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Identification, Syntheses, and Characterization of the Geometric Isomers of 9,11-Hexadecadienal from Female Pheromone Glands of the Sugar Cane Borer *Diatraea saccharalis*

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Chemical analysis of the pheromone glands of the sugar cane borer *Diatraea saccharalis* has shown the presence of the four geometric isomers of 9,11-hexadecadienal (**1**−**4**), in addition to hexadecanal and (*Z*)-hexadec-11-enal. We here report the syntheses and characterization of compounds **1**−**4**. One starting material, 9-decen-1-ol, has been used to obtain all of them via divergent synthetic routes.

Most sex pheromones identified in lepidopteran insects are unsaturated straight-chain aliphatic alcohols, acetates, or aldehydes.[1] The reproductive isolation of the various species is promoted by species-specific mating signals, given by groups of structurally related compounds,[2] such as geometric and positional isomers of acetates, alcohols, or aldehydes.

The main sex pheromone component in a *Diatraea* species is usually a monoenic or dienic aldehyde with a C_{16} carbon skeleton. For example, the pheromone components of *Diatraea considerata* are (*Z*)-hexadec-11-enal, (*Z*)-hexadec-7-enal, and (*Z*)-octadec-13-enal,[3] whereas *D. grandiosella* uses (*Z*)-hexadec-11-enal, (*Z*)-hexadec-9-enal, and (*Z*)-octadec-13-enal as a pheromone blend.[4]

The sugar cane borer *Diatraea saccharalis* (Lepidoptera: Pyralidae) is an economically important pest of sugar cane and is distributed from Argentina to Cuba. In 1980 Hammond[5] and in 1981 Carney and Lui[6] have reported that the pheromone of *D. saccharalis* is (9*Z*,11*E*)-hexadecadienal.

A first step to develop an environmentally safe method to control *D. saccharalis* was the unsuccessful test of (9*Z*,11*E*)-hexadecadienal as a trap lure.[7] The absence of any reports of high trap captures in the literature might be due to a lack of components that, together with the main compound, would constitute the pheromone blend.

To facilitate the optimization of the pheromone lure of *D. saccharalis*, one should investigate the effect of the geometric isomers of (9*Z*,11*E*)-hexadecadienal on male attraction to the main compound, since the MS analysis indicated that the gland contained all four geometric isomers of 9,11-hexadecadienal. Hence we decided to synthesize the four isomers in order to confirm their tentative identification and for coming tests of their pheromonal activity.

In this paper we report the identification of the four 9,11-hexadecadienals as well as two, more saturated, analogues in the glands of *D. saccharalis* and describe the syntheses and characterization of all geometrical isomers of 9,11-hexadecadienal.

A few reports on the synthesis of single isomers of 9,11-hexadecadienal are found in the literature. Carney and Lui have synthesized the (9*Z*,11*E*)-isomer via the synthetic intermediates $Me_3SiO(CH_2)_8C{\equiv}CH$ and (*E*)-dicyclohexyl-1-hexenylborane.[6]

Millar et al. synthesized (9*E*,11*Z*)-hexadecadienal for an investigation of the female-produced sex pheromone of the pecan nut casebearer, *Acrobasis nuxvorella*,[8] by a synthetic route wherein the key step was a Heck coupling reaction between a vinyl iodide and hexyne.

Svirskaya et al. have reported the synthesis of all four isomers of 9,11-hexadecadienal using four separate routes.[9] Many methods are now available for the preparation of conjugated dienes with high isomeric purity. All have advantages and limitations. We have used one compound, 11-(tetrahydro-2-pyranyloxy)-2-undecyn-1-ol (**9**), as starting material for the synthesis of the four geometric isomers of 9,11-hexadecadienal.

Results and Discussion

Gland Analysis. The following six compounds were found by dissection and analysis of pheromone glands from *D. saccharalis* by means of standard procedures:[10] hexadecanal, 0.4 ng/female; (*Z*)-hexadec-11-enal, 0.8 ng/female; (9*E*,11*Z*)-hexadecadienal (*E*9,*Z*11-16:Ald), 0.5 ng/female; (9*E*,11*E*)-hexadecadienal (*E*9,*E*11-16:Ald), 1.5 ng/female; (9*Z*,11*E*)-hexadecadienal (*Z*9,*E*11-16:Ald), 2.5 ng/female; (9*Z*,11*Z*)-hexadecadienal (*Z*9,*Z*11-16:Ald) 0.6 ng/female.

The dienes were identified by comparison of the retention times of the components in the pheromone glands with the retention times of the synthetic standards (produced as described below).

The presence of (*Z*)-hexadec-11-enal was confirmed by comparison with a commercial reference compound and agreed with the reports that the compound had also been found in the glands of the phylogenetically related species *D. grandiosella*[11] and *D. considerata*.[3]

Syntheses. The four isomers of 9,11-hexadecadienal were prepared starting from 9-decen-1-ol (**5**). Protection of the hydroxyl group of **5** with 3,4-dihydropyran (DHP) yielded the corresponding tetrahydropyran derivative **6** in 93% yield (Scheme 1). Bromination of compound **6** at −78 °C provided 1,2-dibromo-10-(tetrahydro-2-pyranyloxy)decane (**7**) in 81% yield. Dehydrobromination of **7** with sodium amide afforded 1-(tetrahydro-2-pyranyloxy)-9-decyne (**8**) in

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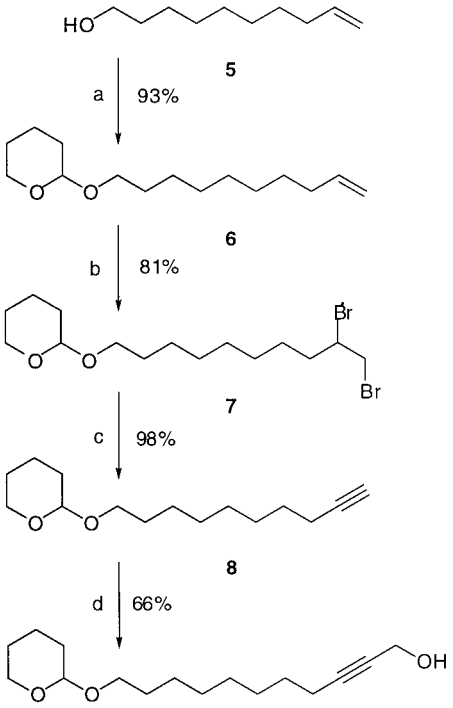
Scheme 1. Synthesis of the Key Intermediate **9**



98% yield. It should be noted that in some experiments the reaction gave a tribromo adduct, probably dependent on hydrogen bromide being produced and leading to replacement of the THP group by bromine atom, yielding a tribromo derivative. The acetylenic proton of compound **8** was removed by means of butyllithium, and paraformaldehyde was then added to provide **9** in 66% yield.

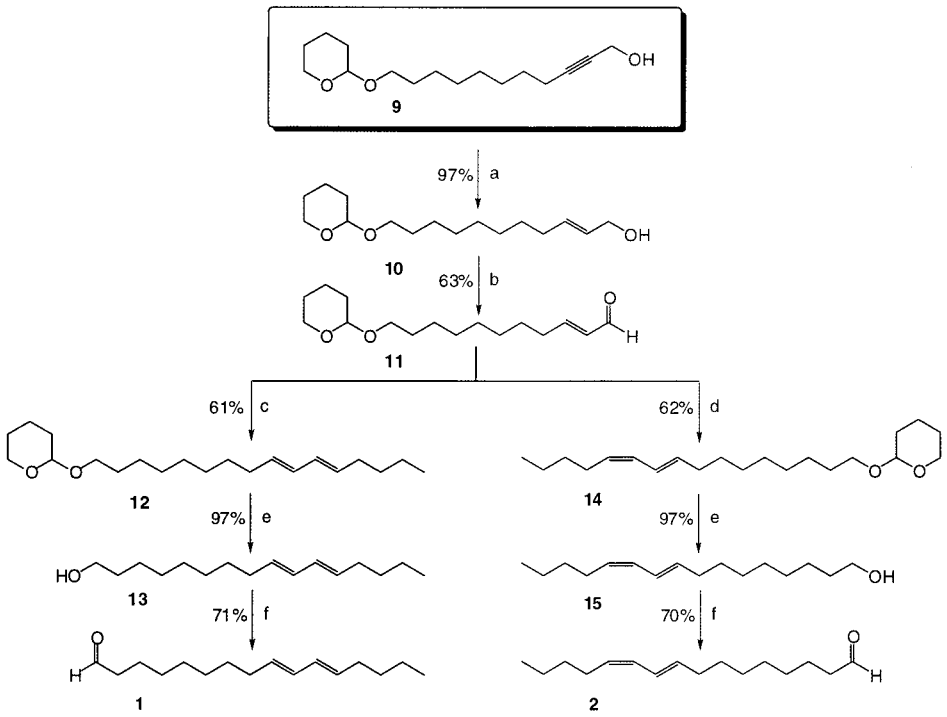
The key intermediate **9** was reduced to the corresponding (*E*)-allylic alcohol **10** by lithium aluminum hydride, and the product was oxidized (MnO_2) to the aldehyde **11** (Scheme 2). The yields were 97% in the reduction step and 63% in the oxidation step. We believe that the high yield in the reduction step compared to what is normally found in the literature for lithium aluminum hydride reductions is a result of the use of the Baeckström procedure for the workup of the reactions.[12] The THP-protected *E*,*E*-**12** and *E*,*Z*-**14** dienes were then formed in separate reactions using normal (*E*,*Z*-**14**/*E*,*E*-**12** = 20:1, yield 62%) or Schlosser Wittig conditions[13] (*E*,*E*-**12**/*E*,*Z*-**14** = 10:1, yield 61%), respectively. After deprotection of the *E*,*E*-**12** and *E*,*Z*-**14** dienes by means of Amberlyst-15 in methanol, the isomeric purity of the *E*,*E*-**13** and *E*,*Z*-**15** was increased to >99% by the urea inclusion complex (clathrate) procedure[14] followed by medium-pressure liquid chromatography using silica gel impregnated with 10% of silver nitrate.[15]

In the final step, (9*E*,11*E*)-hexadecadienal (**1**) and (9*E*,11*Z*)-hexadecadienal (**2**) were formed by oxidation using pyridinium dichromate (PDC) in dichloromethane. The yield was about 70%, and no loss of isomeric purity was observed.

In the syntheses of (9*Z*,11*E*)- and (9*Z*,11*Z*)-hexadecadienal (**3** and **4**, respectively), the key intermediate **9** was oxidized to the aldehyde **16** by means of MnO_2. The yield was 63%.

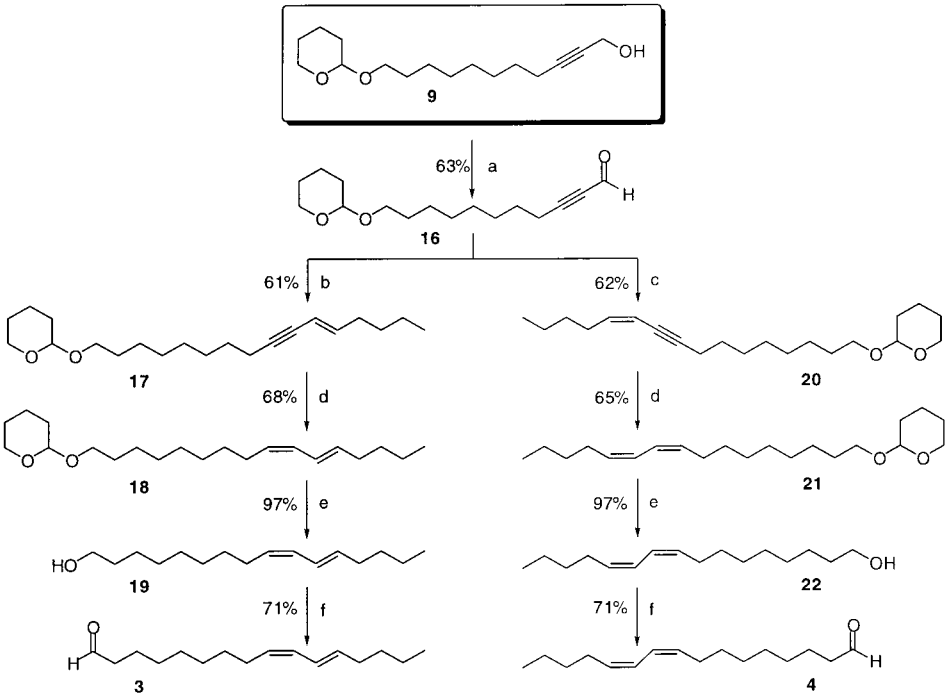
The (9*Z*,11*E*)-hexadecadienal (**3**) was produced by a route starting with a Wittig reaction of the aldehyde **16** with the ylide prepared from pentyltriphenylphosphonium bromide using Schlosser conditions (*E*/*Z* = 7:1).[11] The yield of **17** was 61%. Subsequent hydrogenation of the (*Z*)-enyne (**17**) formed yielded the diene **18** in 68% yield. After deprotection of **18**, the isomeric purity of **19** was increased to >99% as described above for compound **15**. Oxidation using PDC in dichloromethane yielded the *Z*,*E*-dienic aldehyde **3** (in 71% yield) with no loss of isomeric purity.

Scheme 2. Syntheses of the Isomers (9*E*,11*E*)- and (9*E*,11*Z*)-Hexadecadienal



a) $LiAlH_4$, THF; **b)** MnO_2, CH_2Cl_2; **c)** PentylPPh$_3$Br, BuLi, THF/Et_2O, HCl.Et_2O; **d)** PentylPPh$_3$Br, KHMDS, THF ; **e)** *p*-TsOH, EtOH; **f)** PDC, CH_2Cl_2

Scheme 3. Syntheses of the Isomers (9*Z*,11*E*)- and (9*Z*,11*Z*)-Hexadecadienal



a) MnO_2, CH_2Cl_2; **b)** PentylPPh$_3$Br, BuLi, THF/Et_2O, HCl.Et_2O; **c)** PentylPPh$_3$Br, KHMDS, THF; **d)** (Cyclohexyl)$_2$BH, H^+/EtOH; **e)** *p*-TsOH, EtOH; **f)** PDC, CH_2Cl_2

The aldehyde **16** was subjected to a normal Wittig reaction using an ylide prepared from pentyltriphenylphosphonium bromide (yield 62%). The product, the enyne THP ether **20** (*Z*/*E* = 16:1), was then regio- and stereoselectively hydrogenated using a sterically hindered borane, and the (*Z*,*Z*)-diene **21** was obtained in 65% yield. After deprotection, the alcohol **22** was recrystallized at low temperature (−30 °C) from pentane. This increased the isomeric purity to >99% with only a small loss of material. Subsequent oxidation using PDC provided the (*Z*,*Z*)-isomer **4** in 71% yield.

The overall yield of the aldehyde isomers from compound **9** was in the range 17−26%.

Experimental Section

Source of Biological Materials. Field-collected pupae (from Campos dos Goytacazes, Rio de Janeiro State, Brazil) were placed in 10 × 10 × 10 cm cages for emergence. They were held in the laboratory under a photoperiod of 14:8 (L:D) h. The pheromone glands were then excised from the extruded ovipositors of 2 to 3 day old calling virgin females during the first 3 h of the scotophase and were extracted in batches of 19−43 (n = 3) during 1 min, in 5−7 μL of redistilled heptane. The compounds extracted were identified using a Hewlett-Packard 5970B (Hewlett-Packard, Palo Alto, CA) mass spectrometer (MS) with electron impact (EI) ionization, which was interfaced with a Hewlett-Packard 5890 gas chromatograph (GC), with a polar DB-wax column (30 m × 0.25 mm, J&W Scientific, Folsom, CA). In addition, the retention times of the identified gland compounds were compared with those of synthetic compounds on a Hewlett-Packard 5890 GC, with flame ionization detection, on a DB-wax column and on a nonpolar SE-54 column (25 m × 0.32 mm; Kupper & Co., Bonaduz, Switzerland).

Experimental Procedures. The preparative liquid chromatography technique used was the one described by Baeckström et al.[16] It was performed on silica gel (Merck 60, 0.040−0.063 mm) in 15 or 25 mm inner diameter glass columns with gradient elution, using hexane and increasing proportions of ethyl acetate. ^{1}H and ^{13}C NMR spectra of $CDCl_3$ solutions were recorded at 400 and 100 MHz, respectively, using a Bruker AM spectrometer. Chemical shifts were expressed in ppm in relation to tetramethylsilane, followed by numbers of protons, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; m, multiplet; bs, broad singlet; bd, broad doublet; bt, broad triplet; td, triple doublet; tt, triple triplet; dt, double triplet) and coupling constants (Hz). The numbers 1′, 2′, 3′, 4′, and 5′ refer to the tetrahydropyran ring. GC−MS analyses were performed by means of a Finnigan SSQ 7000 mass spectrometer, connected to a Varian 3400 GC, with electron impact ionization (EI). A DB-5 MS fused silica column (J&W Scientific, 30 m, 0.25 mm i.d., 0.25 μm coating layer) and a DB-wax column (J&W Scientific, 30 m, 0.25 mm i.d., 0.25 μm coating layer) were used. The injector was a split/splitless type, closed for 0.5 min at isothermal 225 °C. The elution order of the dienals was (*Z*,*E*), (*E*,*Z*), (*Z*,*Z*), and (*E*,*E*).

The tetrahydrofuran (THF) was treated with sodium/benzophenone and distilled immediately before use. The dichloromethane (CH_2Cl_2) was treated with calcium hydride and, likewise, distilled immediately before use. The other starting materials employed were purchased from commercial suppliers and used without further purification. The reactions involving anhydrous solvents were carried out under an atmosphere of argon.

1-(Tetrahydro-2-pyranyloxy)-9-decene (6). Amberlyst-15 (0.88 g) was added at 0 °C to a solution of 9-decen-1-ol (**5**) (4.30 g, 27.0 mmol) in diethyl ether (80 mL) and followed by 3,4-dihydro-2*H*-pyran (DHP) (2.95 mL, 32.0 mmol). The reaction mixture was stirred for 3 h, the resin was filtered off, and the solution was concentrated. Purification by liquid chromatography afforded the THP ether **6** in 93% yield (6.15 g): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.79 (1H, ddt, J = 17.1 Hz, J = 10.0 Hz, J = 6.7 Hz, H-9), 4.96 (1H, ddt, J = 17.1 Hz, J = 2.1 Hz, J = 1.5 Hz, H-10), 4.90 (1H, ddt, J = 10.0 Hz, J = 2.1 Hz, J = 1.5 Hz, H-10), 4.55 (1H, t, J = 3.5 Hz, O−CH−O), 3.85 (1H, ddd, J = 11.1 Hz, J = 7.4 Hz, J = 3.6 Hz, H_{axial}-5′), 3.71, 3.35 (each 1H, dt, J = 9.4 Hz, 6.6 Hz, H-1), 3.50−3.45 (1H, m, H_{equat}-5′), 2.00 (2H, q, J = 6.7 Hz, H-8), 1.85−1.77 (1H, m), 1.68 (1H, tt, J = 9.4 Hz, J = 3.6 Hz), 1.59−1.47 (6H, m), 1.35−1.27 (10H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) 139.16 (C-9), 114.06

(C-10), 98.79 (O−CH−O), 67.62, (C-1), 62.27 (C-5′), 33.76 (C-8), 30.74 (C-2 and C-2′), 29.38 (2C), 29.03, 28.86, 26.18 (C-3), 25.46 (C-4′), 19.63 (C-3′); EIMS *m*/*z* $[M]^+$ 240 (0.2), 101 (25), 85 (100), 83 (13), 69 (10), 67 (11), 57 (9), 56 (16), 55 (26), 43 (8), 42 (3), 41 (26), 39 (5).

9,10-Dibromo-1-(tetrahydro-2-pyranyloxy)decane (7). Bromine was added dropwise to compound **6** (6.15 g, 25.7 mmol) in CH_2Cl_2 (65 mL) at −78 °C until the first persistence of the halogen color. The solution was shaken with Na_2SO_3 (10% aqueous solution, 3 × 50 mL), and the organic phase was finally washed with brine and dried ($MgSO_4$). The desired compound (**7**) was obtained in 81% yield (8.20 g): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.54 (1H, t, J = 6.7 Hz, O−CH−O), 4.13 (1H, tt, J = 9.1 Hz, J = 4.0 Hz, H-9), 3.85−3.80 (1H, m, H_{axial}-5′), 3.82 (1H, dd, J = 10.1 Hz, J = 4.0 Hz, H-10), 3.70, 3.35 (each 1H, dt, J = 9.4 Hz, J = 6.7 Hz, H-1), 3.59 (1H, t, J = 10.1 Hz, H-10), 3.48−3.42 (1H, m, H_{equat}-5′), 2.13−2.03 (1H, m), 1.84−1.64 (3H, m), 1.55−1.48 (6H, m), 1.31−1.26 (10H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) 98.73 (O−CH−O), 67.52 (C-1), 62.23 (C-5′), 53.02 (C-9), 36.27 (C-8), 35.91 (C-10), 30.70 (C-2 and C-2′), 29.24 (2C), 29.21, 28.65, 26.63 (C-3), 25.43 (C-4′), 19.61 (C-3′); EIMS *m*/*z* 401 $[M]^+$ (1), 400 (3), 399 (2), 137 (9), 109 (5), 101 (5), 95 (11), 85 (100), 84 (8), 83 (6), 81 (12), 69 (13), 67 (16), 57 (13), 56 (21), 55 (31), 53 (9), 43 (8), 42 (6), 41 (37), 39 (9).

1-(Tetrahydro-2-pyranyloxy)-9-decyne (8). Sodium amide (1.95 g, 50.1 mmol) in THF (25 mL) was slowly added to compound **7** (8.20 g, 20.0 mmol) in THF (60 mL) at −78 °C. The reaction mixture was refluxed overnight and then neutralized with aqueous HCl (10%) (3 × 50 mL). The organic layer was separated and dried ($MgSO_4$). The yield of the protected alkynol **8** after chromatography was 98% (4.66 g): ^{1}H NMR ($CDCl_3$, 400 MHz) 4.47 (1H, t, J = 4.2 Hz, O−CH−O), 3.75 (1H, ddd, J = 11.1 Hz, J = 7.7 Hz, J = 3.4 Hz, H_{axial}-5′), 3.62, 3.28 (each 1H, dt, J = 9.4 Hz, J = 6.7 Hz, J = 3.5 Hz, H-1), 3.41−3.34 (1H, m, H_{equat}-5′), 2.07 (2H, td, J = 7.1 Hz, J = 2.6 Hz, H-8), 1.83 (1H, t, J = 2.6 Hz, C≡CH), 1.77−1.69 (1H, m), 1.63−1.57 (1H, m), 1.49 (4H, m), 1.42 (2H, quint, J = 7.1 Hz, H-7), 1.34−1.22 (m, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 98.52 (C-1′), 84.28 (C-9), 67.94 (C-1), 67.31 (C-10), 61.91 (C-5′), 30.59 (C-2 and C-2′), 29.54, 29.10, 28.47 (2C), 26.01 (C-3), 25.37 (C-4′), 19.44 (C-3′), 18.15 (C-8); EIMS *m*/*z* 237 $[M - H]^+$ (1), 101 (31), 95 (10), 86 (5), 85 (100), 84 (6), 81 (15), 79 (6), 67 (14), 56 (15), 55 (17), 41 (19).

11-(Tetrahydro-2-pyranyloxy)undec-2-yn-1-ol (9). Butyllithium (2.5 M in hexane, 9.94 mL) was added dropwise to an ice-cold solution of the protected alkynol **8** (3.94 g, 16.6 mmol) in THF (25 mL), and the mixture was stirred under inert atmosphere for 40 min. Paraformaldehyde (0.74 g, 24.9 mmol) was added in one portion, and the mixture was kept at reflux for 3 h. After cooling and addition of ice−water (20 mL), the organic material was extracted with ethyl acetate (3 × 50 mL). The ethyl acetate extracts were combined, washed with aqueous ammonium chloride (2 × 50 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The crude compound was subjected to medium-pressure liquid chromatography. The yield of **9** was 61% (2.7 g): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.51 (1H, t, J = 3.0 Hz, O−CH−O), 4.15 (2H, bs, H-1), 3.80 (1H, ddd, J = 10.9 Hz, J = 7.4 Hz, J = 3.5 Hz, H_{axial}-5′), 3.65, 3.32 (each 1H, dt, J = 9.7 Hz, 6.7 Hz, H-11), 3.48−3.40 (1H, m, H_{equat}-5′), 2.42 (1H, bs, OH), 2.14 (2H, tt, J = 7.0 Hz, J = 2.1 Hz, H-4), 1.81−1.72 (1H, m), 1.64 (1H, m), 1.56−1.38 (6H, m), 1.35−1.22 (10H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) 98.61 (O−CH−O), 85.84 (C-3), 78.45 (C-2), 67.46 (C-11), 62.04 (H-5′), 50.85 (C-1), 30.54 (C-2′), 29.49, 29.09, 28.82, 28.56, 28.41, 25.96 (C-7), 25.31 (C-9), 19.41 (C-3′), 18.52 (C-4); EIMS *m*/*z* 268 $[M]^+$ (0.14), 267 $[M - H]^+$ (0.9), 101 (36), 95 (6), 91 (4), 86 (4), 85 (100), 83 (6), 81 (11), 79 (9), 70 (5), 69 (6), 67 (14), 57 (13), 55 (7), 43 (4), 41 (7).

11-(Tetrahydro-2-pyranyloxy)-(*E*)-undec-2-en-1-ol (10). A solution of compound **9** (2.66 g, 9.93 mmol) in THF (6.5 mL) was added dropwise to a suspension of $LiAlH_4$ (0.38 g, 9.93 mmol) in THF (10 mL). The resulting mixture was stirred at room temperature for 12 h, and the reaction was then quenched by careful addition of 5 g of a mixture of $Na_2SO_4 \cdot 10H_2O$ and Celite (1:1, v:v). The slurry was filtered through a 1 cm Celite bed on a Büchner funnel. The Celite bed was washed thoroughly with hexane (3 × 20 mL). The combined organic phases were dried with $MgSO_4$, and the solvents were evaporated under reduced pressure. The yield after chromatography was 97% (2.6 g): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.58 (1H, dt, J = 15.5 Hz, J = 6.7 Hz, H-3), 5.62−5.48 (1H, m, H-2), 4.49 (1H, t, J = 2.7 Hz, H-1′), 3.96 (2H, t, J = 5.2 Hz, H-1), 3.78 (1H, ddd, J = 11.4 Hz, J = 7.7 Hz, J = 3.4 Hz, H_{axial}-5′), 3.63, 3.29 (each 1H, dt, J = 9.4 Hz, 6.8 Hz, H-11), 3.43−3.38 (1H, m, H_{equat}-5′), 2.53 (1H, t, J = 5.2 Hz, OH), 1.94 (2H, app. q, J = 6.7 Hz, H-4), 1.77−1.69 (1H, m), 1.61 (1H, m), 1.51−1.41 (6H, m), 1.28−1.20 (10H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 132.64 (C-3), 128.85 (C-2), 98.50 (O−CH−O), 67.41 (C-11), 63.20 (C-1), 61.97 (C-5′), 31.97 (C-4), 30.48 (C-2′), 29.45, 29.16 (2C), 28.87 (2C), 25.96, 25.24, 19.35 (C-3′); EIMS *m*/*z* 237 (4), 107 (5), 101 (36), 95 (10), 93 (11), 85 (100), 84 (13), 83 (8), 81 (13), 79 (14), 77 (6), 70 (9), 69 (7), 67 (21), 56 (9), 55 (27), 43 (10), 41 (29), 39 (8).

11-(Tetrahydro-2-pyranyloxy)-(*E*)-undec-2-enal (11). An excess of MnO_2 was added to a solution of **10** (2.5 g, 9.3 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred at room temperature for 2 h, and the residues containing manganese were filtered off. The yield of the protected alkenal **11** after chromatography was 63% (1.56 g): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.42 (1H, dd, J = 7.9 Hz, J = 1.5 Hz, CHO), 6.78 (1H, dt, J = 15.5 Hz, J = 6.86 Hz, H-3), 6.02 (1H, ddt, J = 15.5 Hz, J = 7.9 Hz, J = 1.5 Hz, H-2), 4.48 (1H, t, J = 3.3 Hz, O−CH−O), 3.78 (1H, ddd, J = 9.0 Hz, J = 7.2 Hz, J = 3.4 Hz, H_{axial}-5′), 3.64, 3.30 (each 1H, dt, J = 9.5 Hz, 6.9 Hz, H-11), 3.43−3.38 (1H, m, H_{equat}-5′), 2.25 (2H, q, J = 7.0 Hz, H-4), 1.77−1.70 (1H, m), 1.66−1.60 (1H, m), 1.52−1.41 (6H, m), 1.24 (10H, bs); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 193.90 (CHO), 158.82 (C-3), 132.78 (C-2), 98.67 (C-1′), 67.40 (C-11), 62.15 (C-5′), 32.53 (C-4), 30.61 (C-2′), 29.53 (s. C-10), 29.12, 29.09, 28.88, 27.62, 25.99 (C-4′), 25.31 (C-9), 19.53 (C-3′); EIMS *m*/*z* 268 $[M]^+$ (0.5), 267 $[M - H]^+$ (0.7), 107 (6), 101 (46), 95 (6), 93 (11), 85 (100), 84 (7), 83 (9), 82 (6), 81 (12), 79 (8), 70 (11), 67 (18), 57 (22), 56 (14), 55 (53), 54 (9), 43 (17), 42 (8), 39 (13), 32 (10).

1-(Tetrahydro-2-pyranyloxy)-(9*E*,11*E*)-hexadecadiene (12). 1-Pentyltriphenylphosphonium bromide (1.09 g, 2.63 mmol) was suspended in THF (4.4 mL) and diethyl ether (2.6 mL) and stirred with BuLi (1.08 M in hexane, 2.44 mL, 2.63 mmol) for 15 min. The solution was cooled to −70 °C, and the aldehyde **11** (0.7 g, 2.6 mmol), dissolved in diethyl ether (1.75 mL), was added. The mixture was stirred vigorously until the yellow coloration disappeared (5 min at −70 to −40 °C), and an additional amount of BuLi (1.08 M, 2.44 mL, 2.63 mmol) was added. The reaction mixture was then stirred at −30 °C for 5 min, whereupon a solution of hydrogen chloride in diethyl ether (1 M, 2.89 mmol, 2.89 mL) and then potassium *tert*-butoxide (0.44 g, 3.95 mmol) in 2-methyl-2-propanol (0.45 mL, 3.95 mmol) were added. The mixture was then stirred at room temperature for 2 h, washed with water until it remained neutral, and dried ($MgSO_4$). After evaporation of the solvent, the crude product (*E*,*E*-**12**:*E*,*Z*-**14**, 10:1) was subjected to medium-pressure column chromatography, yielding 61% (2.7 g) of a 10:1 mixture of the *E*,*E*-diene **12** and the *E*,*Z*-diene **-14**: ^{1}H NMR ($CDCl_3$, 400 MHz) of **12** δ 5.94 (2H, dd, J = 12.5 Hz, J = 1.7 Hz, H-10 and H-11), 5.49−5.46 (2H, m, H-9 and H-12), 4.49 (1H, s, O−CH−O), 3.81−3.76 (1H, ddd, J = 11.0 Hz, 7.3 Hz, J = 3.3, H_{axial}-5′), 3.65, 3.29 (each 1H, dt, J = 9.7 Hz, J = 6.7 Hz, H-1), 3.43−3.40 (1H, m, H_{equat}-5′), 1.97−1.96 (4H, bs), 1.76−1.74 (1H, m), 1.69−1.57 (1H, m), 1.51−1.45 (6H, m), 1.26−1.21 (14H, m), 0.83−0.80 (3H, bs, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) 132.34 (C-9 and C-12), 130.32 (C-10 and C-11), 98.82 (O−CH−O), 67.65 (C-1), 62.30 (C-5′), 32.57 (C-8 or C-13), 32.24 (C-2′), 31.57 (C-8 or C-13), 30.78 (C-14), 29.73, 29.42, 29.40 (2C), 29.14, 26.21 (C-4′), 25.50 (C-3), 22.22 (C-15), 19.68 (C-3′), 13.91 (CH_3); EIMS *m*/*z* 322 $[M]^+$ (2), 304 (8), 101 (9), 95 (17), 93 (9), 85 (100), 81 (23), 79 (15), 67 (29), 57 (10), 54 (30), 43 (11), 41 (20).

(9*E*,11*E*)-Hexadecadien-1-ol (13). Amberlyst-15 (0.23 g) was added to a solution of *E*,*E*-**12**:*E*,*Z*-**14** (10:1) (2.5 g, 7.8 mmol) in MeOH (15.5 mL). The mixture was stirred at 45 °C

for 40 min, the resin was filtered off, and the solution was dried and concentrated under reduced pressure. The yield of the 10:1 mixture of the alcohols **13** and **15** after chromatography was 97% (1.79 g): ^{1}H NMR ($CDCl_3$, 400 MHz) of **13** δ 6.02 (2H, d, J = 17.1 Hz, H-10 and H-11), 5.61−5.56 (2H, m, H-9 and H-12), 3.66 (2H, t, J = 5.3 Hz, H-1), 2.19 (1H, s, OH), 2.07 (4H, m, H-8 and H-13), 1.61−1.57 (2H, m, H-2), 1.31−1.26 (14H, m), 0.91 (3H, t, J = 5.7 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 132.5 (C-12 or C-9), 132.4 (C-12 or C-9), 130.4 (C-10 and C-11), 63.1 (C-1), 32.8 (C-2), 32.6 (C-8 or C-13), 32.3 (C-8 or C-13), 31.6 (C-14), 29.4 (3C), 29.1, 25.7 (C-3), 22.3 (C-15), 14.0 (CH_3); EIMS *m*/*z* 238 $[M]^+$ (16), 136 (12), 135 (10), 124 (8), 122 (6), 121 (5), 110 (12), 109 (15), 108 (10), 107 (7), 98 (9), 97 (7), 96 (22), 95 (9), 94 (23), 93 (21), 92 (7), 91 (17), 83 (9), 82 (31), 81 (45), 80 (40), 79 (50), 77 (11), 68 (14), 67 (97), 66 (10), 65 (11), 57 (9), 56 (6), 55 (61), 54 (9), 53 (22), 51 (10), 41 (63), 39 (18), 31 (100).

Urea Inclusion Complexes. In a typical experiment impure (9*E*,11*E*)-hexadecadien-1-ol (**13**) (91% isomeric purity) (1.25 g, 5.25 mmol) was mixed with a hot solution of urea (1.89 g, 31.5 mmol) in methanol (10 mL). The resulting solution was allowed to cool to room temperature before it was left in the refrigerator overnight. The resulting crystals were rapidly filtered off. The clathrate was dissolved in brine and extracted with diethyl ether. Drying and concentration gave a mixture (1.2 g) containing 97% of the (*E*,*E*)-isomer together with 3% of the (*E*,*Z*)-isomer. This mixture was subjected to medium-pressure liquid chromatography, using silica gel impregnated with 10% of silver nitrate and yielding the (*E*,*E*)-isomer in >99% isomeric purity.

(9*E*,11*E*)-Hexadecadienal (1). The alcohol **13** (1.5 g, 6.3 mmol) was stirred overnight with a slurry of pyridinium dichromate (4.72 g, 12.6 mmol) in CH_2Cl_2 (12 mL). The mixture was then diluted with hexane and filtered through Celite. The filtrate was concentrated and subjected to medium-pressure column chromatography, yielding 71% (1.0 g) of the *E*,*E*-dienal **1** in an isomeric purity of >99%: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.75 (1H, t, J = 1.76 Hz, CHO), 6.01 (2H, d, J = 17 Hz, H-10 and H-11), 5.6−5.55 (2H, m, H-9 and H-12), 2.40 (2H, td, J = 7.3 Hz, J = 1.85 Hz, H-2), 2.1 (4H, m, H-8 and H-13), 1.6 (2H, quint, J = 7.3 Hz, H-3), 1.3−1.25 (12H, m), 0.9 (3H, t, J = 5.7 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 202.90 (CHO), 132.4 (C-9 or C-12), 132.3 (C-9 or C-12), 130.4 (C-10 and C-11), 43.89 (C-2), 32.5 (C-8 or C-13), 32.3 (C-8 or C-13), 31.6 (C-14), 29.5, 29.4 (2C), 29.1, 22.3 (C-15), 22.03 (C-3), 14.03 (CH_3); EIMS *m*/*z* 236 $[M]^+$ (69), 150 (12), 133 (11), 124 (15), 123 (10), 122 (11), 121 (15), 111 (14), 110 (19), 109 (13), 98 (18), 97 (13), 96 (31), 95 (32), 94 (13), 93 (18), 91 (17), 82 (22), 81 (55), 80 (23), 79 (46), 77 (18), 69 (14), 68 (24), 67 (100), 65 (16), 55 (54), 54 (33), 44 (15), 43 (29), 42 (22), 41 (75); HREIMS *m*/*z* 236.214550 (calcd for $C_{16}H_{28}O$, 236.214016).

1-(Tetrahydro-2-pyranyloxy)-(9*E*,11*Z*)-hexadecadiene (14). 1-Pentyltriphenylphosphonium bromide (1.14 g, 2.76 mmol) in THF (3.5 mL) was added to a solution of potassium bis[trimethylsilyl]amide (0.5 M in toluene, 19.56 mL, 9.78 mmol). After refluxing for 1 h the reaction mixture was cooled to −78 °C, and a solution of the aldehyde **11** (1.1 g, 4.14 mmol) in THF (3.5 mL) was added dropwise. The mixture was then stirred for 3 h, before it was poured into aqueous NH_4Cl (10%, 20 mL). The organic phase was separated and the aqueous phase extracted with hexane. The combined organic phases were dried with $MgSO_4$. After evaporation, the crude product (*E*,*Z*-**14**:*E*,*E*-**12**, 20:1) was subjected to medium-pressure column chromatography, yielding 62% (0.82 g) of a 20:1 mixture of the *E*,*Z*-diene **14** and the *E*,*E*-diene **12**: ^{1}H NMR ($CDCl_3$, 400 MHz) of **14** δ 6.27 (1H, ddq, J = 15.2 Hz, J = 11.0 Hz, J = 1.24 Hz, H-11), 5.91 (1H, t, J = 10.9 Hz, H-10), 5.62 (1H, dt, J = 15.0 Hz, J = 7.3 Hz, H-12), 5.27 (1H, dt, J = 11.0 Hz, J = 7.3 Hz, H-9), 4.44 (1H, t, J = 2.4 Hz, O−CH−O), 3.85 (1H, ddd, J = 11.0 Hz, 7.3 Hz, J = 3.3, H_{axial}-5′), 3.71, 3.34 (each 1H, dt, J = 9.7 Hz, J = 6.7 Hz, H-1), 3.50−3.44 (1H, m, H_{equat}-5′), 2.14 (2H, q, J = 7.3 Hz, H-8), 2.06 (2H, q, J = 7.3 Hz, H-13), 1.84−1.76 (1H, m), 1.72−1.66 (1H, m), 1.59−1.47 (6H, m), 1.34−1.27 (14H, m), 0.88 (3H, t, J = 7.2 Hz, H-16); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 134.55 (C-9 or C-12), 129.97 (C-9 or C-12), 128.6 (C-10 or C-11), 125.57 (C-10 or C-11), 98.78 (C-1′), 67.61 (C-1), 62.25 (C-5′), 32.82 (C-8), 31.85 (C-2′), 30.73 (C-14), 29.68, 29.39 (2C), 29.35, 29.13, 27.33 (C-13), 26.18 (C-4′), 25.46 (C-3), 22.26 (C-15), 19.64 (C-3′), 13.91 (CH_3); EIMS *m*/*z* 322 $[M]^+$ (1), 238 (7), 124 (10), 122 (9), 101 (17), 96 (15), 85 (100), 81 (21), 78 (14), 67 (43), 55 (24), 54 (15), 43 (14), 41 (26).

(9*E*,11*Z*)-Hexadecadien-1-ol (15). The alcohol **15** was prepared from compound **14**/compound **12** (20:1) by the same procedure (see above) as was used to hydrolyze compound **12**/**14** (10:1) to compound **13.** The yield was 97%: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.27 (1H, ddq, J = 15.5 Hz, J = 11.0 Hz, J = 1.24 Hz, H-11), 5.92 (1H, t, J = 11.0 Hz, H-10), 5.62 (1H, dt, J = 15.26, J = 7.0 Hz, H-12), 5.27 (1H, dt, J = 11.0 Hz, 7.3 Hz, H-9), 3.60 (2H, t, J = 6.7 Hz, H-1), 2.15 (1H, s, OH), 2.14 (2H, q, J = 7.3 Hz, H-8), 2.06 (2H, q, J = 7.0 Hz, H-13), 1.53 (2H, q, J = 6.7 Hz, H-2), 1.36−1.28 (14H, m), 0.88 (3H, t, J = 7.0 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 134.52 (C-9 or C-12), 130.0 (C-9 or C-12), 128.56 (C-10 or C-11), 125.62 (C-10 or C-11), 62.95 (C-1), 32.80 (C-2 or C-8), 32.73 (C-2 or C-8), 31.86 (C-14), 29.41, 29.33 (2C), 29.10, 27.35 (C-13), 25.69 (C-3), 22.27 (C-15), 13.89 (CH_3); EIMS *m*/*z* 238 $[M]^+$ (8), 135 (10), 110 (12), 109 (15), 108 (10), 107 (7), 98 (9), 97 (7), 96 (22), 95 (9), 94 (23), 93 (21), 92 (7), 91 (17), 83 (9), 82 (31), 81 (45), 80 (40), 79 (50), 77 (11), 68 (14), 67 (97), 66 (10), 65 (11), 57 (9), 56 (6), 55 (61), 54 (9), 53 (22), 51 (10), 45 (7), 44 (5), 43 (18), 42 (7), 41 (42), 39 (10), 31 (100).

(9*E*,11*Z*)-Hexadecadienal (2). The dienal **2** was prepared from the dienol **15** as described before (see preparation of compound **1** from **13**) in an isomeric purity of >99% and 70% yield: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.75 (1H, t, J = 1.8 Hz, CHO), 6.28 (1H, ddq, J = 15.0 Hz, J = 11.0 Hz, J = 1.24 Hz, H-11), 5.92 (1H, t, J = 11.0 Hz, H-10), 5.63 (1H, dt, J = 15.0 Hz, J = 7.0 Hz, H-12), 5.29 (1H, dt, J = 11 Hz, J = 7.6 Hz, H-9), 2.40 (2H, td, J = 7.3 Hz, J = 1.8 Hz, H-2), 2.15 (2H, q, J = 7.3 Hz, H-8), 2.07 (2H, q, J = 7.0 Hz, H-13), 1.63 (2H, quint, J = 7.26 Hz, H-3), 1.38−1.22 (12H, m), 0.89 (3H, t, J = 7.0 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 202.93 (CHO), 134.45 (C-9 or C-12), 130.17 (C-9 or C-12), 128.52 (C-10 or C-11), 125.65 (C-10 or C-11), 43.89 (C-2), 32.81 (C-8 or C-14), 31.89 (C-8 or C-14), 30.93, 29.29, 29.19, 29.09, 27.38 (C-13), 22.31 (C-15), 22.04 (C-3), 13.96 (CH_3); EIMS *m*/*z* 236 $[M]^+$ (29), 175 (10), 151 (10), 147 (12), 137 (15), 135 (25), 124 (10), 111 (12), 110 (20), 109 (26), 108 (13), 107 (13), 98 (12), 97 (16), 96 (32), 95 (34), 94 (17), 93 (13), 91 (16), 83 (16), 82 (39), 81 (82), 80 (26), 79 (50), 77 (10), 69 (14), 68 (26), 67 (100), 66 (17), 55 (34), 55 (48), 54 (41), 45 (20), 4 (19), 42 (75); HREIMS *m*/*z* 236.214348 (calcd for $C_{16}H_{28}O$, 236.214016).

11-(Tetrahydro-2-pyranyloxy)undec-2-ynal (16). The compound **16** was prepared from compound **9** as described before (see oxidation of compound **10** to compound **11**) in 63% yield: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.15 (1H, s, CHO), 4.54 (1H, t, J = 3.9 Hz, OCHO), 3.86−3.81 (1H, m, H_{axial}-5′), 3.70, 3.36 (each 1H, dt, J = 9.2 Hz, J = 7.0 Hz, H-1), 3.49−3.45 (1H, m, H_{equat}-5′), 2.38 (2H, t, J = 7.0 Hz, H-4),1.82−1.77 (1H, m), 1.71−1.66 (1H, m), 1.58−1.51 (6H, m), 1.39−1.29 (10H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 177.31 (C-1), 98.85 (C-1′), 98.80 (C-3), 81.64 (C-2), 67.58 (C-11), 62.30 (C-5′), 30.68 (C-2′), 29.62, 29.18, 28.87, 28.69, 27.43 (C-5), 26.10 (C-4′), 25.40 (C-9), 19.59 (C-3′), 19.06 (C-4); EIMS *m*/*z* 266 $[M]^+$ (2), 105 (14), 101 (22), 100 (8), 95 (15), 94 (6), 93 (6), 91 (6), 85 (7), 85 (100), 84 (8), 81 (13), 80 (9), 79 (21), 69 (6), 68 (7), 67 (19), 66 (10), 64 (8), 57 (11), 56 (25), 55 (13), 55 (14), 53 (14), 52 (8), 49 (6), 44 (5), 43 (12), 41 (9), 41 (65), 40 (16), 39 (10), 38 (23).

1-(Tetrahydro-2-pyranyloxy)-(*E*)-hexadec-11-en-9-yne (17). Compound **17** was prepared from compound **16** as described before (see preparation of compound **12** from **11**). The process yielded 61% of a mixture containing 7:1 of *E*-**17** and *Z*-**20**: ^{1}H NMR ($CDCl_3$, 400 MHz) of **17** δ 6.03 (1H, dt, J = 15.8 Hz, J = 7.1 Hz, H-12), 5.44 (1H, dq, J = 15.8 Hz, J = 1.8 Hz, H-11), 4.57 (1H, dd, J = 4.4 Hz, J = 2.6 Hz, OCHO), 3.87 (1H, ddd, J = 11.0 Hz, J = 7.4 Hz, J = 3.5 Hz, H_{axial}-5′), 3.73, 3.38 (each 1H, dt, J = 9.5 Hz, 6.9 Hz, H-1), 3.52−3.47 (1H, m, H_{equat}-5′), 2.27 (2H, td, J = 7.0 Hz, J = 1.8 Hz, H-8), 2.07 (2H, q, J = 7.0 Hz, H-13), 1.86−1.79 (1H, m), 1.71 (1H,

m), 1.61−1.47 (6H, m), 1.39−1.32 (14H, m), 0.88 (3H, t, J = 7.1 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.33 (C-12), 109.81 (C-11), 98.85 (OCHO), 88.65 (C-9), 79.20 (C-10), 67.66 (C-1), 62.34 (C-5′), 32.66 (C-13), 30.98 (C-14), 30.79, 29.75, 29.37, 29.12, 28.87 (2C), 26.22 (C-4′), 25.52 (C-3), 22.16 (C-15), 19.71 (C-3′), 19.35 (C-8), 13.89 (CH_3); EIMS m/z 320 $[M]^+$ (5), 249 (11), 122 (19), 121 (12), 95 (9), 91 (15), 85 (100), 79 (29), 78 (14), 77 (20), 67 (16), 57 (21), 56 (20), 55 (19), 43 (18), 41 (13).

Dicyclohexylborane. The temperature was kept between −5 and −10 °C, while a solution of borane in tetrahydrofuran (1 M, 3.1 mL, 3.1 mmol) was added slowly over a period of 30 min to a solution of cyclohexene (0.51 g, 6.2 mmol) in THF (3 mL). The resultant milky solution was stirred at 0 to −10 °C for 2 h and then used as such in the next step.

1-(Tetrahydro-2-pyranyloxy)-(9*Z*,11*E*)-hexadecadiene (18). A solution of compound **17** (0.45 g, 1.4 mmol) in THF (2.5 mL) was added dropwise to the above dicyclohexylborane solution (3.1 mmol) at −20 °C. The suspension was stirred at approximately −15 °C for 2 h and then allowed to reach room temperature. After 2 h of stirring at room temperature the precipitate of dicyclohexylborane had disappeared. Glacial acetic acid (1.3 mL) was then added to the mixture, which was stirred overnight at 45 °C. Oxidation of the resulting dicyclohexylborinate was achieved by addition of sodium hydroxide (6 M, 5 mL) followed by dropwise addition of hydrogen peroxide (35%, 1.4 mL) at a rate maintaining the reaction mixture at 30−35 °C. The mixture was stirred for an additional 30 min and was then poured into ice−water (15 mL), extracted with hexane (4 × 30 mL), dried ($MgSO_4$), and chromatographed, providing the desired compound **18** in 65% yield: ^1H NMR ($CDCl_3$, 400 MHz) δ 6.31−6.25 (1H, m, H-11), 5.92 (1H, t, J = 10.9 Hz, H-10), 5.64 (1H, dt, J = 15 Hz, J = 7.2 Hz, H-12), 5.34−5.24 (1H, m, H-9), 4.56 (1H, bs, OCHO), 3.86 (1H, ddd, J = 11.0 Hz, J = 7.7 Hz, J = 3.4 Hz, H_{axial}-5′), 3.71, 3.36 (each 1H, dt, J = 9.6 Hz, J = 7.0 Hz, H-1), 3.51−3.46 (1H, m, H_{equat}-5′), 2.15 (2H, q, J = 7.0 Hz, H-8 or H-13), 2.08 (2H, q, J = 7.0 Hz, H-8 or H-13), 1.85−1.79 (1H, m), 1.73−1.68 (1H, m), 1.59−1.52 (6H, m), 1.37−1.29 (14H, m), 0.88 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 134.65 (C-9 or C-12), 130.06 (C-9 or C-12), 128.57 (C-10 or C-11), 125.58 (C-10 or C-11), 98.83 (C-1′), 67.68 (C-1), 62.34 (C-5′), 32.55 (C-2′ or C-13), 31.55 (C-2′ or C-13), 30.77 (C-14), 29.73, 29.70, 29.44 (2C), 29.20, 27.68 (C-8), 26.21 (C-4′), 25.49 (C-3), 22.27 (C-15), 19.70 (C-3′), 13.94 (CH_3).

(9*Z*,11*E*)-Hexadecadien-1-ol (19). The alcohol **19** was prepared from compound **18** in analogy with compound **13** in 97% yield: ^1H NMR ($CDCl_3$, 400 MHz) δ 6.30−6.23 (1H, m, H-11), 5.92 (1H, t, J = 10.9 Hz, H-10), 5.63 (1H, dt, J = 15 Hz, J = 7.0 Hz, H-12), 5.59−5.23 (1H, m, H-9), 3.60 (2H, t, J = 6.64 Hz, H-1), 2.13 (2H, q, J = 7.0 Hz, H-13), 2.07 (2H, q, J = 7.0 Hz, H-8), 2.02 (1H, bs, OH), 1.57−1.50 (2H, m), 1.30−1.25 (14H, bs), 0.88 (3H, t, J = 7.0 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 134.62 (C-9 or C-12), 129.96 (C-9 or C-12), 128.57 (C-10 or C-11), 125.54 (C-10 or C-11), 62.96 (C-1), 32.72 (C-2), 32.52 (C-13), 31.51 (C-14), 29.66, 29.42, 29.34, 29.13, 27.61 (C-8), 25.68 (C-3), 22.23 (C-15), 13.90 (CH_3); EIMS m/z 238 $[M]^+$ (38), 135 (14), 121 (10), 110 (13), 109 (13), 108 (8), 107 (10), 96 (18), 95 (26), 94 (42), 93 (21), 91 (37), 85 (20), 81 (20), 80 (42), 79 (35), 67 (100), 55 (42), 54 (36), 43 (56), 31 (63).

(9*Z*,11*E*)-Hexadecadienal (3). The dienal **3** was prepared from compound **19** as described before for the preparation of compound **1** (from compound **13**) in an isomeric purity of >99% and 71% yield: ^1H NMR ($CDCl_3$, 400 MHz) δ 9.75 (1H, t, J = 1.81 Hz, CHO), 6.31−6.23 (1H, m, H-11), 5.91 (1H, t, J = 11 Hz, H-10), 5.61 (1H, dt, J = 15.0 Hz, J = 7.0 Hz, H-12), 5.6−5.23 (1H, m, H-9), 2.40 (2H, td, J = 7.0 Hz, J = 1.83 Hz, H-2), 2.1 (2H, q, J = 7.0, H-13 or H-8), 2.01 (2H, q, J = 7.0 Hz, H-8 or H-13), 1.31−1.24 (14H, m), 0.88 (3H, J = 7.0 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 202.91 (CHO), 134.6 (C-9 or C-12), 129.95 (C-9 or C-12), 128.6 (C-10 or C-11), 43.88 (C-2), 32.5 (C-13), 31.85 (C-14), 29.5, 29.4, 29.3, 29.1, 27.5 (C-8), 22.27 (C-15), 22.01 (C-3), 13.93 (s. CH_3); EIMS m/z 236 $[M]^+$ (38), 121 (10), 95 (16), 94 (7), 93 (7), 91 (10), 83 (10), 82 (16), 81 (25), 80 (8), 79 (16), 77 (9), 68 (7), 67 (36), 66 (6), 65 (8), 57 (16), 55 (7), 53 (15), 44 (64), 44 (36), 42 (26), 41 (100), 39 (15), 32 (19); HREIMS m/z 236.220520 (calcd for $C_{16}H_{28}O$, 236.214016).

1-(Tetrahydro-2-pyranyloxy)-(*Z*)-hexadec-11-en-9-yne (20). Compound **20** was prepared, from the aldehyde **16**, in the same manner as compound **14** was prepared from compound **11**. The product obtained was a 62% yield of a mixture containing 20:1 *Z*-**20** and *E*-**17**: ^1H NMR ($CDCl_3$, 400 MHz) of **20** δ 5.78 (1H, dt, J = 10.7 Hz, J = 7.3 Hz, H-12), 5.40 (1H, bd, J = 10.7 Hz, H-11), 4.55 (1H, dd, J = 4.4 Hz, J = 2.4 Hz, OCHO), 3.87−3.82 (1H, m, H_{axial}-5′), 3.70, 3.35 (each 1H, dt, J = 9.7 Hz, J = 6.7 Hz, H-1), 3.50−3.45 (1H, m, H_{equat}-5′), 2.32 (2H, td, J = 7.0 Hz, J = 1.8 Hz, H-8), 2.26 (2H, td, J = 7.2 Hz, J = 1.2 Hz, H-13), 1.84−1.76 (1H, m), 1.68 (1H, m), 1.6−1.45 (6H, m), 1.4−1.3 (14H, m), 0.88 (3H, t, J = 6.7 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.58 (C-12), 109.26 (C-11), 98.80 (OCHO), 94.36 (C-9), 79.10 (C-10), 67.62 (C-1), 62.31 (C-5′), 31.01 (C-14), 30.74, 29.71, 29.68, 29.36, 29.07, 28.81, 28.78 (C-13), 26.18 (C-4′), 25.46 (C-3), 22.2 (C-15), 19.67 (C-3′), 19.47 (C-8), 13.89 (CH_3); EIMS m/z 320 $[M]^+$ (7), 122 (11), 121 (6), 119 (9), 95 (9), 93 (10), 91 (21), 85 (100), 81 (10), 80 (11), 79 (33), 78 (12), 77 (15), 67 (21), 65 (6), 57 (13), 56 (12), 55 (22), 43 (16), 41 (55), 39 (7).

1-(Tetrahydro-2-pyranyloxy)-(9*Z*,11*Z*)-hexadecadiene (21). Compound **21** was prepared from compound **20**, as described before for the preparation of compound **18** from **17**, and in 65% yield: ^1H NMR ($CDCl_3$, 400 MHz) δ 6.21 (2H, bd, J = 9.5 Hz, H-10 and H-11), 5.40 (2H, bq, J = 6.6 Hz, H-10 and H-11), 4.54 (1H, t, J = 2.7 Hz, OCHO), 3.83 (1H, ddd, J = 11.1 Hz, J = 7.6 Hz, J = 3.3 Hz, H_{axial}-5′), 3.69, 3.35 (each 1H, dt, J = 9.4 Hz, J = 7.0 Hz, H-1), 3.43−3.49 (1H, m, H_{equat}-5′), 2.16−2.10 (2H, m, H-8 or H-13), 1.98−1.91 (2H, m, H-8 or H-13), 1.83−1.75 (1H, m), 1.71−1.64 (1H, m), 1.59−1.45 (6H, m), 1.35−1.25 (14H, bs), 0.88 (3H, t, J = 6.7 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 131.9 (C-9 and C-12), 123.56 (C-10 and C-11), 98.74 (C-1′), 67.59 (C-1), 62.20 (C-5′), 31.76 (C-14), 30.73 (C-3′), 29.71, 29.58, 29.53, 29.38, 29.17, 28.92, 27.40 (C-8 or C-13), 27.13 (C-8 or C-13), 26.19 (C-4′), 25.48 (C-3), 19.63 (C-3′), 13.86 (CH_3); EIMS m/z 322 $[M]^+$ (2), 238 (4), 135 (4), 109 (8), 95 (7), 85 (100), 81 (19), 78 (14), 67 (44), 55 (17), 54 (23), 41 (14), 41 (58).

(9*Z*,11*Z*)-Hexadecadien-1-ol (22). The compound **21** was deprotected, in 97% yield, to the alcohol **22** by the method used to prepare compound **13** from **12**: ^1H NMR ($CDCl_3$, 400 MHz) δ 6.22 (2H, bd, J = 9.8 Hz, H-10 and H-11), 5.41 (2H, bq, J = 7.8 Hz, H-9 and H-12), 3.60 (2H, t, J = 6.6 Hz, H-1), 2.18−2.11 (4H, m, H-8 and H-13), 1.65 (1H, bs, OH), 1.52 (2H, quint, J = 6.7 Hz, H-2), 1.39−1.28 (14H, bs), 0.88 (3H, t, J = 6.7 Hz, H-16); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 132.12 (C-9 or C-12), 131.94 (C-9 or C-12), 123.54 (C-10 or C-11), 123.50 (C-10 or C-11), 62.95 (C-1), 32.71 (C-2), 31.76 (C-14), 29.56, 29.41, 29.33, 29.16, 27.40 (C-8 or C-13), 27.13 (C-8 or C-13), 25.67 (C-3), 22.30 (C-15), 13.91 (CH_3); EIMS m/z 238 $[M]^+$ (28), 136 (6), 121 (16), 110 (12), 109 (15), 108 (14), 107 (6), 98 (9), 96 (9), 95 (32), 94 (21), 93 (22), 91 (9), 85 (10), 83 (7), 82 (49), 81 (50), 80 (19), 79 (28), 69 (21), 68 (16), 67 (100), 66 (9), 57 (11), 55 (34), 54 (28), 53 (9), 44 (9), 42 (28).

(9*Z*,11*Z*)-Hexadecadienal (4). The dienol **22** was oxidized to the dienal **4** by PDC, as described above for the oxidation of **13** to compound **1**, in an isomeric purity of >99% and 71%yield: ^1H NMR ($CDCl_3$, 400 MHz) δ 9.75 (1H, t, J = 1.85 Hz, CHO), 6.23 (2H, bd, J = 10.0 Hz, H-10 and H-11), 5.42 (2H, bq, J = 7.8 Hz, H-9 and H-12), 2.40 (2H, td, J = 7.32 Hz, J = 1.86 Hz, H-2), 2.16 (4H, m, H-8 and H-13), 1.61 (2H, quint, J = 7.28 Hz, H-3), 1.40−1.24 (12H, m), 0.88 (3H, t, J = 7.2 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 202.92 (CHO), 132.16 (C-9 or C-12), 131.84 (C-9 or C-12), 123.66 (C-10 or C-11), 123.49 (C-10 or C-11), 43.88 (C-2), 31.78 (C-14), 29.50, 29.17, 29.08, 28.99, 27.37 (C-8 or C-13), 27.16 (C-8 or C-13), 22.32 (C-15), 22.03 (C-3), 13.94 (CH_3); EIMS m/z 236 $[M]^+$ (34), 151 (11), 148 (10), 137 (11), 135 (10), 124 (12), 123 (15), 121 (13), 111 (10), 110 (15), 109 (18), 107 (13), 98 (19), 97 (11), 96 (32), 95 (48), 94 (16), 93 (19), 91 (16), 83 (10), 82 (25), 81 (62), 80 (17), 79 (20), 77 (12), 68 (20), 68 (24), 67 (100), 55 (37), 54 (36),

53 (14), 44 (17), 43 (18), 42 (38), 41 (75); HREIMS *m/z* 236.223457 (calcd for $C_{16}H_{28}O$, 236.214016).

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