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Article

Synthesis of the Minor Sex Pheromone Component of Two Brazilian Soybean Stink Bugs (Het.: Pentatomidae), and an Analogue Compound

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Os percevejos *Euschistus heros* e *Piezodorus guildinii* (Heteroptera: Pentatomidae) são importantes pragas da cultura da soja no Brasil. Uma característica marcante nestas espécies é o fato de que ambas se utilizam das mesmas estruturas químicas como feromônios sexuais, ou seja, os ésteres metílicos 2,6,10-trimetildodecanoato de metila **(1)** (minoritário) e o 2,6,10-trimetiltridecanoato de metila **(2)**. No intuito de se verificar a exata função biológica destas estruturas e melhor entender o sistema de comunicação de cada espécie, realizou-se a síntese do componente minoritário **1** juntamente com um composto análogo, o 2,6,10-trimetiltetradecanoato de metila **(3)**. Tais compostos serão submetidos a testes em laboratório, juntamente com o componente majoritário **2**, já previamente sintetizado.

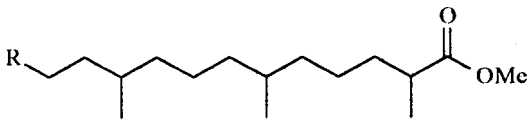
The stink bugs *Euschistus heros* and *Piezodorus guildinii* (Heteroptera: Pentatomidae) are economically important soybean pests in Brazil. An intriguing characteristic of these species is the fact that they use the same chemical compounds as sex pheromone, e.g., methyl 2,6,10-trimethyldodecanoate **(1)** (minor) and methyl 2,6,10-trimethyltridecanoate **(2)**. In order to investigate the specific biological function of these molecules and to increase the knowledge of the communication system of each species, we have synthesized the minor component **1** and an analogue compound, methyl 2,6,10-trimethyltetradecanoate **(3)**. These compounds will be tested on indoor bioassay, in addition with the previously synthesized major component **2**.

Keywords: *Piezodorus guildinii, Euschistus heros,* methyl 2,6,10-trimethyldodecanoate, sex pheromone, synthesis

Introduction

Soybean is damaged by complexes of stink bugs around the world. In Brazil, the species of major importance in practically all soybean growing regions are *Nezara viridula* (L.), *Piezodorus guildinii* (Westwood) and *Euschistus heros* (F.), which attacks has led to the use of more than 4 millions litres of chemical insecticides annually[1,2]. Forming part of a system of integrated pest management, the use of pheromones can be an useful alternative tool for the control of these pests.

Although there are some 35,000 species of Heteroptera worldwide, yet sexual pheromones are fully known only for a few species[3]. The diverse nature of the group itself has hindered progress[3]. In 1994, Aldrich and his co-workers identified methyl 2,6,10-trimethyldodecanoate **(1)** and methyl 2,6,10-trimethyltridecanoate **(2)** as components of the male-produced sex pheromones of *E. heros*[4]. They also identified **2** as the second major component of the male-specific volatile constituents of the Central America stink bug *Euschistus obscurus* (Figure 1).



1 - R = H; **2** - R = Me; **3** - R = Et

Figure 1. Pheromones and analogue compound of stink bugs.

We have recently reported that compounds **1** (minor) and **2** are also male-produced sex pheromones of the stink bug *P. guildinii*[5]. Although the different species liberate a similar pheromone blend, unique ratios of these compounds might be involved in species isolation, since it was previously observed

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on indoor bioassay that the activity of pure synthetic isomers of **2**, in females *E. heros*, does not significantly differ from that of the synthetic racemic mixture[6].

In order to investigate the specific biological function of these compounds and to understand the communication system mechanism of each species, this work is aimed to synthesizing the minor component **1** and an analogue structure, methyl 2,6,10-trimethyltetradecanoate **(3)** (Figure 1). These compounds and the previously synthesized major component **2**[7] will be tested individually and in different ratios on indoor bioassay and the results will be reported in due course.

Experimental

The IR spectra refer to films and were measured on a Bomem M-102 spectrometer. The ^{1}H-NMR spectra were recorded with TMS as an internal standard at 400 MHz on a Bruker ARX 400 spectrometer. The ^{13}C-NMR spectra were recorded with TMS as an internal standard at 100 MHz on a Bruker ARX 400. GC-EIMS (70 eV) analysis was carried out on a Varian Saturn 2000 GC-MS spectrometer in a split injector mode. A VA-5 capillary column (30 m x 0.25 mm x 0.25 μm) was operated at 70° C for 1 min, increased to 270° C at a rate of 7° C/min and held at this temperature for 10 min. All reagents and solvents used in the syntheses were of highest commercially available standard. Chromatographic purifications were carried out on silica gel 60, Merck, 230-400 mesh.

(3RS)-3,7-Dimethyloct-6-enyl-1-acetate **(5)**: To a mixture of pyridine (50 cm^3) and citronellol **4** (15.00 g, 96.15 mmol) cooled at 0 ^{o}C under nitrogen, acetic anhydride (14.15 cm^3, 150 mmol) was added in one portion, and the resulting mixture was stirred for 12 h. The reaction was quenched by addition of hot water (50 cm^3) followed by addition of ethyl ether (100 cm^3). The aqueous layer was extracted with ethyl ether (3 x 60 cm^3) and the organic layer was dried over anhydrous magnesium sulfate and concentrated *in vacuo*. The product was purified by flash chromatography on silica gel using a mixture of hexane/ethyl acetate (24:1 v/v), yielding citronellyl acetate **5** as a colorless oil (17.00 g, 91.40 mmol, 95%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.91 (d, ^3J 6.6 Hz, 3H); 1.16-1.48 (m, 3H); 1.50-1.59 (m, 1H); 1.60 (s, 3H); 1.61-1.68 (m, 1H); 1.69 (s, 3H); 1.90-2.20 (m, 2H); 2.40 (s, 3H); 4.02-4.15 (m, 2H); 5.09 (t, ^3J 7.0 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 17.65; 19.42; 21.05; 25.40; 25.72; 29.50; 35.44; 36.99; 63.05; 124.58; 131.35; 171.24.

(3RS, 6E)-3,7-Dimethyl-8-oxo-6-octenyl-1-acetate **(6)**: To a mixture of selenium dioxide (5.31 g, 48.0 mmol) in methylene chloride (100 cm^3) maintained at 5 – 10°C, *tert*-butyl hydroperoxide (288 mmol) was added dropwise. After 20 minutes at 10 °C, citronellyl acetate **5** (17.8 g, 95.9 mmol) was added in one portion. The resulting mixture was stirred during 30 minutes at 0 °C and then the cooling bath was removed. The mixture was allowed to warm to room temperature, and the stirring of the resulting solution was continued for 2-3 h. After all starting material had been consumed (~ 4 h, detected by gas chromatography), the mixture was carefully concentrated *in vacuo* without heating. The residue was diluted in hexane (50 cm^3) and treated with 10% aqueous potassium hydroxide solution (40 cm^3), yielding an aqueous lemon yellowish solution. The organic layer was treated twice with 10% aqueous potassium hydroxide solution (40 cm^3), followed by treatment with brine (80 cm^3). The organic layer was dried over anhydrous magnesium sulfate and concentrated *in vacuo* to afford an oil. Flash chromatography over silica gel using hexane/ethyl acetate (5:1 v/v) as eluent afforded aldehyde **6** (7.6 g, 38 mmol, 40 %) and the corresponding alcohol (7.5 g, 38 %). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.97 (d, ^3J 6.1, 3H); 1.32-1.74 (m, 5H); 1.75 (s, 3H); 2.05 (s, 3H); 2.32-2.44 (m, 2H); 4.06-4.18 (m, 2H); 6.48 (t, ^3J 7.0 Hz, 1H); 9.40 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 9.20; 19.23; 21.01; 26.47; 29.65; 35.29; 35.37; 62.66; 139.41; 154.57; 171.22; 195.31.

(3RS, 6E)-3,7-Dimethylnona-6,8-dienyl-1-acetate **(7)**: To a mixture of the salt CH_3PPh_3Br (6.25 g, 17.5 mmol) in THF (100 cm^3), cooled at –25 ^{o}C under argon, was added dropwise a solution of ^{n}BuLi (16.9 mmol, 10.6 cm^3, 1.6 mol L^{-1} in hexane). After the addition was completed, the mixture turned dark orange. After 10 min the salt was consumed and a solution of aldehyde **6** (3.0 g, 15 mmol) in THF (30 cm^3) was added to the mixture. After 5 minutes the cooling bath was removed and the mixture was allowed to warm to room temperature. After all starting material had been consumed (~10 min, detected by gas chromatography) the reaction mixture was quenched with saturated aqueous NaCl solution (20 cm^3). The aqueous layer was extracted with petroleum ether (5 x 50 cm^3), and the organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash chromatography over silica gel using a mixture of hexane/ethyl acetate (10:1 v/v), yielding 1.90 g of compound **7** (57 %). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.92 (d, ^3J 6.6 Hz, 3H); 1.20-1.73 (m, 5H); 1.74 (s, 3H); 2.04 (s, 3H); 2.09-2.22 (m, 2H); 4.04-4.15 (m, 2H); 4.93 (d, ^3J 10.7 Hz, 1H); 5.08 (d, ^3J 17.3, 1H); 5.44 (t, ^3J 7.1 Hz, 1H); 6.35 (dd, ^3J 17.3 and 10.7 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 11.66; 19.37; 21.04; 25.60; 29.53; 35.39; 36.55; 62.93; 110.49; 133.06; 134.00; 141.56; 171.22.

(3RS, 6E, 8E)- and (3RS, 6E, 8Z)-3,7-Dimethylundeca-6,8-dienyl-1-acetate **(7a)**: As described above, the reaction of compound **6** (3.50 g, 17.5 mmol), and the salt $CH_3CH_2CH_2PPH_3Br$ (6.49 g, 17.5 mmol) afforded **7a** (2.33 g, 65 %). ^{1}H-NMR (400 MHz, $CDCl_3$) δ [0.92 (d, ^3J 6.6 Hz, 3H); 0.93 (d, ^3J 6.6 Hz, 3H)]; [0.99 (t, ^3J 7.8 Hz, 3H); 1.01 (t, ^3J 7.8 Hz, 3H)]; 1.19-1.29 (m, 1H); 1.35-1.50 (m, 2H); 1.51-1.62 (m, 1H); 1.63-1.70 (m, 1H); [1.73 (s, 3H); 1.76 (s, 3H)]; 2.04 (s, 3H); 2.06-2.17 (m, 2H); 2.20-2.29 (m, 2H); 4.04-4.16 (m, 2H); 5.23-5.38 (m, 1H); [5.58 (t, ^3J 6.6 Hz, 1H); 5.62 (t, ^3J 6.6 Hz, 1H)]; [5.76 (d, ^3J 11.7 Hz, 1H); 6.04 (d, ^3J 15.3 Hz, 1H)]; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 12.44; [13.98; 14.92]; 16.70; 19.40; [21.03; 22.08]; [25.49; 25.86]; [29.51; 29.56]; [35.41; 35.44]; [36.73; 36.77]; 62.96; [129.24; 130.22; 130.24; 131.35; 132.25; 132.72; 133.60; 133.78]; 171.20

(3RS, 6E)-3,7-Dimethylnona-6,8-dien-1-ol **(8)**: To a solution of compound **7** (1.90 g, 9.59 mmol) in methanol (10 cm^3) at 0 ^{o}C, was added a solution of K_2CO_3 (0.5 mol L^{-1}, 19.2 cm^3). The mixture was stirred at room temperature until all starting material had been consumed. This solution was concentrated *in vacuo* and extracted with ether. The organic layer was treated with saturated NaCl solution, dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The product was purified by flash chromatography over silica gel using a mixture of hexane/ethyl acetate (1:5 v/v), yielding 1.48 g of compound **8** (99 %). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.92 (d, ^3J 6.6 Hz, 3H); 1.19-1.31 (m, 1H); 1.35-1.48 (m, 3H); 1.55-1.66 (m, 2H); 1.73 (s, 3H); 2.05-2.25 (m, 2H); 3.64-3.75 (m, 2H); 4.92 (d, ^3J 10.7 Hz, 1H); 5.08 (d, ^3J 17.3 Hz, 1H); 5.47 (t, ^3J 7.1, 1H); 6.35 (dd, ^3J 17.3 and 10.7 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 11.64; 19.47; 25.68; 29.25; 36.80; 39.84; 61.13; 110.43; 133.25; 133.91; 141.59.

(3RS, 6E, 8E)- and (3RS, 6E, 8Z)-3,7-Dimethylundeca-6,8-dien-1-ol **(8a)**: As described above, compound **7a** (2.33 g, 11.0 mmol) was converted into alcohol **8a** (1.82 g, 98 % yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ [0.91 (d, ^3J 6.6 Hz, 3H); 0.92 (d, ^3J 6.6 Hz, 3H)]; [0.99 (t, ^3J 7.1 Hz, 3H); 1.01 (t, ^3J 7.1 Hz, 3H)]; 1.19-1.28 (m, 1H); 1.34-1.46 (m, 2H); 1.55-1.68 (m, 2H); [1.72 (s, 3H); 1.76 (s, 3H)]; 1.84 (br, s, 1H); 2.04-2.16 (m, 2H); 2.20-2.28 (m, 2H); 3.63-3.74 (m, 2H); 5.21-5.40 (m, 1H); [5.58 (t, ^3J 6.1 Hz, 1H); 5.61 (t, ^3J 6.1 Hz, 1H)]; [5.75 (d, ^3J 11.7 Hz, 1H); 6.05 (d, ^3J 16.0 Hz, 1H)]; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 12.43; [13.98; 14.93]; [19.50; 19.54;]; 22.09; [25.55; 25.86]; [29.22; 29.30]; [36.95; 37.00]; 39.86; [61.16; 61.18]; [129.22; 130.41; 130.48; 131.33; 132.26; 132.65; 133.52; 133.78].

(3RS, 6E)-3,7-Dimethylnona-6,8-dienal **(9)**: To a stirred solution of dimethyl sulfoxide (2.21 g, 28.4 mmol) in methylene chloride (8.50 cm^3) cooled at –60 ^{o}C under nitrogen, was added a solution of oxalyl chloride (1.80 g, 14.2 mmol) in methylene chloride (27.4 cm^3), and the reaction mixture was stirred for 20 minutes. Alcohol **8** (1.48 g, 9.48 mmol) dissolved in methylene chloride (67.0 cm^3) was added. The mixture was stirred for 1 h at –60 ^{o}C and then treated with trimethylamine (7.88 cm^3, 57.0 mmol).The cooling bath was removed and the mixture was allowed to warm to room temperature over a period of 30 minutes. After addition of hexane (60 cm^3), the mixture was poured into water (25 cm^3) and extracted with a solution of hexane/ethyl acetate (2:1 v/v). The organic phase was treated with saturated $NaHCO_3$ solution and saturated NaCl solution, dried over anhydrous $MgSO_4$ and concentrated *in vacuo* to give 1.40 g of crude **9**. This unstable aldehyde was directly used for the next step without purification.

(3RS, 6E, 8E)- and (3RS, 6E, 8Z)-3,7-Dimethylundeca-6,8-dienal **(9a)**: As described above, compound **8a** (1.82 g, 10.7 mmol) was converted into aldehyde **9a** (1.70 g).

2,6,10-Trimethyldodecan-1-ol **(11)**: To a mixture of the salt $[HOCH_2CH(CH_3)CH_2PPh_3]Br$ (3.88 g, 9.35 mmol), [prepared by reaction of (2*RS*)-2-methyl-3-hydroxy-1-bromopropane and Ph_3P in benzene[8], 87 % yield] in THF (80 cm^3), cooled at –25 ^{o}C under argon, was added a solution of ^{n}BuLi (18.7 mmol, 11.7 cm^3, 1.6 mol L^{-1} in hexane). After the addition was completed the mixture turned dark orange. In 10 min the salt was consumed and a solution of aldehyde **9** (1.21 g, 7.85 mmol) in THF (10 cm^3) was added to the mixture. After 5 minutes the cooling bath was removed and the mixture was allowed to warm to room temperature. After all starting material had been consumed (~20 min, detected by Gas Chromatography) the reaction mixture was quenched with saturated NaCl solution (20 cm^3). The aqueous layer was extracted with cold petroleum ether (5 x 50 cm^3). The organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was diluted in pentane (~ 20 cm^3) and kept at -10 ^{o}C for 24 h. This was filtrated and the solvent was removed *in vacuo*. The crude product was dissolved in hexane and hydrogenated over Pd/C (100 mg) at room temperature and 25 psi in a Parr® apparatus for 2 h. The mixture was filtered through Celite® and the filtrate was evaporated at reduced pressure. The crude product was purified by flash chromatography over silica gel, using a mixture of hexane/ethyl acetate (7:1 v/v), to afford 1.25 g of alcohol **11**, 75 % yield as a mixture of stereoisomers. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.84-0.91 (m, 9H); 0.92 (d, ^3J 6.8 Hz, 3H), 1.10-1.17 (m, 4H); 1.24-1.42 (m, 12H); 1.60-1.67 (m, 2H); 3.42 (dd, ^3J 10.4 and 6.4 Hz, 1H); 3.50-3.54 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 11.4; 16.6; [19.2, 19.3]; 19.7; 24.4; 24.5; [29.4, 29.6]; 32.7; 33.4; 34.4; 35.8; 37.0; 37.3; 37.5; 68.5.

2,6,10-Trimethyltetradecan-1-ol **(11a)**: As described above, compound **9a** (1.64 g, 9.76 mmol) was converted into alcohol **11a** (1.40 g, 65 %) as a mixture of stereoisomers. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.79-0.89 (m, 9H); 0.94 (d, ^3J 7.0 Hz, 3H), 0.98-1.12 (m, 4H); 1.18-1.40 (m, 16H); 1.55-1.66 (m, 2H); 3.41 (dd, ^3J 10.4 and 6.8 Hz, 1H); 3.44-3.52 (m, 1H)

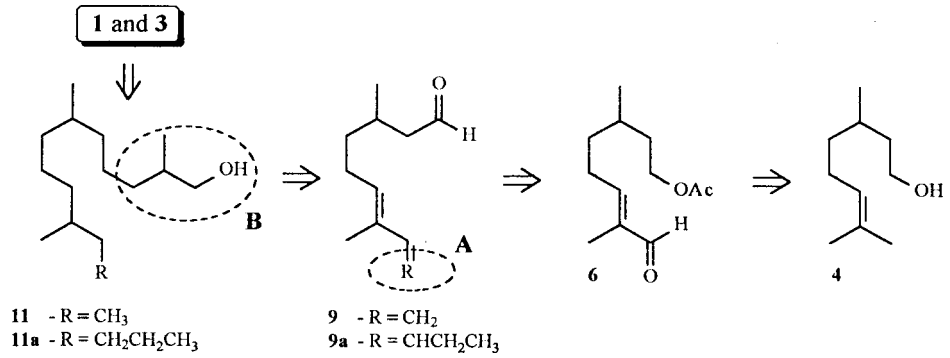
Methyl-2,6,10-trimethyldodecanoate **(1)**: Jones reagent (~20.0 cm^3) was added to a solution of the alcohol **11** (1.30 g, 5.70 mmol) in acetone (100 cm^3), and the mixture was stirred for 30 min at –5 °C. Excess of oxidant was destroyed with *i*-PrOH, and the mixture was concentrated *in vacuo*, diluted with water, and extracted with ether. The ether extract was washed with H_2O and satd NaCl solution, dried with $MgSO_4$, and concentrated. The residue obtained was diluted in ether (50 cm^3) and treated with ethereal CH_2N_2 at 0° C, until the reaction mixture turned yellow. The solution was stirred for 30 min, concentrated, and the residual oil was chromatographed on silica gel using hexane/ethyl acetate (9.5:0.5 v/v) as eluent, yielding 1.10 g of **1** (75 %) as a mixture of stereoisomers. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.84 (d, ^3J 7.2 Hz, 3H); 0.85 (d, ^3J 6.8 Hz, 3H); 0.86 (t, ^3J 7.2 Hz, 3H); 1.01-1.10 (m, 3H); 1.14 (d, ^3J 6.8 Hz, 3H); 1.18-1.45 (m, 13H); 2.45 (sext, ^3J 6.8 Hz, 1H); 3.67 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ [11.42, 11.43]; [17.03, 17.14]; [19.21, 19.27]; [19.60, 19.65]; 24.47; 24.71; [29.47, 29.58]; 32.65; [34.12, 34.16]; 34.43; 36.84; [36.93, 36.97]; [37.31, 37.35, 37.36, 37.39]; [39.47, 39.50]; 51.44; 177.43; GC-EIMS *m/z* 256 (M$^+$, 0.6 %); 232 (0.6); 203 (1.3); 152 (0.5); 119 (9.6); 101 (29.8); 88 (100); 69 (18.3); 55 (29.8).

Methyl-2,6,10-trimethyltetradecanoate **(3)**: As described above, compound **11a** (1.40 g, 5.47 mmol) was converted into **3** (1.32 g, 82 %) as a mixture of stereoisomers. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.83 (d, ^3J 6.1 Hz, 3H); 0.84 (d, ^3J 6.6 Hz, 3H); 0.89 (t, ^3J 7.1 Hz, 3H); 1.00-1.12 (m, 4H); 1.14 (d, ^3J 7.1 Hz, 3H); 1.18-1.31 (m, 13H); 1.32-1.44 (m, 3H); 2.44 (sext, ^3J 7.1 Hz, 1H); 3.67 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.58; [17.43, 17.53]; [20.00, 20.05]; [20.10, 20.16]; 23.45; 24.85; [25.09, 25.11]; 29.76; 33.04; [33.14, 33.17]; [34.51, 34.56]; [37.15, 37.25]; [37.26, 37.33]; [37.71, 37.74]; [37.77, 37.82]; [39.87, 39.89]; 51.84; 177.44; GC-EIMS *m/z* 284 (M$^+$, 1.0 %); 227 (0.6); 194 (2.0); 157 (6.7); 129 (3.66); 101 (34.3); 97 (14.4); 88 (100); 69 (24.3); 55 (45.5); 43 (73.0).

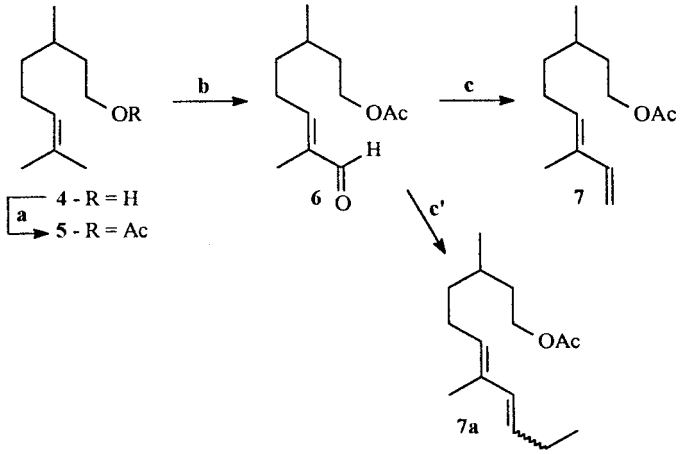
Results and Discussion

A brief retrosynthetic analysis is depicted for compounds **1** and **3** (Scheme 1). (±) – Citronellol **4** serves as starting material to the synthesis of the key and common intermediate for both target molecule, aldehyde **6**. From here, we have mainly utilized two Wittig reaction to build the skeleton of each molecule. The first one was employed to generate compounds **9** and **9a**, which have the correct numbers of carbon atoms at the A portions of the molecules, and the second Wittig reaction afforded the B portions of alcohol **11** and **11a**, the direct precursors of the desired molecules.

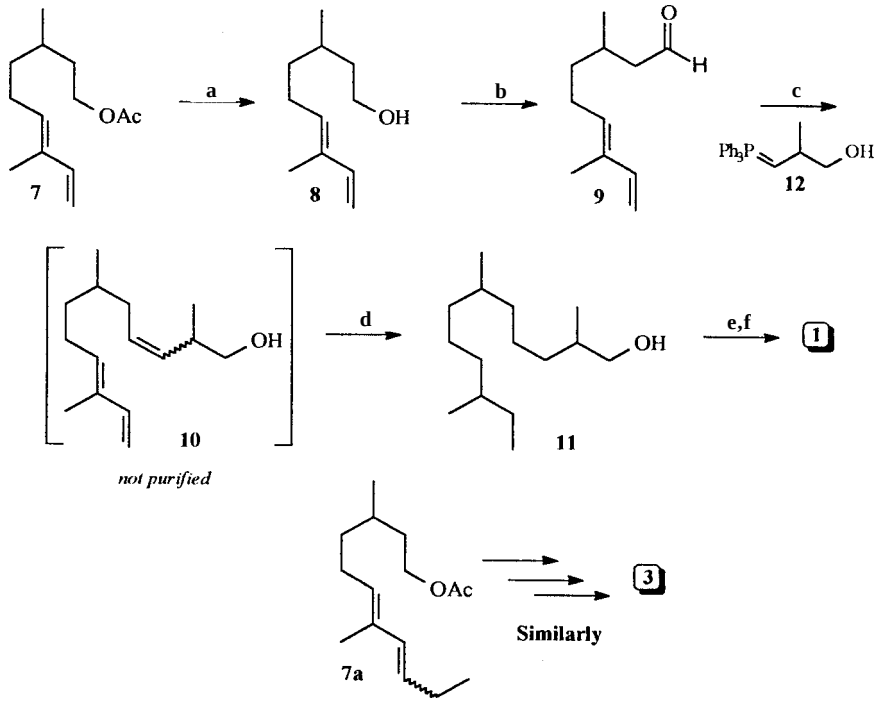
The transformation of (±)-citronellol **4** to the aldehyde **6** was performed according to Scheme 2. The first step involves the acetylation of **4** with Ac_2O-Py[9] resulting in the respective acetate **5** in 95 % yield. This was oxidised by SeO_2 / ^{t}BuOOH to afford a mixture of the aldehyde **6** (40 % yield) and the corresponding allylic alcohol (38 % yield)[10,11]. After purification by flash chromatography, the pure aldehyde **6** was subjected to the Wittig reaction with (triphenylphosphonium)methanide (CH_2=PPh_3) or (triphenylphosphonium)propanide (CH_3CH_2CH=PPh_3) to give compounds **7** (57 % yield) or **7a** (65 % yield), respectively. These new acetates intermediates were straightforward transformed into methyl 2,6,10-trimethyl-dodecanoate **(1)** and methyl 2,6,10-trimethyltetradecanoate **(3)**, as indicated in Scheme 3. Hydrolysis of **7** under basic condition yielded alcohol **8** in 99 % yield. Swern oxidation[12] of **8** gave the unstable aldehyde **9**, which without purification was readily



Scheme 1. Retrosynthetic analysis.



Scheme 2. Synthesis of aldehyde **6** and intermediates **7** and **7a**. Reagents: a)Ac_2O - Py, 95%; b)SeO_2 / ^tBuOOH, CH_2Cl_2, 40%; c)CH_3PPh_3Br, BuLi, THF, 57%; c')$CH_3CH_2CH_2PPh_3Br$, BuLi, THF, 65 %.



Scheme 3. Synthesis of methyl 2,6,10-trimethyldodecanoate **(1)** and methyl 2,6,10-trimethyltetradecanoate **(3)**. Reagents: a)K_2CO_3, MeOH, 99%; b)Swern oxidation; c)$HOCH_2CH(CH_3)CH_2PPh_3Br$(12), BuLi, THF; d)$H_2$, Pd/C, 25 psi, 75% from **9**; e)Jones oxidation; f)CH_2N_2, Et_2O, 75% from **11**.

transformed in to the alcohol **10**, by employing the second Wittig reaction of our synthetic plan, with ylide **12**. Compound **10** and the respective analogue **10a**, derived from acetate **7a**, could not be adequately purified. The GC and TLC analyses of the crude residue obtained in this reaction shows a number of products, which are certainly related to the mixture of stereoisomers (resulting from the methyl branches and the double bonds). Thus, crude **10** was hydrogenated over Pd/C furnishing the alcohol **11** in 75 % yield over two steps. Finally, the routine Jones oxidation of **11** afforded the respective carboxylic acid, which was treated with CH_2N_2 to give the desired pheromone **1** in 75 % yield[13] as a mixture of stereoisomers. Similarly, acetate **7a** was converted into **3**.

We have previously described the first synthesis of (2*R*, 6*S*, 10*S*) and (2*S*, 6*S*, 10*S*) isomers of methyl 2,6,10-trimethyldodecanoate **(1)**[13], and recently we developed a new synthesis of a mixture of stereoisomers of pheromone **2**[7]. A stereoisomeric mixture of methyl 2,6,10-trimethyltridecanoate **(2)** was firstly synthesized by Mori and Murata[14], which later have described the synthesis of all of the eight possible isomers of pheromone **2**[15].

We have now achieved a new approach to the synthesis of these stink bugs pheromones. A positive feature of our synthesis is the fact that the starting material **4** and the bromide utilized to prepare ylide **12** (3-bromo-2-methyl-1-propanol), are commercially available in both enantiomeric forms. So, a number of stereoisomers of the final compounds **1** and **3** (even for **2**) could be obtained.

However, we intend in to use the racemic compounds to carry out the bioassays, since these stink bugs are responding to the racemic mixture at the same level as to the pure isomers, as already mentioned[6]. This characteristic can be an economically important issue to define the usefulness of synthetic pheromones as an alternative method in pest management control for *P. guildinii* and *E. heros*.

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