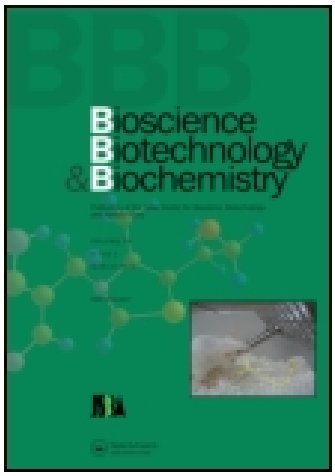

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Synthesis of (*R*,*Z*)-7,15-Hexadecadien-4-olide, the Sex Pheromone of the Yellowish Elongate Chafer (*Heptophylla picea*)

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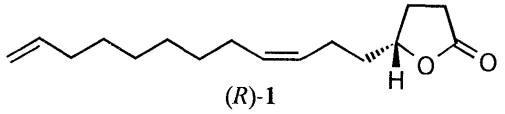
(*R*,*Z*)-7,15-Hexadecadien-4-olide, the sex pheromone of the yellowish elongate chafer (*Heptophylla picea*), was synthesized from L-malic acid in 15 steps. The synthetic pheromone was identical with the natural product in its MS, IR, GLC retention time, and biological activity.

Key words: sex pheromone; yellowish elongate chafer; *Heptophylla picea*; 7,15-hexadecadien-4-olide

Leal *et al.* have recently reported the isolation of the sex pheromone of the yellowish elongate chafer, *Heptophylla picea* Motshulsky (Coleoptera, Scarabaeidae, Mololonthinae), an important agricultural pest, especially for tea and flower production.[1] They deduced its structure to be (*Z*)-7,15-hexadecadien-4-olide (**1**) from the mass and infrared spectral data of the pheromone and its derivatives (Fig. 1). Our enantioselective synthesis of (*R*,*Z*)-7,15-hexadecadien-4-olide [(*R*)-**1**] from L-malic acid was accomplished, and the identity of the synthetic pheromone against the natural material was established by comparing their mass and infrared spectra, as well as their biological activities. Furthermore, GLC analyses of samples of 4-hexadecanolide prepared by catalytic hydrogenation of the natural pheromone, synthetic (*R*)-**1** and racemic 7,10-hexadecadien-4-olide were carried out in a chiral stationary phase, the results of which confirmed the (*R*)-configuration of the natural pheromone.[1] Another synthesis of the enantiomers of **1** by Nakayama and Mori led to the same structural assignment.[2] In this paper, we describe the details of our synthesis of (*R*)-**1**.

Our synthesis began with alkylation of the anion of 1,3-dithiane with iodide **2a** which is known to be obtainable from L-malic acid in 4 steps[3] (Fig. 2). The resultant dithiane derivative (**2b**) was deketalized under acidic conditions to give **3a**. The primary hydroxyl group of **3a** was selectively sulfonylated by treating with mesitylenesulfonyl chloride[4] and triethylamine in dichloromethane at 0°C to afford **3b** in a 65% isolated yield. Under these conditions, a 16% yield of the disulfonylated product was also isolated, but no monosulfonylation at the secondary hydroxyl functionality took place, as checked by a ^{1}H-NMR analysis of the crude product. After chromatographic purification, **3b** was subjected to basic conditions to give epoxide **4**, which was then ring-opened with the carbanion of acetonitrile[6] to yield **5a**. Protection of **5a** as its *t*-butyldimethylsilyl ether (**5b**) was followed by reduction with diisobutylaluminum hydride to give **5c**. (*Z*)-Selective Wittig olefination[6] of **5c** with (8-nonenylidene)triphenylphosphorane gave **6a** [*Z*/*E* = 93 : 7, as judged by the capillary GLC analysis of the final product, (*R*)-**1**], whose dithiane moiety was then hydrolyzed by treating with mercuric chloride and calcium carbonate in aqueous acetonitrile[7] to afford **6b**, together with a small amount of **7**. The mixture was treated with tetrabutylammonium fluoride to give lactol **7** as a diastereomeric mixture at the hemiacetal position (*ca.* 3 : 2 by a ^{1}H-NMR analysis). Finally, Jones oxidation of **7** yielded (*R*)-**1**, which showed the same MS, IR, GLC retention time, and GC-EAD response as those of the natural pheromone. The ^{1}H-NMR spectrum of the synthetic pheromone accorded with the structure, although the synthetic sample contained 7% of the corresponding (*E*)-isomer that originated from the incomplete geometric selectivity of the Wittig olefination step. The optical purity of the synthetic sample was evaluated by analyzing the corresponding hydrogenated lactone, 4-hexadecanolide, in a chiral GLC column as previously reported,[1] which showed the absence of the unnatural (*S*)-enantiomer.

In our previous synthesis,[1] we protected **5a** as its 1-ethoxyethyl ether (**5b**, R^1 = 1-ethoxyethyl) and deprotected it together with the dithiane moiety for the conversion of **6a** (R = 1-ethoxyethyl) to **7** by treating with *N*-chlorosuccinimide and silver nitrate, resulting in complication of the reaction and isolation of **7** in only a 25% yield. Other deprotecting methods such as mercuric chloride–calcium carbonate[7] and cupric chloride–cupric oxide[8] were also unsuccessful. Thus, the protective group of **5a** was changed from 1-ethoxyethyl to *t*-butyldimethylsilyl, and the two protective groups of **6a** were removed stepwise (trimethylenedithio and then *t*-butyldimethylsilyl) as already



(*R*)-**1**

Fig. 1. Sex Pheromone of *Heptophylla picea*.

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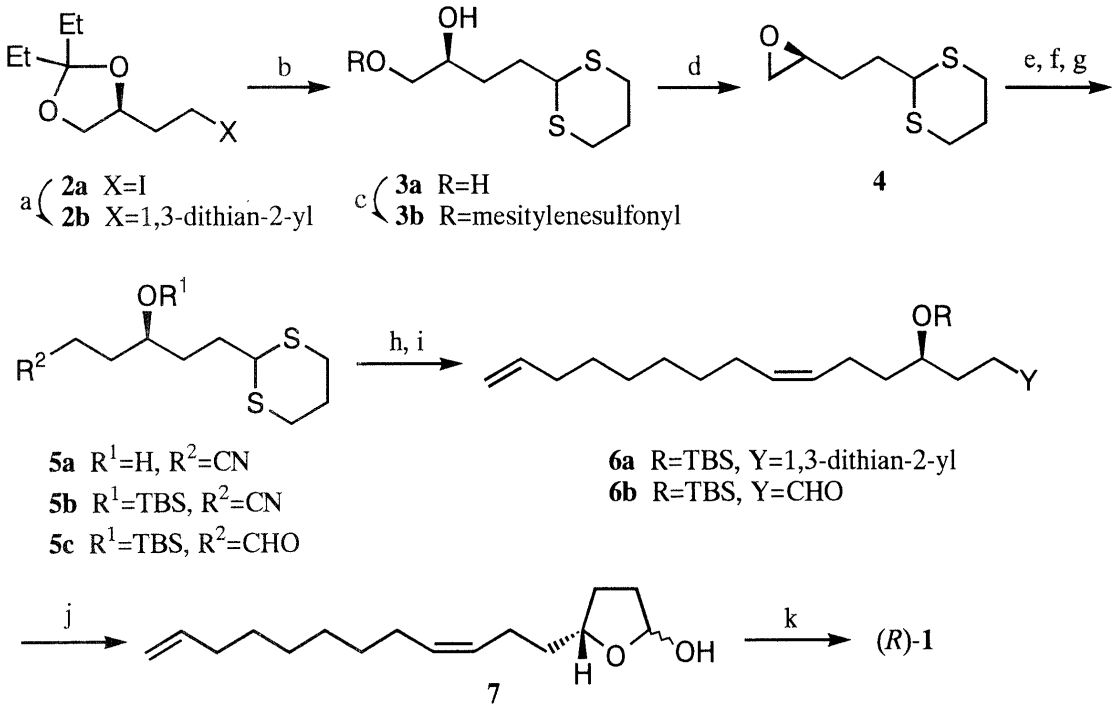
Abbreviation: GC-EAD, gas chromatography-electroantennographic detection.



Reagents: a) 1,3-dithiane, *n*-BuLi, THF; b) *p*-TsOH, MeOH; c) MSCl, Et_3N, CH_2Cl_2; d) K_2CO_3, MeOH; e) CH_3CN, *n*-BuLi, THF; f) TBSCl, imidazole, DMF; g) DIBAL, toluene; h) $CH_2{=}CH(CH_2)_7P(C_6H_5)_3Br$, *t*-BuOK, THF; i) $HgCl_2$, $CaCO_3$, CH_3CN-H_2O; j) $(n\text{-}Bu)_4NF$, THF; k) Jones reagent, acetone

Fig. 2. Synthesis of (*R*,*Z*)-7,15-Hexadecadien-4-olide.

described. These modifications enabled us to obtain **7** in a much better yield of 61% from **6a**.

Experimental

IR spectra were measured as films for oils or as KBr discs for solids with a JASCO FT/IR-5000 spectrometer. ^{1}H-NMR spectra were recorded with TMS as an internal standard in $CDCl_3$ with a JEOL JNM-A500 spectrometer. High-resolution mass spectra (70 eV) were measured with a Shimadzu GCMS 9020-DF spectrometer, and optical rotation values were measured with a JASCO DIP-370 polarimeter. Tetrahydrofuran was purified by distilling from benzophenone ketyl, while dichloromethane was purified by drying with P_2O_5 and then distilling from CaH_2. Merck Kieselgel 60 Art 7734 was used for silica gel column chromatography.

(S)-2,2-Diethyl-4-[3,3-(trimethylenedithio)propyl]-1,3-dioxolane (**2b**). To a stirred solution of 1,3-dithiane (3.4 g, 32.6 mmol) in tetrahydrofuran (32 ml) was added dropwise butyllithium (1.70 M in hexane, 19.3 ml, 32.9 mmol) at −25°C. After 2 h, a solution of **2a** (6.22 g, 21.9 mmol) in tetrahydrofuran (41 ml) was added dropwise, and the mixture was gradually warmed to 10°C over 1.5 h. The reaction mixture was quenched with saturated NH_4Cl and extracted with ether. The ethereal solution was successively washed with water and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed over silica gel (170 g, hexane : ether = 15 : 1) to give 4.70 g (78%) of **2b**, $[\alpha]_D^{25}$ +2.69° (*c* = 5.84, $CHCl_3$). IR ν_{max} cm^{-1}: 2970 (s), 2930 (s), 2900 (m), 2880 (s), 1460 (m), 1420 (m), 1280 (m), 1200 (m), 1180 (m), 1080 (s), 920 (m). ^{1}H-NMR δ: 0.89 (3H, t, *J* = 7.3 Hz, CH_3), 0.90 (3H, t, *J* = 7.3 Hz, CH_3), 1.61 (2H, q, *J* = 7.3 Hz, CH_3CH_2), 1.63 (2H, q, *J* = 7.3 Hz, CH_3CH_2), 1.68–1.82 (3H, m, 1′-H, 2′-H_2), 1.87 (1H, dtt, *J* = 14.2, 10.8, 3.9 Hz, SCH_2CH), 1.93–1.99 (1H, m, 1′-H), 2.12 (1H, dtt, *J* = 14.2, 4.5, 2.8 Hz, SCH_2CH), 2.81–2.91 (4H, m, $SCH_2 \times 2$), 3.49 (1H, t, *J* = 7.1 Hz, 5-H), 4.04–4.11 (3H, m, 4-H, 5-H, 3′-H). HRMS *m/z* (M^+): calcd. for $C_{13}H_{25}O_2S_2$, 277.1295; found, 277.1250.

(S)-5,5-(Trimethylenedithio)-1,2-pentanediol (**3a**). A solution of **2b** (4.90 g, 17.8 mmol) in methanol (50 ml) containing *p*-toluenesulfonic acid monohydrate (1.01 g, 5.33 mmol) and water (7.3 ml) was stirred for 1.5 h at 40°C. The reaction mixture was neutralized with solid $NaHCO_3$ (1.5 g) and concentrated *in vacuo*. The residue was diluted with ether, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed over silica gel (70 g, hexane : ethyl acetate = 1 : 2 to 1 : 3) to give 2.85 g (71%) of **3a** as a solid, which upon recrystallization from hexane afforded colorless needles, mp 53–54°C, $[\alpha]_D^{25}$ −5.02° (*c* = 1.18, $CHCl_3$). IR ν_{max} cm^{-1}: 3350 (s), 2940 (m), 2910 (m), 1420 (m), 1280 (m), 1090 (m), 1050 (s), 860 (m). ^{1}H-NMR δ: 1.61–1.74 (2H, m, 4-H_2), 1.79 (1H, dd, *J* = 5.0, 6.3 Hz, 1-OH), 1.81–1.91 (2H, m, 3-H, SCH_2CH), 1.95–2.02 (1H, m, 3-H), 2.12 (1H, dtt, *J* = 14.2, 4.5, 2.8 Hz, SCH_2CH), 2.10 (1H, d, *J* = 4.3 Hz, 2-OH), 2.82–2.91 (4H, m, $SCH_2 \times 2$), 3.46 (1H, ddd, *J* = 11.0, 7.7, 5.0 Hz, 1-H), 3.66 (1H, ddd, *J* = 11.0, 6.3, 3.3 Hz, 1-H), 3.70–3.77 (1H, m, 2-H), 4.08 (1H, t, *J* = 6.7 Hz, 5-H). HRMS *m/z* (M^+): calcd. for $C_8H_{16}O_2S_2$, 208.0591; found, 208.0499.

2-[(S)-3,4-Epoxybutyl]-1,3-dithiane (**4**). To a solution of **3a** (13.77 g, 66.2 mmol) and triethylamine (23 ml, 165 mmol) in dichloromethane (70 ml) was added portionwise 2-mesitylenesulfonyl chloride (17.95 g, 82 mmol) at 0°C. After being stirred overnight at 0–5°C, the mixture was diluted with water and extracted with ether. The ethereal solution was successively washed with 0.5 M HCl, saturated $NaHCO_3$ and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed over silica gel (200 g, hexane : ether = 5 : 1 to 2 : 1) to give 16.81 g (43.1 mmol) of **3b** as a sticky oil. The sulfonate was dissolved in methanol (168 ml), and solid potassium carbonate (6.25 g, 45.3 mmol) was then added. After being stirred for 40 min at room temperature, the mixture was diluted with hexane–ether (2 : 1, 60 ml). The diluted mixture was filtered through a Celite pad, and the filtrate was concentrated *in vacuo*. The residue was triturated with hexane–ether (2 : 1), filtered and concentrated *in vacuo* to give 10.1 g (44% from **3a**) of **4**. ^{1}H-NMR δ: 1.70 (1H, ddt, *J* = 13.7, 9.2, 6.0 Hz, 1′-H), 1.81–2.00 (4H, m, 5-H, 1′-H, 2′-H_2), 2.12 (1H, dtt, *J* = 14.2, 4.5, 2.8 Hz, 5-H), 2.50 (1H, dd, *J* = 5.0, 2.8 Hz, 4′-H), 2.75 (1H, dd, *J* = 5.0, 4.0 Hz, 4′-H), 2.81–2.91 (4H, m, $SCH_2 \times 2$), 2.92–2.96 (1H, m, 3′-H), 4.08 (1H, t, *J* = 6.7 Hz, 2-H). Since this epoxide was unstable to silica gel chromatographic purification, the crude product was used in the next step without further purification.

(R)-4-Hydroxy-7,7-(trimethylenedithio)heptanenitrile (**5a**). To a solution of butyllithium (1.69 M in hexane, 50.1 ml, 84.6 mmol) in tetrahydrofuran (50 ml) was added dropwise a solution of acetonitrile (4.42 ml, 84.6 mmol) in tetrahydrofuran (80 ml) at −78°C. After 1.5 h, a solution of **4** (10.1 g, 52.9 mmol) in tetrahydrofuran (100 ml) was added dropwise at −15°C,

and the mixture was stirred for 1.8 h at about −10°C. The mixture was poured into saturated NH_4Cl and extracted with ether. The ethereal solution was successively washed with water and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed over silica gel (150 g, hexane : ethyl acetate = 5 : 1 to 2 : 1) to give 5.03 g (43%) of **5a** as a solid, which upon recrystallization from hexane–ether afforded colorless microcrystals, mp 35–37°C, $[\alpha]_D^{25}$ +13.3° (c = 1.23, $CHCl_3$). IR ν_{max} cm^{-1}: 3450 (s), 2930 (s), 2250 (w), 1640 (m), 1610 (m), 1420 (s), 1275 (m), 1090 (s), 910 (m), 735 (m). ^{1}H-NMR δ: 1.61 (1H, d, J = 5.7 Hz, OH), 1.63–1.79 (3H, m, 5-H, 6-H_2), 1.81–1.90 (3H, m, 3-H, 5-H, $SCH_2C\underline{H}$), 1.94 (1H, dddd, J = 13.7, 10.0, 6.8, 5.8 Hz, 3-H), 2.13 (1H, dtt, J = 14.2, 4.5, 2.8 Hz, $SCH_2C\underline{H}$), 2.49 (1H, ddd, J = 17.0, 7.5, 5.8 Hz, 2-H), 2.53 (1H, ddd, J = 17.0, 8.3, 6.8 Hz, 2-H), 2.82–2.92 (4H, m, $SCH_2 \times 2$), 3.73–3.81 (1H, m, 4-H), 4.07 (1H, t, J = 6.7 Hz, 7-H). HRMS m/z (M^+): calcd. for $C_{10}H_{17}NOS_2$, 231.0751; found, 231.0792.

(R)-4-(t-Butyldimethylsilyl)oxy-7,7-(trimethylenedithio)heptanenitrile (**5b**). To a stirred solution of **5a** (4.66 g, 20.2 mmol) and imidazole (2.75 g, 40.4 mmol) in *N,N*-dimethylformamide (10 ml) was added portionwise *t*-butyldimethylsilyl chloride (4.32 g, 28.7 mmol). The mixture was stirred overnight at room temperature, diluted with saturated $NaHCO_3$ and extracted with ether. The ethereal solution was successively washed with water and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed over silica gel (200 g, hexane : ether = 5 : 1) to give 5.8 g (83%) of **5b** as a solid, which upon recrystallization from hexane–ether afforded colorless microcrystals, mp 31–32°C, $[\alpha]_D^{25}$ +23.7° (c = 1.20, $CHCl_3$). IR ν_{max} cm^{-1}: 2960 (s), 2920 (s), 2900 (m), 2860 (m), 2250 (vw), 1350 (m), 1090 (s), 990 (m), 830 (s), 770 (s). ^{1}H-NMR δ: 0.09 (3H, s, CH_3), 0.10 (3H, s, CH_3), 0.89 (9H, s, *t*-butyl), 1.67–1.72 (2H, m, 6-H_2), 1.73–1.82 (4H, m, 3-H_2, 5-H_2), 1.86 (1H, dtt, J = 14.2, 10.8, 3.9 Hz, $SCH_2C\underline{H}$), 2.12 (1H, dtt, J = 14.2, 4.5, 2.8 Hz, $SCH_2C\underline{H}$), 2.38 (1H, dt, J = 17.0, 7.1 Hz, 2-H), 2.42 (1H, dt, J = 17.0, 7.6 Hz, 2-H), 2.81–2.91 (4H, m, $SCH_2 \times 2$), 3.79–3.84 (1H, m, 4-H), 4.01 (1H, t, J = 6.7 Hz, 7-H). HRMS m/z (M^+): calcd. for $C_{16}H_{31}NOS_2$, 345.1615; found, 345.1661.

(R)-4-(t-Butyldimethylsilyl)oxy-7,7-(trimethylenedithio)heptanal (**5c**). To a stirred solution of **5b** (520 mg, 15.1 mmol) in toluene (2.6 ml) was added dropwise diisobutylaluminum hydride (1.01 M in toluene, 2.24 ml, 22.6 mmol) at −40°C. The mixture was gradually warmed to 10°C over 3 h. To this mixture was added saturated NH_4Cl, ethyl acetate and Celite, and the resultant slurry was stirred for 30 min. The mixture was filtered, and the filtrate was concentrated *in vacuo*. The residue was chromatographed over silica gel (15 g, hexane : ether = 15 : 1) to give 278 mg (53%) of **5c**, $[\alpha]_D^{25}$ +12.5° (c = 2.77, hexane). IR ν_{max} cm^{-1}: 2960(s), 2930 (s), 2900 (s), 2860 (s), 2730 (w), 1725 (s), 1255 (s), 1090 (s), 1055 (m), 1000 (m), 870 (s), 775 (s). ^{1}H-NMR δ: 0.05 (3H, s, CH_3), 0.77 (3H, s, CH_3), 0.89 (9H, s, *t*-butyl), 1.63–1.69 (2H, m, 6-H_2), 1.71–1.85 (4H, m, 3-H_2, 5-H_2), 1.86 (1H, dtt, J = 14.2, 10.8, 3.9 Hz, $SCH_2C\underline{H}$), 2.12 (1H, dtt, J = 14.2, 4.5, 2.8 Hz, $SCH_2C\underline{H}$), 2.49 (2H, dt, J = 1.6, 7.4 Hz, 2-H_2), 2.80–2.91 (4H, m, $SCH_2 \times 2$), 3.75 (1H, qui, J = 5.6 Hz, 4-H), 4.02 (1H, t, J = 6.7 Hz, 7-H), 9.78 (1H, t, J = 1.6 Hz, 1-H). HRMS m/z (M^+): calcd. for $C_{16}H_{32}O_2S_2Si$, 348.1612; found, 348.1573.

2-[(R,Z)-3-(t-Butyldimethylsilyl)oxy-6,14-pentadecadienyl]-1,3-dithiane (**6a**). A mixture of 9-bromo-1-nonene (1.02 g, 4.98 mmol) and triphenylphosphine (1.30 g, 4.98 mmol) in acetonitrile (6 ml) was stirred for 24 h under reflux. The mixture was concentrated *in vacuo*, and the residue was diluted with ether. The ethereal supernatant solution was removed, and the residue was diluted with dry benzene and concentrated to give 2.12 g (4.94 mmol) of (8-nonenyl)triphenylphosphonium bromide, which was then dissolved in tetrahydrofuran (23 ml). To the solution was added a solution of potassium *t*-butoxide (0.55 g, 4.94 mmol) in tetrahydrofuran (11 ml) while cooling with a water bath. After 30 min, **5c** (0.89 g, 2.56 mmol) in tetrahydrofuran (9 ml) was added dropwise. The mixture was stirred for 10 min, poured into saturated NH_4Cl and extracted with ether. The ethereal solution was successively washed with water and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The resulting residue was triturated with hexane–ether (10 : 1) and filtered. The filtrate was concentrated *in vacuo*, and the residue was chromatographed over silica gel (55 g, hexane : ether = 200 : 1 to 100 : 1) to give 0.95 g (81%) of **6a**, $[\alpha]_D^{25}$ +4.92° (c = 1.46, hexane). IR ν_{max} cm^{-1}: 3090 (w), 3010 (w), 2930 (s), 2860 (s), 1640 (w), 1255 (m), 1090 (m), 830 (s), 775 (s). ^{1}H-NMR δ: 0.05 (3H, s, CH_3), 0.06 (3H, s, CH_3), 0.89 (9H, s, *t*-butyl), 1.26–1.36 (8H, m, 9′-H_2, 10′-H_2, 11′-H_2, 12′-H_2), 1.44–1.51 (2H, m, 1′-H_2), 1.59–1.88 (4H, m, 2′-H_2, 4′-H_2), 1.86 (1H, dtt, J = 14.2, 10.8, 3.9 Hz, 5-H), 1.95–2.10 (6H, m, 5′-H_2, 8′-H_2, 13′-H_2), 2.10 (1H, dtt, J = 14.2, 4.5, 2.8 Hz, 5-H), 2.80–2.90 (4H, m, $SCH_2 \times 2$), 3.69 (1H, qui, J = 5.7 Hz, 3′-H), 4.02 (1H, t, J = 6.7 Hz, 2-H), 4.93 (1H, ddt, J = 10.0, 1.9, 1.2 Hz, 15′-H), 4.99 (1H, ddt, J = 17.0, 1.9, 1.5 Hz, 15′-H), 5.33 (1H, dt, J = 10.0, 5.6 Hz, 7′-H), 5.36 (1H, dt, J = 10.0, 5.6 Hz, 6′-H), 5.81 (1H, ddt, J = 17.0, 10.0, 6.7 Hz, 14′-H). HRMS m/z ($M^+ - C_6H_{15}OSi$): calcd. for $C_{25}H_{33}S_2$, 325.2022; found, 325.2066.

(2R,5R)- and (2R,5S)-2-[(Z)-3,11-Dodecadienyl]-5-hydroxyoxolane (**7**). Mercuric chloride (980 mg, 3.62 mmol) and calcium carbonate (390 mg, 3.95 mmol) were added to a solution of **6a** (400 mg, 0.877 mmol) in acetonitrile–water (10 : 1, 4.4 ml), and the mixture was stirred for 2 h under reflux conditions. The mixture was diluted with ether and filtered. The filtrate was successively washed with water and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was triturated with ether, and the ethereal solution was concentrated *in vacuo* to give 288 mg of **6b**, which was then dissolved in tetrahydrofuran (0.58 ml). To the solution was added tetrabutylammonium fluoride (1 M in tetrahydrofuran, 1.5 ml, 1.5 mmol), and the mixture was stirred for 30 min. The mixture was diluted with ether, successively washed with water and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed over silica gel (25 g, hexane : ethyl acetate = 15 : 1 to 10 : 1) to give 134 mg (61%) of **7**, $[\alpha]_D^{25}$ +14.5° (c = 0.85, hexane). IR ν_{max} cm^{-1}: 3420 (m), 3080 (w), 3020 (w), 2930 (vs), 2860 (s), 1640 (w), 1460 (m), 1440 (m), 1060 (s), 1010 (s), 990 (s), 910 (s). ^{1}H-NMR δ: 1.27–1.41 (8H, m, 6′-H_2, 7′-H_2, 8′-H_2, 9′-H_2), 1.45–1.52 (1H, m, 1′-H), 1.58–1.65 (1H, m, 1′-H), 1.70–2.18 (10H, m, 3-H_2, 4-H_2, 2′-H_2, 5′-H_2, 10′-H_2), 2.39 (1H, br, OH), 3.97–4.03 (0.4H, m, 5-H), 4.21 (0.6H, qui, J = 6.6 Hz, 5-H), 4.93 (1H, ddt, J = 10.2, 1.9, 1.2 Hz, 12′-H), 4.99 (1H, ddt, J = 17.0, 1.9, 1.5 Hz, 12′-H), 5.33–5.42 (2H, m, 3′-H, 4′-H), 5.46 (0.4H, d, J = 4.3 Hz, 2-H), 5.55 (0.6H, dd, J = 5.0, 1.8 Hz, 2-H), 5.81 (1H, ddt, J = 17.0, 10.0, 6.7 Hz, 11′-H). HRMS m/z (M^+): calcd. for $C_{16}H_{28}O_2$, 252.2088; found, 252.2099.

(R,Z)-7,15-Hexadecadien-4-olide (**1**). To a stirred solution of **7** (28.2 mg, 11.2 mmol) in acetone (0.2 ml) was added Jones reagent (40 μl) at 0°C. After 30 min, the mixture was diluted with water and extracted with ether. The ethereal solution was successively washed with water and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed over silica gel (15 g, hexane : ethyl acetate = 10 : 1) to give 18.9 mg (68%) of **1**, $[\alpha]_D^{25}$ +38.6° (c = 1.45, $CHCl_3$). GLC: (HP 5890 Series II Plus, HP-INNOWAX 30 m × 0.25 mm × 0.25 μm at 70°C + 10°C/min to 150°C, He at 1 ml/min) Rt 20.92 min (*Z*-isomer, 93%) and 21.21 min (*E*-isomer, 7%). IR ν_{max} cm^{-1}: 3080 (w), 3010 (w), 2930 (vs), 2870 (s), 1775 (vs), 1640 (w), 1460 (m), 1350 (m), 1220 (m), 1180 (vs), 990 (m), 960 (m), 910 (s). ^{1}H-NMR δ: 1.26–1.41 (8H, m, 10-H_2, 11-H_2, 12-H_2, 13-H_2), 1.64 (1H, dddd, J = 13.7, 8.3, 6.8, 5.2 Hz, 5-H), 1.80 (1H, dddd, J = 13.7, 8.3, 8.3, 5.2 Hz, 5-H), 1.87 (1H, dddd, J = 12.7, 9.7, 9.7, 8.3 Hz, 3-H), 2.00–2.07 (4H, m, 9-H_2, 14-H_2), 2.15–2.23 (2H, m, 6-H_2), 2.32 (1H, dddd, J = 12.7, 7.7, 6.7, 6.7 Hz, 3-H), 2.51–2.56 (2H, m, 2-H_2), 4.50 (1H, dddd, J = 8.3, 8.3, 6.7, 5.2 Hz, 4-H), 4.93 (1H, ddt, J = 10.2, 1.9, 1.2 Hz, 16-H), 4.99 (1H, ddt, J = 17.0, 1.9, 1.5 Hz, 16-H), 5.33 (1H, dtt, J = 10.8, 7.3, 1.4 Hz, 8-H), 5.43 (1H, dtt, J = 10.8, 7.3, 1.4 Hz, 7-H), 5.81 (1H, ddt, J = 17.0, 10.0, 6.7 Hz, 15-H). HRMS m/z (M^+): calcd. for $C_{16}H_{26}O_3$, 250.1932; found, 250.1907.

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