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An Expedient Synthesis of the Sugarcane Borer Pheromone Components

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Abstract: A practical synthesis of the title compounds has been developed. The salient features of the synthesis were i) use of easily accessible starting materials *viz*. aleuritic acid, 10-undecenoic acid, cyclohexanone *etc*. and ii) fixation of the required olefinic geometry *via* Wittig and acetylenic routes.

Keywords: Sugarcane pest, pheromone, total synthesis

Introduction

Sugarcane is one of the important commercial crop cultivated in various parts of India. However, the productivity of sugarcane is drastically lowered due to the damage caused by several pests [1-4]. The most important amongst the pests are the stem and top shoot, as well as the internode borers, *Chilo auricilius*, *C. sacchariphagus* and *C. indicus* and pyrilla which are of regularly occurr. The stem borers especially are cosmopolitan in nature and are widespread in Java, Formosa, Philippines, Japan, India et*c.*

Due to the concealing habit of the pests, they are not exposed to parasitation or predation by natural enemies or to contact with insecticides. Hence, effective control of these seems only possible by reducing the fertility of wild females *via* their pheromone which has been isolated [5] as a four component mixture composed of (7*Z*)-dodecenyl acetate **1**, (8*Z*)-tridecenyl acetate **2**, (9*Z*)-tetradecenyl acetate **3** and (10*Z*)-pentadecenyl acetate **4**. The best formulation for mass trapping was found to be a 8:16:1 ratio of **1**: **2**: **4**, while for communication disruption a mixture of **1**, **2**, **3** and **4** in a combination of 4:8:4:1 [5] cocktail was the most efficient.

Although an efficient pheromone-based strategy for the protection of sugar cane requires a multiple blend system of all the pheromone components, little effort has so far been directed towards their syntheses. To the best of our knowledge, only the syntheses of **1** [6-9] and **3** [10-12] have so far been reported. Earlier, we synthesised [6] the pheromone component **1**. The syntheses of the other components are reported herein.

Results and Discussion

*Synthesis of **2***

For the synthesis, 1-hexyne (**5**) was first prepared [13] by alkylation of acetylene with 1-bromobutane. For the preparation of the required C_7-synthon **7,** cycloheptanone was subjected to the Bayer-Villager reaction with HCO_3H [14] to give the hydroxy acid **6** which on bromination with

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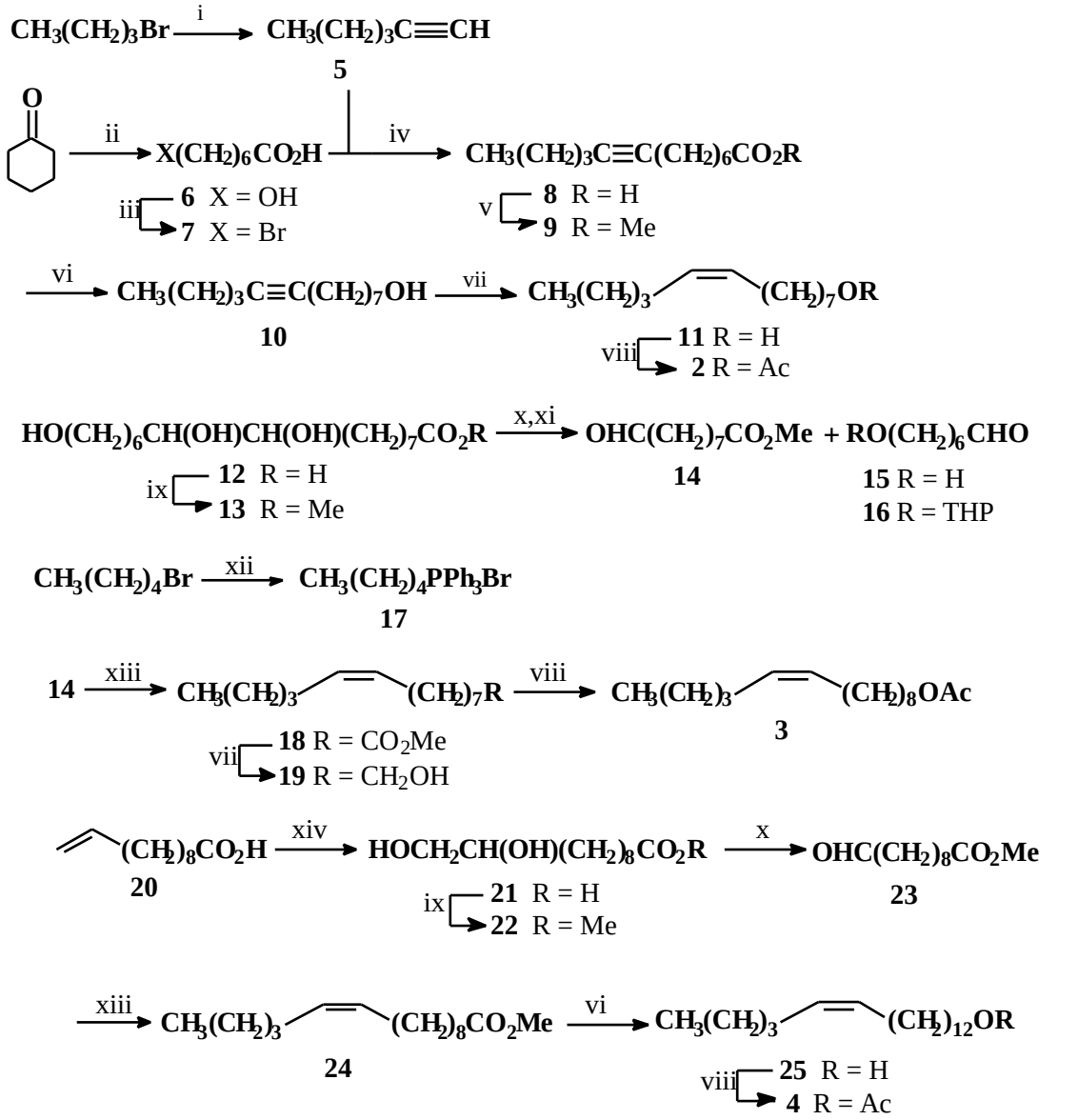
HBr furnished **7**. Alkylation of **5** with **7** using $LiNH_2$ as the base gave the acid **8** which after esterification to **9** was reduced with LAH to give the alcohol **10**. Its semi-hydrogenation over the P-2 Ni [15] catalyst gave the *cis*-alcohol **11** which was converted to the pheromone **2** by acetylation (**Scheme**).



i) NaC≡CH/NH_3, ii) H_2O_2/HCO_2H; alc. KOH, iii) HBr-H_2SO_4, iv) $LiNH_2$, v) MeOH/H^+, vi) LAH/ether, vii) H_2/P-2 Ni/EDA/EtOH, viii) Ac_2O/py, ix) MeOH/$BF_3.Et_2O$/D, x) $NaIO_4$/CH_3CN/H_2O, xi) DHP/PPTS/CH_2Cl_2, xii) Ph_3P/D, xiii) Dimsyl ion/**17**/DMSO; MeOH/H^+, xiv) H_2O_2/HCO_2H; Alcoholic KOH,

Scheme 1.

*Synthesis of **3***

Aleuritic acid (**12**), available from shellac was converted to the known ester **13** [16] and subjected to $NaIO_4$ cleavage to give the desired C_9- and C_7-components [16], **14** and **15** respectively. Although, the individual components could be separated by column chromatography, the protocol did not seem suitable for a large-scale synthesis. Hence, we attempted their separation by distillation under reduced pressure which gave the

aldehyde **14** in excellent yield. However, the high temperature required for the distillation of **15** led to substantial polymerization. Consequently, the product mixture containing **14** and **15** was directly treated with dihydropyran (DHP) in the presence of pyridinium *para*-toluenesulphonate (PPTS) to afford the pyranylated aldehyde **16** along with **14** which could be easily separated by distillation. The *Z*-selective Wittig reaction between the C_5-phosphonium salt **17** [17] with **14** in the presence of dimsyl anion as the base gave the ester **18**. Its LAH reduction to the alcohol **19** followed by acetylation furnished the pheromone **3** which was characterized by comparing its physicochemical data with those reported in the literature [12].

*Synthesis of **4***

For this synthesis, 10-undecenoic acid (**20**), easily available by cracking castor oil [18] was chosen as the starting material. Its dihydroxylation with HCO_3H [14] furnished the known [19] diol acid **21**, which was esterified to the ester **22**. After its $NaIO_4$ cleavage, the resultant aldehyde **23** was subjected to the *Z*-selective Wittig reaction with **17** to furnish the ester **24**. Its LAH reduction and subsequent acetylation furnished the pheromone **4**.

Experimental

General

All bp's and mp's were uncorrected. The IR spectra were scanned with a Perkin-Elmer 783 spectrophotometer and only the pertinent values are expressed, in cm^{-1}. The ^{1}H-NMR spectra were recorded, either with a Varian EM 360L (60 MHz) or a Bruker AC-200 (200 MHz) spectrometer, using $CDCl_3$ as the solvent. The chemical shift (δ) and coupling constant (J) values are expressed in ppm and Hz only. The GLC analyses were carried out on a Shimadzu GC-7A chromatograph fitted with a flame ionization detector and glass packed column for routine analysis and a capillary column for the determination of isomeric compositions. The mass spectra (EI) were recorded at 70 eV with a Shimadzu GC-MS QP-1000A spectrometer. Unless otherwise mentioned, the organic extracts were dried over anhydrous Na_2SO_4.

*1-Hexyne (**5**)*

Acetylene (gas) was bubbled through a stirred suspension of $NaNH_2$ [20] [prepared from Na (21.0 g, 0.98 mol) using $Fe(NO_3)_3$ (0.5 g) as the catalyst] in liquid ammonia (750 mL) for 2 h. To the resultant grey solution of NaC≡CH, 1-bromobutane (96.0 g, 0.7 mol) was added over a period of 4 h. Stirring was continued for a further 4 h, the temperature of the cooling bath raised to -30° C, kerosene (200 mL) added and the mixture left overnight. Next day, the reaction mixture was transferred into a separating funnel, washed with cold dil. HCl (2N), water, and dried over $MgSO_4$. The hexyne was distilled off (55° C) from the extract under a slow stream of Ar. Redistillation of the fraction gave pure **5**. Yield: 41.0 g (71.1%); bp: 70° C, [lit [13]. 71° C]; GLC (60° C, neat sample): R_t = 0.95 min (98%); IR: 3320, 2140 cm^{-1}; PMR: δ 0.9 (dist. t, 3H), 1.3-1.8 (m, 6H), 2.1 (s, 1H).

*6-Bromoheptanoic acid (**7**)*

To a stirred solution of performic acid [prepared by addition of 30% H_2O_2 (150 mL) to HCO_2H (300 mL) at 0° C] was added cycloheptanone (47.1 mL, 0.4 mol) over a period of 1.5 h. After 24 h, most of the HCO_3H was removed in vacuo, water (200 mL) added and the mixture extracted with $CHCl_3$ by continuous liquid-liquid extraction. Most of the solvent and excess performic acid were removed at atmospheric pressure and at 0.1 mm to give 6-hydroxyheptanoic acid (**6**). Yield 40.7 g (69.7%); IR: 3400-3000, 2800-2500, 1720 cm^{-1}; ^{1}H-NMR: δ 1.45 (br. s, partially D_2O exchangeable OH, 9H), 2.4 (t, *J* = 6 Hz, 2H), 3.60 (t, *J* = 6 Hz, 2H), 10.2 (br. s, D_2O exchangeable, 1H).

The above acid (36.5 g, 0.25 mol) was introduced into an acid mixture [prepared by slow addition of conc. H_2SO_4 (15 mL) to 48% HBr (48.1 g)] at 0° C]. After refluxing for 8 h, the mixture was brought to room temperature, diluted with water and extracted with ether. The extract was washed with water, brine, dried and concentrated. The crude product was purified by vacuum distillation to furnish pure **7**. Yield: 26.0 g (62%); bp: 120-125°C/ 0.2 mm; IR: 3400-3000, 2800-2500, 1710 cm^{-1}; ^{1}H-NMR: δ 1.3-1.9 (br. s and m, 8H), 2.4 (t, *J* = 6 Hz, 2H), 3.43 (t, *J* = 6 Hz, 2H), 11.2 (s, D_2O exchangeable, 1H).

*Methyl tridec-8-ynoate (**9**)*

To a stirred solution of $LiNH_2$ [prepared from Li (3.2 g, 0.45 mol) using $Fe(NO_3)_3$ (0.1 g) as the catalyst] in liquid ammonia (300 mL) was added the alkyne **5** (24.6 g, 0.3 mol) and the mixture stirred for 1 h. A solution of the acid **7** (20.9 g, 0.1 mol) in THF (150 mL) was then added dropwise over the course of 1 h. The reaction mixture was stirred for 4 h at the same temperature and left overnight. The residue was treated with dil. HCl (10:1) and extracted with ether. The ether layer was extracted thoroughly with 5% aqueous NaOH, then the ether layer separated and the aqueous layer acidified with dil. HCl. This was then re-extracted with ether, the new organic extract was washed with water, brine and dried. Concentration of the extract gave the crude acid **8** which was used for the next step without any purification .

Thus, a solution of the above acid in MeOH (100 mL) was refluxed in the presence of PTS (0.1 g) to furnish the ester **9** after the usual isolation and purification by column chromatography (silica gel, 5% EtOAc/hexane). Yield: 18.1 g (81%); IR: 1750, 1060, 720 cm^{-1}; ^{1}H-NMR: δ 0.9 (dist. t, 3H), 1.32 (br. s, 12H), 2.1-2.2 (m, 4H), 2.32 (t, *J* = 6 Hz, 2H), 3.5 (s, 3H).

*Tridec-8-yn-1-ol (**10**)*

Reduction of the ester **9** (9.0 g, 0.04 mol) with LAH (1.15 g, 0.03 mol) in ether (100 mL) gave pure **10**. Yield: 7.1 g (89.6%); bp: 110° C (bath)/ 0.3 mm; IR: 3440, 3005, 1660 cm^{-1}; ^{1}H-NMR: δ 0.9 (dist. t, 3H), 1.1-1.5 (br. s & m, 14H), 1.8-2.1 (m, 4H), 2.8 (s, D_2O exchangeable, 1H), 3.3-3.5 (m, 3H), 5.3-5.5 (m, 2H).

*(Z)-Tridec-8-en-1-ol (**11**)*

To a stirred suspension of nickel acetate (1.24 g, 5.0 mmol) in EtOH (50 mL), a solution of $NaBH_4$ (295.0 mg, 75.0 mmol) was added. A black colloidal suspension of P-2 Ni appeared immediately with the evolution of hydrogen. When the evolution of gas ceased, a mixture of the alkynol **10** (11.2 g, 0. 05 mol) and ethylenediamine (0.9 g) was added and the mixture stirred under a slight positive pressure of hydrogen. After the required hydrogen uptake, the mixture was diluted with hexane and passed through a pad of celite to remove the catalyst. The clear solution was concentrated and the product purified by distillation to afford **11**. Yield: 9.6 g (85%); bp: 90° C/0.3 mm; IR: 3350, 3010, 1650 cm^{-1}; ^{1}H-NMR: δ 0.95 (dist. t, 3H), 1.2-1.7 (m, 14H), 1.9 (s, D_2O exchangeable OH, 1H), 2.0-2.3 (m, 4H), 3.65 (t, *J* = 6 Hz, 2H), 5.3-5.5 (m, 2H).

*(Z)-8-Tridecenyl acetate (**2**)*

A mixture of **11** (5.94 g, 0.03 mol), Ac_2O (10.0 mL, 0.01 mol) and pyridine (15 mL) was stirred for 12 h at room temperature. Ice-cold water was added to the mixture and stirring continued for 1 h. The mixture was extracted with ether, the ether layer washed successively with water, aqueous $NaHCO_3$, water, aqueous HCl, water and brine and finally dried. Removal of the solvent followed by distillation furnished pure **2**. Yield: 6.0 g (83%); bp: 130° (bath) C/0.3 mm; GLC (3% OV-17, 40 mL N_2/min, temp. 180° C): R_t = 5.04 min (98%); IR: 3010, 1740, 1240 cm^{-1}; ^{1}H-NMR: δ 0.9 (dist. t, 3H), 1.3 (br. s, 14H), 2.0-2.3 (m containing a s at δ 2.1, 7H), 4.3 (t, *J* = 6 Hz, 2H), 5.2-5.5 (m, 2H).

*Methyl aleuritate (**13**)*

A solution of aleuritic acid (**12**) (76.0 g, 0.25 mol) in MeOH (300 mL) containing $BF_3.Et_2O$ (15 mL) was refluxed for 4 h. Most of the solvent was removed in vacuo, the residue taken up in ether and the ether layer washed with water, brine, dried and concentrated. The product was purified by chromatography (silica gel, 0-10% EtOAc/hexane) to furnish **13**. Yield: 62.8 g (79.5%); mp: 75-78°C, (lit. [16] mp: 73° C); IR: 3440, 1750 and 1480 cm^{-1}; ^{1}H-NMR: δ 1.32 (br. s, 22H), 2.21 (t, *J* = 7 Hz), 3.68 (t, *J* = 7 Hz, 2H), 3.7 (s, 3H), 3.8-4.0 (m, 2H).

*Methyl 8-formyloctanoate (**14**)*

To a cooled (0° C) and stirred solution of **13** (30.4 g, 0.1 mol) in a mixture of CH_3CN-H_2O (6:4, 200 mL) was added $NaIO_4$ (22.0 g, 0.1 mol) in portions. The mixture was stirred for 30 min and then filtered to remove $NaIO_3$. The filtrate was then extracted with $CHCl_3$, the extract washed with water, brine, dried and evaporated in vacuo. The residue was distilled under reduced pressure to give the pure ester **14**. However, the other required aldehyde component **15** could not be distilled and decomposed at high temperature. Yield: 16.17 g (87%); bp: 55-60° C/0.05 mm, (lit. [21] bp: 86-92° C/0.2 mm); IR: 2740, 1750, 1720 cm^{-1}; ^{1}H-NMR: δ 1.3 (s, 10H), 2.0-2.6 (m, 4H), 3.6 (s, 3H), 9.7 (t, *J* = 1.5 Hz, 1H).

*Pentyltriphenylphosphonium bromide (**17**)*

A solution of triphenylphosphine (262.0 g, 1.0 mol) and 1-bromopentane (151.0 g, 1.0 mol) in CH_3CN (500 mL) was refluxed for 30 h. After removing most of the solvent, benzene (300 mL) was added and the mixture refluxed for 3 h. After cooling, the upper layer was decanted to remove the unreacted reactants, the separated white crystalline solid was collected, washed with benzene and dried under vacuum (0.1 mm) to afford **17**. Yield: 367.0 g (88.8%), mp 165° C, (lit. [17] mp: 167-168°C).

*Methyl (Z)-9-tetradecenoate (**18**)*

The aldehyde **14** (11.2 g, 0.06 mol) was reacted with the phosphorane generated from the phosphonium salt **17** (27.2 g, 0.066 mol) using a dimsyl ion as the base (0.072 mol) in DMSO (100 mL). Subsequent work-up followed by column chromatography of the residue (silica gel, 0-10% EtOAc/hexane) gave **18**. Yield: 7.5 g (52%); bp: 140° C (bath)/ 0.5 mm; IR: 3010, 1745, 1650 cm^{-1}; ^{1}H-NMR: δ 0.9 (dist. t, 3H), 1.3 (br. s, 14H), 2.0-2.5 (m, 6H), 3.65 (s, 3H), 5.35 (t, *J* = 7 Hz, 2H).

*(Z)-9-Tetradecen-1-ol (**19**)*

To a stirred suspension of $LiAlH_4$ (1.14 g, 0.03 mol) in anhydrous ether (100 mL) compound **18** (7.2 g, 0.03 mol) in ether (50 mL) was slowly added. The mixture was refluxed untill the completion of the reaction (*cf*. TLC, 8 h)

and quenched by dropwise addition of aqueous saturated Na_2SO_4 solution (7-8 mL). The organic layer was separated from the white granular solid which was thoroughly washed with ether. After drying, the organic layer was concentrated and the resulting alcohol **19** purified by evaporative distillation. Yield: 5.5 g (86.5%); bp: 125° C/0.3 mm; IR: 3330, 3010, 1640, 1080 cm^{-1}; ^{1}H-NMR: δ 0.9 (dist. t, 3H), 1.3 (br. s, 16H), 1.5 (s, D_2O exchangeable, 1H), 1.8-2.2 (m, 4H), 3.45 (t, *J* = 7 Hz, 2H), 5.5 (t, *J* = 7 Hz, 2H).

*(Z)-9-Tetradecenyl acetate (**3**)*

A mixture of **19** (4.24 g, 0.02 mol) and Ac_2O (15 mL) in pyridine (10 mL) was stirred for 12 h at room temperature. Water was added to the mixture which was stirred for another 1 h and extracted with ether. The ether layer was washed with 5% aqueous HCl, water, 10% aqueous $NaHCO_3$, water and brine. After drying, the extract was concentrated in vacuo and the residue distilled to obtain pure **3**. Yield: 4.2 g (83%); bp: 130° C/0.1 mm; GLC (3% OV-17, 40 mL N_2/min, temp. 180° C): R_t = 7.4 min (96%); GLC (capillary, OV-17, 50 M x 0.25 mm, split (1:100), 2 mL N_2/min, temp. 210° C): R_t = 13.2 min; IR: 3020, 1740, 1650, 1240 cm^{-1}; ^{1}H-NMR: δ 0.9 (dist. t, 3H), 1.3 (br. s, 16H), 1.9-2.3 (m containing a s at δ 2.1, 7H), 4.05 (t, *J* = 7 Hz, 2H), 5.2-5.5 (m, 2H). Anal. Calcd. for $C_{16}H_{30}O_2$: C 75.6, H 11.8; Found: C 75.5, H 11.9.

*Methyl 10,11-dihydroxyundecanoate (**22**)*

A solution of HCO_3H [prepared from 30% H_2O_2 (25 mL) and HCO_2H (15 mL) at 0° C] was slowly added to 10-undecenoic acid (**20**) (18.4 g, 0.1 mol). The reaction mixture was stirred for 8 h at 40° C and subsequently at room temperature overnight. The mixture was distilled in vacuo (10 mm), the residue diluted with water and extracted with ether. The ether layer was washed with water, dried ($MgSO_4$) and concentrated.

The residue was treated with 5% aqueous KOH (100 mL) and heated on a steam bath for 1 h, cooled and poured into excess cold dil. HCl (1N) under vigorous stirring (maintaining the temperature ~20° C). The mixture was extracted with ether which was washed with water, dried and concentrated to give the crude diol acid **21** which was recrystallized from EtOH/H_2O. Yield: 13.2 g (55%); mp: 86-87° C, (lit. [19] mp: 84-85° C); IR: 3500-3300, 1710, 1460 cm^{-1}; ^{1}H-NMR: δ 1.3 (br. s, 14H), 1.9-2.4 (m partially D_2O exchangeable, 4H), 3.5-3.8 (m, 3H), 9.8 (s, D_2O exchangeable, 1H).

Esterification of **21** (13.0 g, 0.06 mol) with MeOH (100 mL) in the presence of $BF_3.Et_2O$ (5 mL) gave the diol-ester **22**. A part of this was distilled to prepare an analytical sample. Yield: 6.0 g (~ quant.); bp: 145° (bath) C/0.2 mm; IR: 3450, 1750 cm^{-1}; ^{1}H-NMR: δ 1.33 (m, 14H), 2.2-2.5 (m, 2H), 3.2-3.7 (m, partially D_2O exchangeable, 5H), 3.8 (s, 3H). Anal. Calcd. for $C_{12}H_{24}O_4$: C 62.03, H 10.41; Found: C 62.12, H 10.31.

*Methyl 9-formylnonanoate (**23**)*

The diol **22** (11.6 g, 0.05 mol) was cleaved with $NaIO_4$ (11.0 g, 0.05 mol) in CH_3CN (50 mL)-CH_2Cl_2 (50 mL)-H_2O (10 mL) to furnish the aldehyde **23** after the usual isolation. The product aldehyde **23** was purified by distillation. yield: 9.8 g (84.5%); bp: 100° C/0.5 mm (lit. [19] bp: 120-121° C/0.3 mm); IR: 2950, 2870, 2730, 1750, 1730 cm^{-1}; PMR: δ 1.1-1.9 (m, 12H), 2.0-2.4 (m, 4H), 3.7 (s, 3H), 9.1 (t, *J* = 1.5 Hz, 1H). Anal. Calcd. for $C_{11}H_{20}O_3$: C 66.0, H 10.1; Found: C 65.8, H 9.9.

*Methyl (10Z)-pentadecenoate (**24**)*

As described earlier, the Wittig reaction between the aldehyde **23** (9.0 g, 0.045 mol) and the phosphorane generated from **17** (20.7 g, 0.05 mol) using a dimsyl ion as the base (0.054 mol) in DMSO (50 mL) and subsequent work-up gave **24**. The ester was purified by column chromatography over silica gel (10% EtOAc/hexane). Yield: 5.8 g (51%); bp: 135-140° C (bath)/1 mm; GLC (3% OV-17, 180° C): R_t = 7.2 min (98%); IR: 3010, 2950, 2870, 1745 cm^{-1}; ^{1}H-NMR: δ 0.9 (dist. t, 3H), 1.3 (br. s, 16H), 2.0-2.4 (m, 4H), 2.3 (t, *J* = 6 Hz, 2H), 3.59 (s, 3H), 5.2-5.3 (m, 2H).

*(Z)-Pentadec-10-en-1-ol (**25**)*

Reduction of **24** (5.0 g, 0.02 mol) with LAH (0.5 g, 0.026 mol) in ether (100 mL) gave the alcohol **25**. Yield: 3.6 g (80%); bp: 110-120° C/0.3 mm; IR: 3350, 3010, 1660, 1070 cm^{-1}; ^{1}H-NMR: δ 0.9 (dist. t, 3H), 1.33 (br. s, 18H), 1.62 (s, D_2O exchangeable, 1H), 1.8-2.2 (m, 4H), 3.68 (t, *J* = 6 Hz, 2H), 5.33 (t, *J* = 5 Hz, 2H).

*(Z)-Pentadec-10-en-1-yl acetate (**4**)*

Acetylation of **25** (3.4 g, 0.015 mol) with Ac_2O (8.0 mL) and pyridine (12.0 mL) gave the pheromone **4**. yield: 3.3 g (82%); bp: 110° C (bath)/0.5 mm; GLC (180° C): R_t = 9.6 min (96%); IR: 3000, 1740, 1240 cm^{-1}; PMR: δ 0.85 (dist. t, 3H), 1.32 (br. s, 18H), 1.95 (s, 3H), 2.0-2.2 (m, 4H), 3.8-4.1 (m, 2H), 5.2-5.3 (m, 2H).

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Sample Availability: Samples available from the authors.