) CH_3SO_2Cl; (d) LiBr; (e) HCl in CH_3OH/H_2O; (f) Pd on $CaCO_3$/quinoline; (g) KOH.

as well. We now report a convergent approach to the synthesis of **2** and **3** which provides good access to pure samples of these unstable hydrocarbons, and which in addition lends itself to the preparation of analogously constituted molecules.

The new synthesis of **2**, summarized in Scheme I, relies on the coupling of the Grignard reagent derived from a protected C-7 diynol (**6**) with a C-11 propargylic halide (**8**), giving a crystalline C-21 triynol (**10**) after deprotection. Catalytic hydrogenation of **10** yields the corresponding (*Z,Z,Z*)-trienol **11**, which is converted to the desired C-21 tetraene **2** in three steps.

The conversion of the tetrahydropyranyl (THP) derivative of 3-butynol (**4**), via its magnesium bromide, into the THP-protected 3,6-heptadiynol (**5**) was accomplished in 76% yield. Its C-14 partner (**8**) for the subsequent Grignard coupling was best prepared from 2-tetradecynol (**7**) in 92% yield by mesylation followed by displacement of the mesyl group using lithium bromide in THF. 1-Bromo-2-tetradecyne (**8**) coupled with the Grignard derivative of the protected C-7 diynol **6** to give the desired C-21 triynol **10** as colorless crystals in 44% overall yield after removal of the THP protecting group.

We were successful, in the course of our original synthesis of **2**, in partially reducing two acetylenic bonds in skipped conjugation with P-2 nickel catalyst to give the corresponding (*Z,Z*)-diene.[3] It was our hope that the three acetylenic bonds in **10** could be similarly reduced. However, we were unable to achieve a comparably successful partial reduction in this case. TLC analysis of the reduction product showed that there were at least four components formed in comparable amounts in the hydrogenation product. The "modified" Lindlar's catalysts, i.e., Pd on barium sulfate in methanol containing quinoline,[6] and Pd on calcium carbonate in hexane containing

(6) Cram, D. J.; Allinger, N. L. *J. Am. Chem. Soc.* **1956**, *78*, 2518.

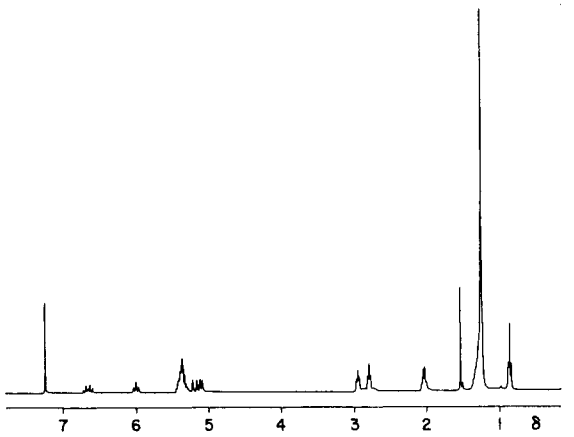


Figure 1. ^1H NMR spectrum of (*Z,Z,Z*)-1,3,6,9-heneicosatetraene (**2**).

triethylamine,[7] gave results almost the same as those obtained on using P-2 nickel catalyst.[8] Nevertheless, it turned out that the classical Lindlar catalyst provided a simple solution to this problem. The partial reduction of **10** proceeded smoothly in absolute ethanol to give the desired trienol **11** in 83% yield after purification by preparative TLC. The 300-MHz ^1H NMR spectrum of this product was in accord with expectations for a pure sample of the desired (*Z,Z,Z*)-trienol **11**. TLC analyses of **11** itself and of the products from subsequent steps in our reaction sequence all suggested homogeneity.

The dehydration of **11** to give the terminal conjugated diene system present in the desired pheromone was accomplished in three final steps. The mesylate (**12**) of **11** was prepared in a standard fashion (98% yield) and was converted into the corresponding bromide (**13**) in 82% yield by treatment with lithium bromide in dry THF. After several exploratory experiments, it was found that relatively brief treatment of **13** with potassium hydroxide in alcohol at about 65 °C gave the desired product of dehydrohalogenation (**2**) in 66% yield, after purification by preparative TLC. This product, which was indistinguishable from the natural material on the basis of electroantennogram responses,[9] GLC analysis, and mass spectrometry, showed infrared, ultraviolet, and 300-MHz ^1H NMR spectra (see Figure 1) consistent with expectations for structure **2**.

The synthesis of the winter moth female pheromone, **3**, followed the same pattern as that described for **2** but used 1-bromo-2-dodecyne (**14**) in place of **8**. Once again, the intermediate triynol **15** proved to be a crystalline solid, whose partial reduction over Lindlar catalyst gave the desired trienol **16**. Since the chemistry in this preparation of the C-19 pheromone follows that already described for **2**, we have simply reported physical and spectral data for each of the characterized intermediates in the reaction sequence.

While neither infrared spectroscopy nor GLC analyses have shown the presence of impurities containing *E* double bonds in samples of **2** and **3** prepared via triynes as described above, it is possible that small amounts of such stereoisomers may be present. The detection and removal of such stereoisomers, which might be accomplished with appropriate GLC or HPLC techniques, would become important only if biological responses to these pheromones

(7) Corey, E. J.; Kang, J. *J. Am. Chem. Soc.* **1981**, *103*, 4618.
(8) For an example of a triyne reduction using P-2 Ni, see: Mori, K. "Les Médiateurs Chimiques"; INRA: Versailles, 1981; Les Colloques de l'INRA, 7.
(9) We thank Mr. David Dussourd for making these measurements.

turn out to be more sensitive to such contaminants than now seems to be the case.

Experimental Section

Thin-layer chromatography (TLC) was performed on Polygram Sil G/UV_{254} plates (0.25-mm silica gel with fluorescent indicator on 40 × 80 mm plastic sheets) for qualitative assays or on Uniplate silica gel GF plates (1- or 2-mm silica gel on 20 × 20 cm glass plates) for preparative work. Components were located by inspection under UV light or by development with an ethanolic solution of phosphomolybdic acid (ca. 4%) on the qualitative plates and on the edges of the preparative plates. Solvent mixtures are described as ratios by volume, and removal of solvents was performed at reduced pressure by using a rotary evaporator. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl; dichloromethane was dried over Davison 4A molecular sieves for several days before being used.

Infrared (IR) spectra were obtained on a Perkin-Elmer Model 299B spectrophotometer. Proton nuclear magnetic resonance (^{1}H NMR) spectra were determined in deuteriochloroform and obtained either on a Varian EM-390 spectrometer (90 MHz) with tetramethylsilane as an internal standard or on a Bruker WM-300 spectrometer (300 MHz) without an additional standard. ^{1}H NMR data are expressed in parts per million downfield from Me_4Si (δ 0).

Mass spectra were recorded on an AEI MS 902/CIS-2 mass spectrometer. Electron-impact mass spectra (EI MS) were obtained at 70 eV, and chemical ionization mass spectra (CI MS) were recorded by using methane as the ionizing gas. Only ions with relative intensities higher than 10% are tabulated.

1-(2-Tetrahydropyranyloxy)-3,6-heptadiyne (5). A solution of ethylmagnesium bromide in 15 mL of THF was prepared in the usual way from 3.38 g (31 mmol) of ethyl bromide and 0.76 g of magnesium turnings. To the resulting Grignard reagent was added slowly a solution of 4.35 g (28 mmol) of the adduct of 2,3-dihydropyran and 3-butynol in 10 mL of THF. After the addition, the reaction mixture was warmed in a water bath (55–60 °C) for 40 min. The solution was then cooled to room temperature, and 120 mg of cuprous chloride was added. Twenty minutes thereafter, 3.17 mL of an 80% solution of propargyl bromide in toluene (corresponding to 28.2 mmol of propargyl bromide) was added gradually. After being stirred at room temperature for 12 h, the reaction mixture was warmed on a water bath (55–60 °C) for 2 h. After cooling to room temperature, the reaction mixture was treated with a solution of 4.5 g of ammonium chloride and 0.2 g of potassium cyanide in 15 mL of water with vigorous shaking in a separatory funnel. The upper layer was separated, and the aqueous layer was extracted twice with ether. The combined organic layers were washed with a concentrated solution of ammonium chloride and dried over anhydrous sodium sulfate. The solvents were removed under vacuum. The residue was distilled under vacuum, giving a colorless liquid [bp 83–88 °C (0.06 mmHg); 4.06 g (76%)] which became pale yellow within a few minutes after being exposed to air: IR (film) 3286, 2122 (w), 1135, 1122, 1080 (sh), 1070, 1060, 645 cm^{-1}; ^{1}H NMR (90 MHz) 1.35–2.04 (m, 6 H, 3 CH_2 in pyran), 2.07 (t, 1 H, J = 3.0 Hz, HC≡C), 2.46 (m, 2 H, C≡C**C**H_2CH$_2$), 3.13 (m, 2 H, C≡CC**H**$_2$C≡C), 3.36–4.20 (m, 4 H, CH_2CH_2O and 2 C-6 Hs of tetrahydropyran-2-yl), 4.65 (t, 1 H, J = 3.3 Hz, OCHO); CI MS, m/e (relative intensity) 193 (34, M$^+$ + 1), 85 (100).

1-Bromo-2-tetradecyne (8). The sample of 8 obtained by following the literature procedure[10] (treating 2-tetradecynol with phosphorus tribromide) showed an impurity having a higher R_f value than that of the desired bromide on TLC (hexane). An improved preparation consisted of the mesylation of 2-tetradecynol (7) followed by displacement of the methanesulfonyl group by bromide using a THF solution of lithium bromide. The procedures were analogous to that used for converting (*Z,Z,Z*)-3,6,9-heneicosatrienol to (*Z,Z,Z*)-1-bromo-3,6,9-heneicosatriene, described below: yield 92% (based on the 7 used); IR (film) 2232, 1210, 610 cm^{-1}; ^{1}H NMR (90 MHz) 0.88 (t, 3 H, J = 6 Hz, C**H**$_3$CH$_2$), 1.16–1.66 (m, 18 H, $(CH_2)_9$), 2.23 (m, 2 H, CH_2C**H**$_2$C≡CCH$_2$Br), 3.91 (m, 2 H, CH$_2$C≡CC**H**$_2$Br); CI MS, m/e (relative intensity) 193 (11, n-$C_{11}H_{23}$C≡CC$^+$H$_2$), 137 (15), 123 (26), 111 (18), 109 (49), 97 (24), 95 (100), 83 (23), 81 (40), 69 (16), 67 (12).

3,6,9-Heneicosatriynol (10). A solution of ethylmagnesium bromide in 20 mL of THF was prepared in the usual way from 2.33 g (20.5 mmol) of ethyl bromide and 0.52 g of magnesium turnings. To this solution was added (in 15 min) a solution of 3.89 g (20 mmol) of 5 in 10 mL of THF. After the addition, the reaction mixture was stirred for 2 h, and then 69 mg of cuprous chloride was added. Half an hour thereafter, a solution of 5.10 g (18.7 mmol) of 8 in 10 mL of THF was added over 20 min. After the mixture was stirred for 24 h at room temperature, 30 mL of 1.2 N methanolic hydrochloric acid was added to the solution. To make sure of the completeness of the hydrolysis, which took about 30 minutes, we checked the reaction mixture by TLC (silica gel plate; hexanes/ether, 5:1) intermittently. The reaction mixture was transferred to a separatory funnel and extracted twice with saturated aqueous sodium chloride. The upper layer was separated, and the aqueous layer was extracted with ether several times. The combined organic layers were dried ($MgSO_4$) and then evaporated in vacuo. The residue was crystallized from hexane, affording 2.23 g of 3,6,9-heneicosatriynol. An additional 0.23 g of the product was recovered from the mother liquor by concentration. The yield was 44% based on 8 used. An analytical sample was obtained by recrystallization of the product from ethanol, giving colorless crystals of 10: mp 60–61 °C; IR (KBr) 3350, 3265 (br), 1408, 1311, 722 cm^{-1}; ^{1}H NMR (300 MHz) 0.86 (t, 3 H, J = 6.8 Hz, C**H**$_3$CH$_2$), 1.18–1.50 (m, 18 H, $(CH_2)_9$), 1.70 (t, 1 H, J = 6.3 Hz, CH$_2$O**H**), 2.13 (m, 2 H, CH$_2$C≡C), 2.43 (m, 2 H, C≡CC**H**$_2$CH$_2$OH), 3.13 (m, 4 H, 2 ≡CC**H**$_2$C≡), 3.69 (dt, 2 H, $J = J_2$ = 6.3 Hz, CH$_2$C**H**$_2$OH); EI MS, m/e (relative intensity) 300 (0.34, M$^+$), 173 (12), 171 (10), 161 (10), 160 (40), 159 (18), 157 (16), 155 (26), 145 (24), 144 (10), 143 (48), 142 (19), 141 (44), 133 (11), 132 (10), 131 (52), 130 (24), 129 (91), 128 (74), 127 (26), 119 (16), 118 (16), 117 (62), 116 (22), 115 (63), 109 (11), 105 (35), 104 (18), 103 (16), 96 (10), 95 (31), 93 (24), 92 (16), 91 (95), 89 (12), 83 (17), 82 (24), 81 (43), 79 (47), 78 (18), 77 (35), 69 (12), 67 (53), 66 (27), 65 (21), 63 (15), 57 (34), 55 (67), 53 (21), 51 (16), 43 (100).

CI MS, m/e (relative intensity) 301 (95, M$^+$ + 1), 299 (28), 283 (19), 257 (15), 255 (15), 217 (27), 215 (22), 213 (10), 203 (16), 201 (24), 199 (23), 197 (14), 189 (23), 187 (22), 185 (38), 183 (21), 179 (11), 177 (37), 175 (34), 174 (10), 173 (31), 172 (11), 171 (51), 169 (18), 163 (13), 162 (10), 161 (69), 160 (30), 159 (40), 158 (10), 157 (66), 155 (21), 149 (21), 148 (10), 147 (51), 146 (12), 145 (78), 144 (16), 143 (79), 142 (12), 141 (18), 137 (10), 135 (36), 133 (62), 132 (14), 131 (100), 130 (15), 129 (60), 128 (25), 123 (19), 121 (67), 119 (72), 118 (13), 117 (65), 115 (17), 111 (11), 109 (38), 107 (47), 105 (65), 97 (33), 95 (82), 93 (69), 91 (67), 85 (18), 83 (52), 82 (11), 81 (83), 79 (50), 71 (36), 69 (56), 67 (66), 66 (11).

(*Z,Z,Z*)-3,6,9-Heneicosatrienol (11). To a solution of 100 mg (0.333 mmol) of 10 in 4 mL of absolute ethanol was added 8 mg of Lindlar catalyst (5% Pd on $CaCO_3$) and 2 drops of quinoline. The mixture was vigorously stirred under a slight positive pressure of hydrogen. After 24.3 mL of hydrogen had been absorbed (in about 18 min), the mixture was filtered and concentrated in vacuo. The residue was dissolved in methylene choride. The solution was washed with dilute hydrochloric acid and water, dried ($MgSO_4$), and concentrated to give an oily liquid. The yield of crude product was nearly quantitative. Preparative thin-layer chromatography on a 20 × 20 cm silica gel plate, with methylene chloride/ether (18:1) as developing solvent, afforded 84 mg (83%) of pure 11 as a colorless oil: IR (film) 3320 (br), 3018, 1659, 1650, 1645, 1050, 720, 685 (sh) cm^{-1}; ^{1}H NMR (300 MHz) 0.86 (t, 3 H, J = 6.6 Hz, C**H**$_3$CH$_2$), 1.20–1.38 (m, 18 H, $(CH_2)_9$), 1.52 (s, 1 H, OH), 2.03 (m, 2 H, C**H**$_2$(C=C—$CH_2)_3CH_2$OH), 2.34 (m, 2 H, CH$_2$C=C—C**H**$_2$CH$_2$OH), 2.82 (m, 4 H, 2 =CC**H**$_2$C=), 3.63 (m, 2 H, CH$_2$C**H**$_2$OH), 5.35 (m, 5 H), 5.52 (m, 1 H) (3 *cis*-HC=CH); EI MS, m/e (relative intensity) 306 (5, M$^+$), 124 (29), 123 (13), 121 (15), 119 (27), 109 (23), 107 (15), 106 (12), 105 (22), 97 (16), 96 (19), 95 (45), 94 (38), 93 (58), 92 (19), 91 (63), 83 (30), 82 (26), 81 (60), 80 (74), 79 (77), 78 (28), 77 (22), 71 (15), 69 (32), 68 (25), 67 (94), 66 (11), 58 (16), 57 (36), 55 (63), 54 (16), 53 (12), 43 (100); CI MS, m/e (relative intensity) 308 (24, M$^+$ + 2), 307 (100, M$^+$ + 1), 290 (11), 289 (44), 135 (15), 121 (10).

(10) Ames, D. E.; Covell, A. N.; Goodburn, T. G. *J. Chem. Soc.* **1963**, 5891.

Mesylate of (*Z,Z,Z*)-3,6,9-Heneicosatrienol (12). To an ice-cooled solution of 459 mg (1.5 mmol) of **11** in 5 mL of methylene chloride containg 0.42 mL (ca. 3 mmol) of triethylamine was added 0.2 mL (ca. 2.6 mmol) of methanesulfonyl chloride over a period of 10 min with stirring. The reaction was completed after further stirring for an additional 10 min. The reaction mixture was washed with ice–water followed by 2 N hydrochloric acid, water, aqueous sodium bicarbonate, and water. Evaporation of the solvent followed by drying of the residue in vacuo gave mesylate **12** as an oil, 564 mg (98%). An analytical sample was obtained by preparative TLC on a silica gel plate with methylene chloride/ether (95:5) as the developing solvent: IR (film) 3015, 1659, 1650, 1645, 1357, 1177 (SO_3), 720, 685 (sh) cm^{-1}; ^1H NMR (300 MHz) 0.86 (t, 3 H, J = 6.6 Hz, CH_3CH_2), 1.17–1.40 (m, 18 H, $(CH_2)_9$), 2.03 (m, 2 H, $CH_2CH_2C{=}C$), 2.52 (m, 2 H, $CH_2C{=}CCH_2CH_2OMs$), 2.80 (m, 4 H, 2 $=CCH_2C=$), 2.98 (s, 3 H, SO_3CH_3), 4.21 (t, 2 H, J = 6.8 Hz, CH_2CH_2OMs), 5.35 (m, 5 H), 5.56 (m, 1 H) (olefinic protons); EI MS, m/e (relative intensity) 384 (14, M^+), 133 (22), 123 (13), 121 (14), 120 (22), 119 (41), 109 (26), 107 (23), 106 (80), 105 (38), 97 (18), 96(19), 95 (40), 94 (31), 93 (56), 92 (29), 91 (68), 83 (29), 82 (28), 81 (61), 80 (85), 79 (100), 78 (22), 77 (25), 71 (12), 69 (19), 68 (19), 67 (100), 57 (32), 55 (59), 54 (17), 53 (11), 43 (68), 41 (75), 39 (11); CI MS, m/e (relative intensity) 386 (22, $M^+ + 2$), 385 (80, $M^+ + 1$), 384 (44, M^+), 383 (47), 345 (14), 290 (23), 289 (100), 288 (13), 287 (18), 207 (10), 163 (10), 149 (14), 135 (36), 123 (14), 121 (23), 109 (13), 107 (12), 106 (11), 95 (15), 81 (14).

(*Z,Z,Z*)-1-Bromo-3,6,9-heneicosatriene (13). A mixture of 67 mg (0.175 mmol) of **12** and 61 mg (0.70 mmol) of lithium bromide was dried under vacuum overnight at room temperature. To the mixture was added 0.6 mL of THF with stirring. The reaction mixture was checked intermittently by TLC to ensure completion of the reaction. The reaction time, ranging from 20 min to several hours, was significantly affected by the dryness of the reaction mixture. After removal of the solvent in vacuo, the residue was digested with hexane. The hexane solution was evaporated in vacuo to give crude bromide. Purification of the product by preparative TLC on a silica gel plate, with hexane as the developing solvent, afforded the pure bromide: 53 mg (82%); IR (film) 3012, 1659, 1650, 1645, 1210, (CH_2Br), 720, 690 (sh), 644 (CH_2Br) cm^{-1}; ^1H NMR (300 MHz) 0.86 (t, 3 H, J = 6.6 Hz, CH_3CH_2), 1.18–1.39 (m, 18 H, $(CH_2)_9$), 2.04 (m, 2 H, $CH_2CH_2C{=}CCH_2$), 2.63 (m, 2 H, $CH_2C{=}CCH_2CH_2Br$), 2.80 (m, 4 H, 2 $=CCH_2C=$), 3.36 (t, 2 H, J = 7.0 Hz, CH_2CH_2Br), 5.35 (m, 5 H), 5.51 (m, 1 H) (olefinic protons); EI MS, m/e (relative intensity) 370 (22) and 368 (21) (M^+), 235 (13), 234 (38), 216 (10), 214 (10), 208 (11), 202 (14), 201 (11), 200 (13), 199 (12), 189 (17), 188 (100), 187 (17), 186 (97), 135 (11), 121 (19), 109 (17), 107 (17), 105 (19), 97 (15), 96 (15), 95 (28), 94 (14), 93 (29), 91 (25), 83 (22), 82 (21), 81 (39), 80 (43), 79 (78), 78 (10), 77 (15), 71 (14), 68 (12), 67 (54), 57 (31), 55 (33), 54 (10), 53 (10), 43 (36), 41 (40), 39 (10); CI MS, m/e (relative intensity) 371 (31) and 369 (100) ($M^+ + 1$), 370 (40), 367 (73), 290 (14), 289 (58), 277 (11), 263 (11), 243 (12), 235 (10), 234 (20), 231 (12), 229 (15), 221 (12), 217 (15), 215 (16), 211 (34), 207 (12), 203 (17), 201 (16), 189 (19), 188 (40), 187 (16), 186 (39), 149 (15), 139 (11), 137 (16), 135 (43), 125 (19), 123 (27), 121 (33), 111 (25), 109 (26), 107 (14), 97 (30), 95 (25), 93 (18), 85 (10), 83 (22), 81 (27), 79 (14), 71 (11), 67 (17).

(*Z,Z,Z*)-1,3,6,9-Heneicosatetraene (2). To 53 mg (0.14 mmol) of **13** was added a solution of 45 mg of potassium hydroxide in 5 mL of a 1:2 methanol/ethanol mixture. The reaction mixture was heated in a water bath (65–70 °C) for 15 min. After removal of the solvent in vacuo, the residue was treated with water and then extracted with hexane several times. The concentrated extracts were loaded on a silica gel plate followed by development with hexane. The strongly UV-absorbing zone of the preparative TLC plate was eluted with hexane. Removal of the solvent in vacuo afforded 26.5 mg (66%) of **2**. This material showed a single peak upon GLC analysis [145 °C, XF-1150 (10%) on Chromsorb W-AW-DMCS]: UV (hexane) λ_{max} 230 nm (log ϵ 4.415); IR (film) 3016, 1658, 1651, 1642, 1466, 992, 905, 720 cm^{-1}; ^1H NMR (300 MHz) 0.86 (t, 3 H, J = 6.8 Hz; CH_3CH_2), 1.20–1.39 (m, 18 H, $(CH_2)_9$), 2.03 (m, 2 H, $CH_2CH_2CH{=}$), 2.80 (m, 2 H) and 2.95 (m, 2 H) (2 $=CCH_2C=$), 5.15 (m, 2 H), 5.36 (m, 5 H), 6.00 (m, 1 H) and 6.65 (m, 1 H) (olefinic protons); EI MS, m/e (relative intensity) 288 (5, M^+), 234 (13), 133 (11), 106 (38), 105 (25), 95 (12), 94 (20), 93 (48), 92 (49), 91 (62), 83 (13), 83 (14), 81 (27), 80 (100), 79 (99), 78 (33), 77 (28), 71 (13), 68 (10), 67 (55), 66 (18), 57 (31), 55 (34), 54 (11), 53 (10), 43 (44), 41 (64), 39 (13); CI MS, m/e (relative intensity) 289 (100, $M^+ + 1$), 288 (36), 287 (54), 275 (19), 261 (11), 247 (22), 235 (13), 234 (25), 215 (21), 207 (11), 177 (12), 163 (20), 161 (12), 149 (40), 147 (13), 137 (14), 135 (68), 133 (19), 125 (17), 123 (25), 121 (49), 119 (28), 111 (26), 109 (33), 107 (44), 106 (20), 105 (13), 99 (11), 97 (35), 95 (41), 93 (40), 92 (16), 91 (15), 85 (20), 83 (30), 81 (42), 80 (22), 79 (29), 75 (10), 71 (26), 69 (11), 67 (35).

1-Bromo-2-dodecyne (14): CI MS, m/e (relative intensity) 165 (6), 123 (16), 109 (45), 107 (10), 97 (10), 95 (100), 93 (11), 83 (24), 81 (47), 69 (14), 67 (18); EI MS, m/e (relative intensity) 165 (1.5), 123 (10), 109 (35), 95 (100), 93 (14), 83 (14), 81 (58), 79 (21), 77 (10), 69 (20), 67 (46), 57 (16), 55 (46), 54 (10), 53 (21), 52 (13), 51 (10), 43 (43), 41 (47), 39 (18); IR (film) 2235, 1210, 610 cm^{-1}; ^1H NMR (90 MHz) 0.87 (t, 3 H, J = 6 Hz, CH_3CH_2), 1.15–1.70 (m, 14 H, $(CH_2)_7$), 2.28 (m, 2 H, n-$C_8H_{17}CH_2C{\equiv}CCH_2Br$), 3.93 (m, 2 H, $C{\equiv}CCH_2Br$).

3,6,9-Nonadecatriynol (15): mp 52–53 $C{\equiv}CCH_2CH_2OH$), EI MS, m/e (relative intensity) 173 (13), 171 (10), 161 (10), 160 (44), 159 (21), 157 (16), 156 (10), 155 (30), 145 (26), 144 (12), 143 (51), 142 (23), 141 (50), 133 (13), 132 (10), 131 (56), 130 (27), 129 (100), 128 (76), 127 (25), 124 (11), 119 (15), 118 (16), 117 (67), 116 (25), 115 (60), 107 (11), 105 (39), 104 (19), 103 (16), 95 (32), 93 (24), 92 (17), 91 (98), 83 (10), 82 (25), 81 (40), 79 (45), 78 (16), 77 (27), 69 (15), 67 (51), 66 (30), 65 (16), 63 (10), 57 (20), 55 (50), 53 (15), 51 (11), 43 (59), 41 (58), 39 (15); CI MS, m/e (relative intensity) 274 (10), 273 (45, $M^+ + 1$), 271 (11), 255 (14), 229 (10), 227 (13), 215 (10), 201 (19), 199 (10), 197 (13), 189 (34), 187 (24), 185 (28), 183 (18), 175 (27), 173 (29), 172 (12), 171 (48), 169 (19), 163 (10), 161 (60), 160 (24), 159 (41), 158 (13), 157 (65), 156 (11), 155 (23), 151 (16), 149 (46), 148 (10), 147 (56), 146 (11), 145 (76), 144 (16), 143 (93), 142 (16), 141 (21), 135 (28), 133 (58), 132 (14), 131 (100), 130 (19), 129 (70), 128 (27), 123 (12), 121 (65), 119 (77), 118 (11), 117 (65), 116 (11), 115 (19), 109 (26), 107 (46), 106 (10), 105 (70), 99 (11), 97 (14), 95 (75), 93 (67), 92 (11), 91 (80), 83 (48), 82 (12), 81 (86), 79 (56), 71 (29), 69 (68), 67 (65), 60 (12); IR (KBr) 3355, 3270, 1406, 1311, 723 cm^{-1}; ^1H NMR (300 MHz) 0.87 (t, 3 H, J = 6.7 Hz, CH_2CH_3), 1.16–1.50 (m, 14 H, $(CH_2)_7$), 1.69 (t, 1 H, J = 6.2 Hz, CH_2OH), 2.13 (m, 2 H, n-$C_8H_{17}CH_2C{\equiv}$), 2.43 (m, 2 H, $C{\equiv}CCH_2CH_2OH$), 3.13 (m, 4 H, 2 $=CCH_2C{\equiv}$), 3.69 (dt, 2 H, $J = J_2$ = 6.2 Hz, CH_2CH_2OH).

(*Z,Z,Z*)-3,6,9-Nonadecatrienol (16): EI MS, m/e (relative intensity) 278 (8, M^+), 206 (14), 205 (12), 193 (17), 165 (10), 163 (10), 151 (10), 149 (14), 139 (10), 138 (10), 137 (21), 135 (16), 133 (21), 125 (13), 124 (34), 123 (19), 122 (11), 121 (30), 120 (20), 110 (16), 109 (22), 108 (13), 107 (25), 106 (18), 105 (34), 97 (10), 96 (19), 95 (56), 94 (34), 93 (72), 92 (12), 91 (66), 85 (16), 84 (11), 83 (34), 82 (39), 81 (81), 80 (80), 79 (71), 78 (49), 77 (31), 71 (17), 68 (35), 67 (100), 66 (21), 65 (10), 57 (45), 56 (15), 55 (68), 54 (12), 53 (10), 42 (15), 41 (56), 39 (13); CI MS m/e (relative intensity) 280 (15, $M^+ + 2$), 279 (69, $M^+ + 1$), 278 (18), 277 (35), 262 (22), 261 (93), 259 (20), 233 (17), 219 (12), 193 (17), 179 (19), 177 (10), 165 (17), 163 (20), 151 (21), 149 (42), 147 (10), 139 (11), 137 (30), 136 (12), 135 (94), 133 (17), 125 (23), 124 (21), 123 (49), 122 (12), 121 (100), 119 (21), 111 (27), 109 (69), 107 (52), 105 (13), 97 (43), 95 (93), 94 (14), 93 (41), 91 (20), 85 (15), 83 (44), 81 (77), 80 (18), 79 (28), 71 (79), 69 (25), 67 (50); IR (film) 3320, 3012, 1665, 1658, 1652, 1050 (CH_2OH), 725 cm^{-1}; ^1H NMR (300 MHz) 0.87 (t, 3 H, J = 6.5 Hz, CH_2CH_3), 1.17–1.39 (m, 14 H, $CH_2)_7$), 1.51 (s, 1 H, OH), 2.03 (m, 2 H, $CH_2(CH{=}CHCH_2)_3CH_2OH$), 2.35 (m, 2 H, $CH_2CH{=}CHCH_2CH_2OH$), 2.81 (m, 4 H, 2 $=CCH_2C=$), 3.66 (m, 2 H, CH_2CH_2OH), 5.35 (m, 5 H) and 5.51 (m, 1 H) (olefinic protons).

Mesylate of (*Z,Z,Z*)-3,6,9-Nonatrienol (17): EI MS, m/e (relative intensity) 356 (26, M^+), 147 (14), 134 (12), 133 (27), 123 (13), 121 (16), 120 (30), 119 (31), 109 (28), 107 (30), 106 (100), 105 (42), 97 (17), 96 (21), 95 (49), 94 (35), 93 (60), 92 (34), 91 (64), 83 (24), 82 (31), 81 (62), 80 (84), 79 (74), 78 (22), 77 (17), 71 (12), 68 (18), 67 (89), 66 (13), 57 (21), 55 (40), 54 (14), 43 (13), 41 (34); CI MS, m/e (relative intensity): 357 (29, $M^+ + 1$), 356 (11), 355 (13), 262 (21), 261 (100), 259 (16), 219 (13), 179 (14), 165 (11), 163 (13), 151 (11), 149 (25), 137 (15), 135 (54), 123 (22), 121 (53), 111 (15), 109 (30), 107 (29), 106 (11), 97 (22), 95 (38), 93 (20), 82 (20), 81 (35), 79 (13), 71 (10), 69 (10), 67 (26); IR (film) 3008, 1655, 1647,

1640, 1350, 1171, 730 cm^{-1}; ^1H 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}; ^1H 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}; ^1H 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).

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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)

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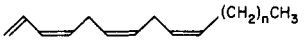
We have recently characterized the first sex attractant from a female geometrid moth (*Operophtera brumata*, the winter moth) as (*Z,Z,Z*)-1,3,6,9-nonadecatetraene (**1A**).[2]

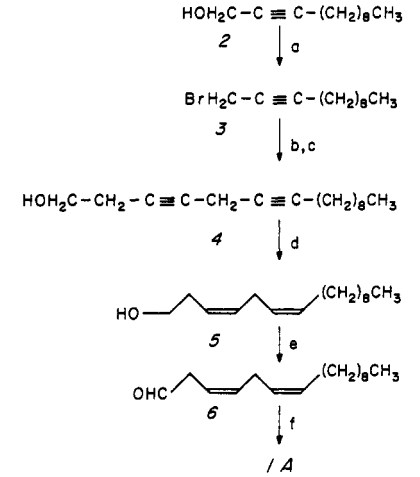


1A: n = 8
1B: n = 10

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]

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

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



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

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(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.

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