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Improved Synthesis of (3*E*,7*Z*)-3,7-Tetradecadienyl Acetate, the Major Sex Pheromone Constituent of the Potato Pest *Symmetrischema tangolias* (Gyen)

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An efficient six-step synthesis of (3*E*,7*Z*)-3,7-tetradecadienyl acetate, the major component of the sex pheromone of the potato pest *Symmetrischema tangolias* (Gyen), is described, starting from the commercially available dihydropyran. The stereoselective formation of the 7*Z* double bond is accomplished by a Wittig reaction, while the 3*E* double bond is formed by a modified Knoevenagel condensation. The overall yield of the synthesis is 28%, giving the final product in high stereochemical purity (95%). The simplicity and the low cost of the herein reported synthesis suggest the potential practical use of the above pheromone in integrated management programs, for this serious insect pest.

KEYWORDS: Pheromone synthesis; potato tuber moth; tomato stem borer; *Symmetrischema tangolias* (Gyen); (3*E*,7*Z*)-3,7-tetradecadienyl acetate; Knoevenagel condensation

INTRODUCTION

The potato plant *Solanum tuberosum* L., an important plant for human nutrition cultivated extensively in most countries around the world, is extremely susceptible to various insect attacks (*1*). At present, one of the most devastating pest of potatoes in South America and especially in Andean valleys of Bolivia, Colombia, and Peru, as well as in Australia, is the tuber moth *Symmetrischema tangolias* (Gyen) (Lepidoptera: Gelechiidae), (synonym: *Symmetrischema plaesiosema*, Turner) (*2*). Damage is caused by larvae, which burrow into tubers and stems, making them unsuitable for human consumption or for seed. A population survey showed that it remains in potato fields after harvesting, even in the absence of a host plant, threatening the next crop. Furthermore, this destructive pest became the most dominant enemy in potato storehouses or in open facilities, where harvested tubers are commonly stored for up to 4 months before marketing. The accidental introduction of infested tubers into stores allows the development and reproduction of tuber moths. *S. tangolias* is also reported as a pest of tomatoes worldwide (*3*) and that is why it is also known with the systematic name "tomato stem borer" (*4*).

Chemical and biological control applications, including the use of the soil bacterium *Bacillus thuringiensis*, have been used by farmers worldwide. However, leaf mining and tuber burrowing, the feeding behavior of *S. tangolias*, make the use of insecticides low and inefficient. Moreover, the general utility of insecticides is limited by high cost, persistence of residue in tubers, and the environment and development of this insecticide-resistant pest. Considerable efforts have been made for the development and evaluation of the efficacy of alternative control methods (*5, 6*). The use of an insect's pheromone by the mass trapping technique has shown promising results (*1, 2, 7*).

Griepink et al. isolated and identified the sex pheromone constituents from the female moth's gland extract in 1995 (*7*). The amounts of the same pheromone constituents were also measured later by direct pheromone glands introduction into two-dimensional gas chromatography (GC) (*8*). The main constituent of the female-produced pheromone is the (3*E*,7*Z*)-3,7-tetradecadienyl acetate, **1** (**Figure 1**), which was identified in the pheromone as a 2:1 mixture with (3*E*)-tetradecenyl acetate. In the sex pheromone glands, two additional minor

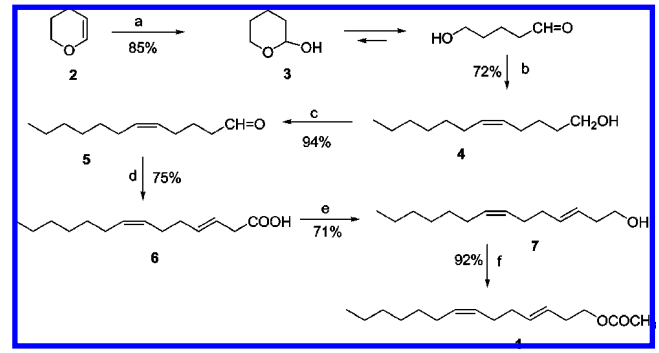

Figure 1. Reagents and conditions: (a) HCl/H_2O. (b) $CH_3(CH_2)_5$-$CH_2P^+(Ph)_3Br^-$; $KN[Si(Me)_3]_2$, THF −78 °C. (c) PCC/Celite, CH_2Cl_2. (d) $CH_2(COOH)_2$, piperidinium acetate, DMSO. (e) Red-Al/ether. (f) Ac_2O, pyridine.

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alkenyl constituents, (7*Z*) and (5*Z*)-tetradecenyl acetates, have been identified but have proved nonsignificant in attractiveness. The ratio of the above four C14 components in the sex pheromone gland is (3*E*,7*Z*):(3*E*):(7*Z*):(5*Z*) = 63:31:5:1. To confirm the structural assignment and to provide samples of suitable size for laboratory and field bioassay, the above scientists carried out a stereospecific six-step synthesis of compound **1** (*7*). The synthetic active compound was found to be highly attractive to males in field tests and, applied in traps, caught large numbers of insects. Therefore, the availability of high-purity synthetic pheromone, by the development of a practical chemical synthesis, would aid integrated pest management programs in monitoring or control of the above noxious insect.

(*E*,*Z*)-Diene structures are widespread in insect pheromones, which are responsible for special functions (*9*), but pose great challenges for their stereoselective synthesis. The 3,7-dienyl moiety is not common in Lepidoptera pheromones, other than *S. tangolias*. To our knowledge, the only synthetic report found in the literature (*7*) for the creation of the 3*E*,7*Z* double bond system of this main component of the pheromone is based on the partial reduction of suitable acetylenic precursors. However, this synthesis is lacking in experimental details and structural description of the intermediates. The reported overall yield is a few percent; therefore, the method is unsuitable for large-scale preparation. An alternative approach for the synthesis of the title compound has therefore been developed in this study.

MATERIALS AND METHODS

Spectroscopic data were obtained on the following instruments: ^{1}H NMR spectra, in $CDCl_3$ solution on a Varian 600 MHz spectrometer; ^{13}C NMR spectra, in $CDCl_3$ solution on a Varian Mercury 200 MHz spectrometer. IR spectra were obtained in CCl_4 solutions (5%) on a Perkin-Elmer 247 spectrophotometer. Gas chromatography−mass spectrometric (GC-MS) analyses were carried out with a Hewlett-Packard 5890-5970 system, equipped with a SPB-1 capillary column (20 m × 0.25 mm, 0.33 μm film thickness, Supelco, Sigma-Aldrich Ltd., Greece); carrier gas, helium, 1 mL/min; injector temperature, 230 °C; oven temperature, 50 °C for 5 min isothermal and then raised to 250 °C at a rate of 4 °C/min and then held for 10 min; ion source temperature, 220 °C; interface temperature, 250 °C; mass range, 40−500 amu; and EI, 70 eV. GC analyses were carried out with Agilent 6890 N chromatograph either in a polar capillary column CP-Wax 52 CB (30 m × 0.32 mm, 0.25 μm film thickness, Varian Inc., CA) or in a nonpolar capillary column SPB1 (20 m × 0.32 mm, 1.0 μm film thickness, Supelco, Sigma-Aldrich Ltd.): carrier gas, helium, 1 mL/min; injector temperature, 200 °C; oven temperature, 60 °C for 5 min isothermal and then raised to 250 °C at a rate of 4 °C/min and then held for 15 min. Thin-layer chromatography (TLC) was performed on 0.25 mm precoated silica gel 60 F_{254} aluminum sheets and column chromatography on silica gel 60 (0.063−0.2 mm) as well as silica gel 60 (<0.063 mm Merck & Co., Darmstadt, Germany). All commercial reagents and solvents were used as supplied. Petroleum ether was the light fraction bp 40−60 °C. Piperidinium acetate was prepared in situ by mixing equivalent quantities of piperidine and glacial acetic acid in dimethyl sulfoxide (DMSO). Red-Al was a solution of sodium *bis*(2-methoxyethoxy) aluminum hydride, 65 wt % in toluene (Sigma-Aldrich Ltd.). $KN[Si(Me)_3]_2$ was a solution of potassium *bis*(trimethylsilyl)-amide, 0.5 M in toluene (Sigma-Aldrich Ltd.).

5-Hydroxytetrahydropyran (3). This lactol was prepared in 85% yield from 1,3-dihydropyran (**2**), according to a literature procedure (*10*). After the workup of the reaction mixture, the product was directly used for the Wittig reaction without further purification.

5*Z*-Dodecenol (4). (a) The *n*-heptylphosphonium bromide was prepared in 75% yield (mp 172−174 °C) from 1-bromoheptane and triphenylphosphine, by a previously described procedure (*11*), using toluene as the solvent instead of xylene. (b) Potassium *bis*(trimethylsilyl)amide (11.7 mL, 5.87 mmol, 0.5 M solution in toluene) was added dropwise over 5 min to a suspension of freshly prepared $[Ph_3P^+CH_2(CH_2)_5CH_3]Br^-$ (2.58 g, 5.87 mmol) in dry THF (15 mL) at 0 °C, under nitrogen. The resulting orange solution was stirred for 1 h at 0 °C and then cooled to −78 °C. A solution of the lactol **3** (0.40 g, 3.92 mmol) in dry THF (9 mL) was added dropwise over 30 min, maintaining the temperature below −70 °C. The resulting yellow solution was allowed to warm slowly to room temperature over a period of 1 h and left overnight. Then, the reaction mixture was quenched with a saturated solution of NH_4Cl (20 mL) and extracted with ether (3 × 15 mL). The combined organic phases were washed with brine (15 mL), dried over Na_2SO_4, and concentrated. The residue was chromatographed (petroleum ether/diethyl ether 6:1 to 1:1) to give practically pure **4** (0.52 g, 72%, purity by GC 98%, *Z*/*E* 98/2), as a colorless oil. IR ν_{max}/cm^{-1}: 3640 (w), 3009 (w), 2932 (s), 2861 (s), 1550 (s), 1440 (w). ^{1}H NMR: δ 0.87 (t, 3, J = 7.2 Hz), 1.21−1.35 (m, 8), 1.41 (qt, 2, J = 7.2 Hz), 1.57 (qt, 2, J = 7.2 Hz), 2.00 (qd, 2, J = 6.6 Hz), 2.05 (qd, 2, J = 7.2 Hz), 3.64 (t, 2, J = 6.6 Hz), 5.30−5.40 (m, 2). ^{13}C NMR 14.2, 22.8, 26.1, 27.1, 27.4, 29.2, 29.9, 32.0, 32.5, 62.9, 129.5, 130.5. MS *m*/*z* (%): 166 ($M^+ - H_2O$, 3), 110 (11), 95 (33), 82 (43), 81 (45), 67 (87), 55 (80), 41 (100). The NMR spectra are in accordance with those reported in the literature (*12*).

5*Z*-Dodecenal (5). A 50 mL round-bottom flask, equipped with a magnetic stirring bar, was charged with pyridinium chlorochromate (0.7 g, 3.25 mmol), Celite (0.7 g), and anhydrous CH_2Cl_2 (6 mL). The alcohol **4** (0.4 g, 2.17 mmol) in anhydrous CH_2Cl_2 (3 mL) was added to the stirred suspension at room temperature. Progress of the reaction was monitored by TLC. When the starting material disappeared (2 h), the mixture was diluted with Et_2O (25 mL) and filtered through a pad of Florisil. The filter cake was washed with Et_2O (2 × 8 mL). After evaporation of the solvent, the crude product was purified by column chromatography (petroleum ether/diethyl ether 4:1 to 2:1) producing **5** (372 mg, 94%, purity by GC 97%, *Z*/*E* ratio 98/2) as a colorless oil. IR ν_{max}/cm^{-1}: 3011 (w), 2931 (s), 2859 (s), 2718 (w), 1728 (s), 1550 (s), 1460 (w). ^{1}H NMR δ 0.81 (t, 3, J = 7.2), 1.16−1.30 (m, 8), 1.63 (qt, 2, J = 7.2 Hz), 1.93 (qd, 2, J = 7.2 Hz), 2.02 (qd, 2, J = 7.2 Hz), 2.36 (dt, 2, J_1 = 7.2 Hz, J_2 = 1.8 Hz), 5.24 (dtt, 1, J_1 = 10.8 Hz, J_2 = 7.2 Hz, J_3 = 1.2 Hz), 5.35 (dtt, 1, J_1 = 10.8 Hz, J_2 = 7.2 Hz, J_3 = 1.2 Hz), 9.70 (t, 1, J = 1.8 Hz). ^{13}C NMR δ 14.3, 22.2, 22.8, 26.6, 27.4, 29.2, 29.8, 31.9, 43.5, 128.4, 131.6, 202.8. MS *m*/*z* (%): 164 ($M^+ - H_2O$, 3), 138 (13), 110 (13), 98 (23), 81 (25), 67 (52), 55 (61), 41 (100). The NMR spectra of **5** are consistent with the literature (*12*). The IR and mass spectra of **5** matched those of the literature (*13*).

(3*E*,7*Z*)-3,7-Tetradecadienoic Acid (6). To a stirred solution of piperidine (0.033 mmol) and AcOH (0.033 mmol) (one drop from each one) in DMSO (3 mL) was added malonic acid (0.4 g, 3.85 mmol). To the resulting clear solution, the aldehyde **5** (0.35 g, 1.92 mmol) was added, and the mixture was stirred at room temperature for 30 min. Then, it was heated at 85 °C under stirring, until the evolution of CO_2 had stopped (2−3 h). The mixture was poured into H_2O (10 mL) and extracted with Et_2O (3 × 8 mL). The combined organic phases were dried over Na_2SO_4, and the solvent was concentrated under vacuum. Column chromatography (petroleum ether/diethyl ether 8:1 to 3:1) gave acid **6** (320 mg, 75%, purity by GC 97%) as a colorless oil. IR ν_{max}/cm^{-1}: 3011 (w), 2931 (s), 2860 (s), 1712 (s), 1548 (s), 969 (m). ^{1}H NMR: δ 0.87 (t, 3, J = 6.6 Hz), 1.20−1.35 (m, 8), 2.00 (qt, 2, J = 7.2 Hz), 2.09 (m, 4), 3.07 (d, 2, J = 6.6 Hz), 5.32 (dt, 1, J_1 = 10.8 Hz, J_2 = 7.2 Hz), 5.37 (dt, 1, J_1 = 10.8 Hz, J_2 = 7.2 Hz), 5.52 (dt, 1, J_1 = 15.0 Hz, J_2 = 6.6 Hz), 5.60 (dt, 1, J_1 = 15.6 Hz, J_2 = 6.0 Hz). ^{13}C NMR: δ 14.3, 22.9, 27.3, 27.5, 29.2, 29.8, 32.0, 32.8, 38.0, 121.3, 128.8, 130.9, 135.1, 179.1. MS *m*/*z* (%): 224 (M^+, 1), 164 (10), 112 (8), 100 (10), 84 (45), 69 (92), 55 (100), 41 (80). Anal. calcd for $C_{14}H_{24}O_2$: C, 74.94; H, 10.79. Found: C, 74.60; H, 10.67.

(3*E*,7*Z*)-3,7-Tetradecadienol (7). To a cold (0−4 °C) stirred solution of Red-Al (1 mL, 3.21 mmol, 65 wt % in toluene) in anhydrous diethyl ether (5 mL), a solution of **6** (0.3 g, 1.34 mmol) in diethyl ether (2 mL) was added dropwise under nitrogen. Stirring was continued for 1 h at the same temperature, and then, the solution was left overnight at room temperature. The end of the reaction was checked by TLC. The reaction mixture was hydrolyzed by dropwise addition of cold solution of 5% HCl (10 mL), under inert atmosphere, and then diluted with water and extracted with diethyl ether (3 × 10 mL). The organic

phase was dried over anhydrous Na_2SO_4, and the solvent was evaporated under vacuum. The resultant crude product was purified by column chromatography, over silica gel, to give (3*E*,7*Z*)-tetradecadienol (**7**) (200 mg, 71%, purity by GC 95%) as a viscous oil. IR ν_{max}/cm^{-1}: 3640 (w), 3010 (w), 2930 (s), 2860 (s), 1550 (s), 972 (m). ^{1}H NMR δ 0.82 (t, 3, $J = 7.2$ Hz), 1.15−1.30 (m, 8), 1.94 (qd, 2, $J = 6.6$ Hz), 2.03 (qt, 4, $J = 6.6$ Hz), 2.19 (qd, 2, $J = 6.6$ Hz), 3.56 (t, 2, $J = 6.6$ Hz), 5.26 (dt, 1, $J_1 = 10.8$ Hz, $J_2 = 6.6$ Hz), 5.29−5.36 (m, 2), 5.49 (dt, 1, $J_1 = 15.6$ Hz, $J_2 = 6.6$ Hz). ^{13}C NMR δ 14.3, 22.9, 27.3, 27.5, 29.2, 29.9, 32.0, 33.0, 36.1, 62.1, 126.4, 129.1, 130.7, 133.7. MS (*m*/*z*) 210 (M^+, 1), 192 (2), 124 (5), 95 (10), 83 (32), 69 (60), 55 (100), 41 (72).

(3*E*,7*Z*)-3,7-Tetradecadienyl Acetate (1). To a solution of acetic anhydride (1.0 mL, 10 mmol) in pyridine (4.0 mL), at 0−4 °C, the dienol **7** (0.25 g, 1.19 mmol) was added under stirring. The reaction was maintained at the same temperature for 1 h and then was brought to room temperature and monitored by TLC. When the reaction was finished (5 h), the mixture was poured in cold water (20 mL) and was extracted with diethyl ether (2 × 10 mL). The organic phase was washed by dilute 5% HCl, then by saturated $NaHCO_3$, and finally dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, and the crude product was purified by column chromatography over silica gel to give **1** (275 mg, 92%, purity by GC 95%) as a viscous liquid. IR ν_{max}/cm^{-1}: 3008 (w), 2931 (s), 2859 (s), 1741 (s), 1550 (s), 1239 (s), 972 (m). ^{1}H NMR: δ 0.82 (t, 3, $J = 6.6$ Hz), 1.15−1.30 (m, 8), 1.97 (s, 3), 1.92−2.04 (m, 6), 2.24 (qd, 2, $J = 7.2$ Hz), 3.99 (t, 2, $J = 7.2$ Hz), 5.24−5.36 (m, 3), 5.46 (dt, 1, $J_1 = 15.6$ Hz, $J_2 = 6.6$ Hz). ^{13}C NMR: δ 14.3, 21.1, 22.8, 27.3, 27.5, 29.2, 29.9, 32.0, 32.1, 32.9, 64.3, 125.6, 129.0, 130.6, 133.1, 171.2. MS *m*/*z* (%): 192 (M^+ − 60, 3), 149 (3), 135 (4), 121 (12), 83 (17), 67 (69), 55 (28), 43 (100). NMR and MS spectra of **1** were in agreement with those described in the literature (*7*).

RESULTS AND DISCUSSION

The main pheromone component **1** of the potato tuber moth *S. tangolias* was synthesized by an unambiguous stereoselective route, as outlined in **Figure 1**. This method involves the following six steps: Hydration of the 2,3-dihydropyran (**2**) in wet acid according to the literature (*10*) afforded 2-hyroxytetrahydropyran (**3**) in 85% yield. The carbonyl olefination of the lactol **3** with phosphorus ylids is a general method for the preparation of 5*Z*-alkenols (*14*). To ensure *cis* selectivity of this Wittig olefination, potassium *bis*(trimethylsilyl)amide was chosen as the base. The ylide, prepared from heptyltriphenylphosphonium bromide (*11*) by reaction with potassium *bis*(trimethylsilyl)amide as the base (*15*), in a stoichiometric ratio of reagents, reacted with **3** in THF at −78 °C to give the alkenol **4**. Pure 5*Z*-dodecenol (**4**) was isolated from the reaction mixture by column chromatography in good yield (72%) and excellent purity (98%, *Z*/*E* ratio 98/2). Oxidation of **4** with pyridinium chlorochromate/Celite in dichloromethane (*16*) afforded the required 5*Z*-dodecenal (**5**), which was purified by column chromatography. The yield was 94%, and the *Z* geometry of the double bond of **5** was confirmed by the vicinal vinyl hydrogen coupling constant $J = 10.8$ Hz. It must be mentioned here that the 5*Z*-dodecenol (**4**) and 5*Z*-dodecenal (**5**) are found as components in the chemical communication system of various species. For example, these compounds are major volatile constituents in the sex pheromone glands of females of the lappet moth *Gastropacha quercifolia* (Lepidoptera: Lasiocampidae) (*17*) and of other species in the genus Dendrolimus (*18*). The 5*Z*-dodecenal (**5**) was also identified in the anal gland of the male wild rabbit (*13*).

The aldehyde **5** was subsequently treated under modified Knoevenagel condensation conditions with malonic acid (*19*), in the presence of catalytic amount of piperidinium acetate in DMSO, for 4 h at 85 °C. The crude reaction product, purified by column chromatography, gave the (3*E*,7*Z*)-tetradecadienoic acid (**6**) in 75% yield. This procedure provides higher than 97% configurational purity of the 3*E* bond. The regio- and stereoselectivity of the product **6** were unambiguously confirmed by values of chemical shifts and coupling constants in the ^{1}H NNR, which exhibited resonances attributable to vinyl hydrogens on two different double bonds. The presence of a coupling constant of 15.0 Hz at 5.52 ppm and another one of 15.6 Hz at 5.60 ppm revealed two *trans* olefinic protons at C4 and C3, respectively. A second vinyl resonance coupling constant of 10.8 Hz, at both 5.32 and 5.37 ppm, confirmed the presence of two *cis* olefinic protons at C8 and C7, respectively. The transformation of (3*E*,7*Z*)-3,7-tetradecadienoic acid (**6**) into the target compound was done by reduction to the corresponding alcohol **7** and subsequent acetylation to the final acetate **1**. The reduction of the acid **6** to (3*E*,7*Z*)-3,7-alkadienol (**7**) was effected in 71% yield, with an excess of Red-Al in ether (*20*), without affecting the double bonds. The acetylation was carried out in 92% yield, under standard conditions by acetic anhydride in pyridine solution to give the final product (3*E*,7*Z*)-tetradecadienyl acetate (**1**) in high purity (95%) (*21*). The system of the olefinic protons appears as follows: one doublet of triplet at 5.46 ppm ($J_1 = 15.6$) attributed to C3 proton and one multiplet at 5.24−5.36 ppm, attributed to C4, C7, and C8 protons, respectively. Although the complexity of the second vinyl resonance did not allow measurement of a coupling constant, the described conditions of reduction and acetylation do not affect the geometry of the system of the double bonds, which remain unchanged as in the precursors **5** and **6**. The values of chemical shifts in the ^{1}H NNR and those of ^{13}C NMR of the synthetic acetate **1** were consistent with those reported for the isolated natural product and also with the reported synthetic compound (*7*).

In conclusion, (3*E*,7*Z*)-3,7-tetradecadienyl acetate (**1**), the main pheromone component of the potato tuber moth *S. tangolias* (Gyen), was prepared in six experimentally simple steps and an overall yield of 28% from commercially available 2,3-dihydropyran (**2**). The products can be easily purified in sufficient quantities by rapid column chromatography, and no efforts have been made to optimize the yields. The simplicity of the operation along with the high regio- and stereoselectivity obtained, the low cost of reagents, and the easily scalable procedure suggest the potential practical use of the above pheromone for the development of alternative environmentally safe control methods for this serious insect pest.

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