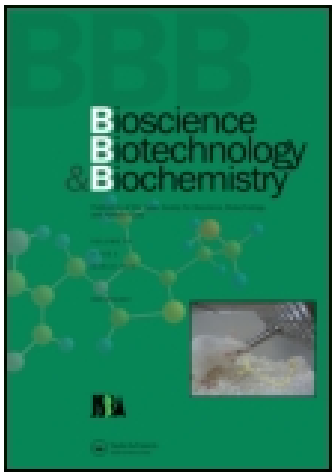


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# Concise Synthesis of a Racemic and Diastereomeric Mixture of the Sex Pheromones of Matsucoccus Pine Scales

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# Concise Synthesis of a Racemic and Diastereomeric Mixture of the Sex Pheromones of *Matsucoccus* Pine Scales

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**A short (3–5 steps) synthesis of a racemic and diastereomeric mixture of *Matsucoccus* sex pheromones (1–3) is described. The key reaction is Lewis acid-mediated cyanation of symmetric tertiary alcohol 6 to afford common intermediate 7.**

**Key words:** sex pheromone; pine scale; *Matsucoccus*; cyanation of allylic alcohol



In 1989, Silverstein *et al.* isolated and identified matsuone (**1**) as the primary component of the female-produced sex pheromone of three species of *Matsucoccus* pine scales, *M. resinosae*, *M. matsumurae*, and *M. thumbergianae*.[1] Subsequently, the analogous sex pheromone components were isolated from the two different species, *M. feytaudi* and *M. josephi*, and identified as **2**[2] and **3**,[3] respectively (Fig. 1). The absolute configurations of these pheromones have already been assigned as depicted in Fig. 1 by our enantioselective syntheses of the stereoisomers of **1**,[4] **2**,[5] and **3**[6] and by their bioassays or a GC comparison with natural pheromones. Several synthetic efforts have been reported for the stereoisomer(s) of **1**,[7–10] **2**,[10–12] and **3**[10,13] up to the present time. As no inhibitory activities of unnatural isomers were observed, it was thought worth while to develop a simple method for synthesizing **1–3**, even as a stereoisomeric mixture, for a study of practical pest control.[10] We report a short (3 steps for **1′** and **2′**, and 5 steps for (±)-**3**) synthesis of a racemic and diastereomeric mixture of *Matsucoccus* pheromones.

Our synthetic strategy is shown in Fig. 2. By paying attention to the common skeleton, a $\beta,\gamma,\delta,\varepsilon$-unsaturated ketone, of these pheromones, and disconnecting the C–C bond between the carbonyl and $\alpha$-carbon, the symmetric delocalized carbanion (**B**) or carbenium ion (**C**) was thought to be a simple and readily preparable species to give **A** by a reaction with the equivalent of **D** or **E**, respectively.*[1]

First, we adopted the carbanion strategy (**4**→**B**→**5**), but deprotonation at the doubly allylic position of **4** by various bases (*e.g.*, *n*-BuLi–TMEDA or *t*-BuLi) resulted in failure (Fig. 3). We then moved to the carbenium ion (**C**) strategy. The Grignard reaction between 1-propenylmagnesium bromide and ethyl acetate afforded tertiary alcohol **6** in a 95% yield. Although **6** was contaminated with *ca.* 11% of 4-methyl-5-hepten-2-one, it could be used for the next reaction as a mixture. The delocalized cation (**C**) generated by treating **6** with a catalytic amount (0.1 eq) of TMSOTf was trapped with TMSCN in $CH_2Cl_2$[14] at $-35\sim-30$°C to give unsaturated nitriles **7** and **7′** as a 5.3 : 1 mixture in a 56% yield. These isomers were carefully separated by $SiO_2$ chromatography, and **7** of 98.7% purity was obtained. It should be noted that an inexpensive *E*, *Z* mixture of 1-propenyl bromide could be used in the first Grignard reaction, because the geometry of the two double bonds of **6** was equilibrated during the cationic reaction. In practice, both (*E*, *E*)- and (*Z*, *Z*)-**6** gave mixtures of **7** and **7′** in the same ratio.

Nucleophilic addition of (±)-3,5-dimethylhexyllithium to **7** in ether and subsequent acid treatment afforded **1′** as a racemic and diastereomeric mixture in a 70% yield. During the course of this reaction, slight isomerization of the geometry at the $\beta,\gamma$-double bond was observed ($E/Z = 60:1$, determined by $^1$H-NMR; see Experimental section). Similarly, the reaction of **7** with (±)-3-methylpentyllithium afforded **2′** in a 73% yield ($E/Z = 53:1$, determined by $^1$H-NMR or GLC; see Experimental section). A comparison of the $^1$H-NMR and IR data for **1′** and **2′** with the

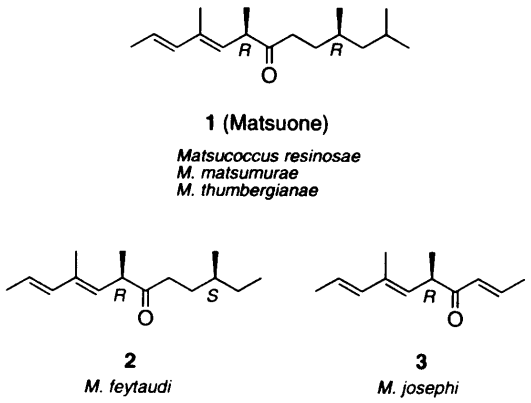


**Fig. 1.** Sex Pheromones of *Matsucoccus* Pine Scales.

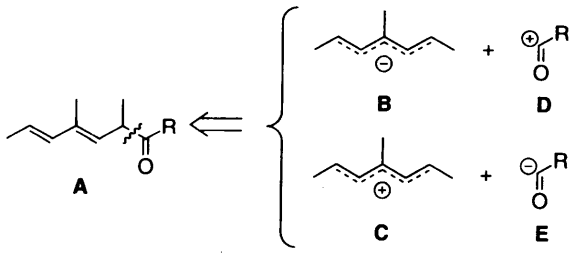


**Fig. 2.** Synthetic Strategy for the *Matsucoccus* Pheromones.

*[1] For syntheses of **1–3** on the same basis of symmetry, see ref. 10.

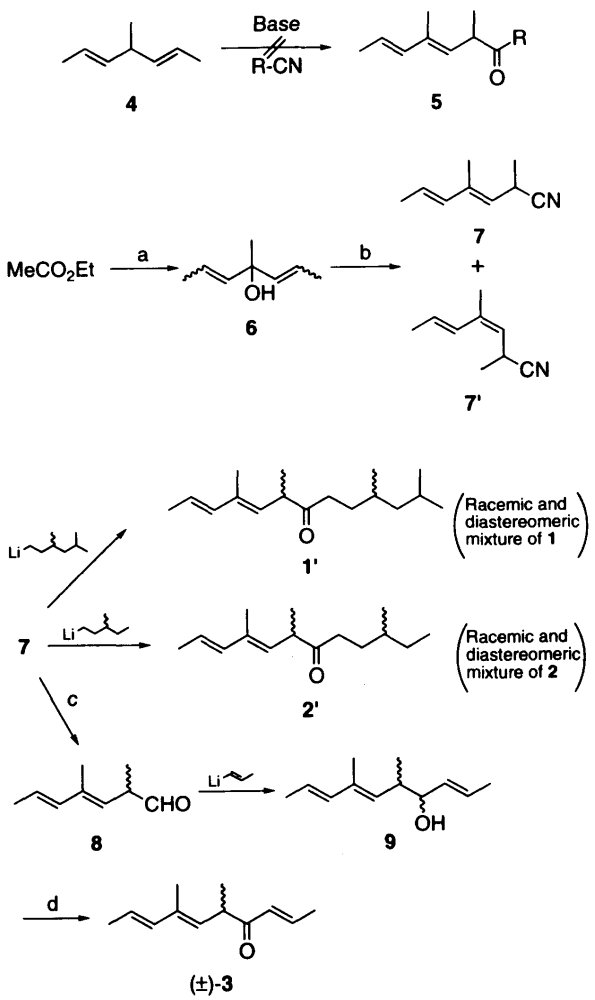


**Fig. 3.** Synthesis of **1**–**3** (as a racemic and diastereomeric mixture).

Reagents: (a) 1-propenylmagnesium bromide (95%); (b) $Me_3SiCN$, $Me_3SiOTf$ (44–58%, 7/7′ = 4.5–5.7 : 1); (c) DIBAL; $H_3O^+$; (d) PDC (49%).

previously reported data[4,5,8,10] confirmed their structures.

On the other hand, the reaction of **7** with (*E*)-1-propenyllithium resulted in the recovery of **7**. Presumably due to the low nucleophilicity of this lithium reagent, deprotonation of **7** is thought to have predominantly taken place. We then employed aldehyde **8** as an electrophile.[10] Nitrile **7** was successfully reduced with DIBAL in pentane at −20°C and then hydrolyzed with aqueous tartaric acid to give an unstable aldehyde (**8**), which was immediately subjected to a reaction with (*E*)-1-propenyllithium, **9** being obtained as an inseparable diastereomeric mixture in a 67% yield. The relative stereochemistry of the major component of **9** was assigned to be *syn* by comparing its $^1$H-NMR data with those previously reported by us,[6] and the ratio was determined to be *syn*/*anti* = 4 : 1. Oxidation of **9** with PDC gave (±)-**3** in 49% yield. Its IR and $^1$H-NMR spectral data were identical with those reported by us previously.[6]

In conclusion, we developed a new and simple synthetic method for *Matsucoccus* pheromones **1**, **2**, and **3** as racemic and diastereomeric mixtures. The overall yield was 28% (in 3 steps), 29% (in 3 steps), and 13% (in 5 steps), respectively.

## Experimental

Infra-red spectra were recorded with a JASCO FT/IR-230 spectrometer. $^1$H- and $^{13}$C-NMR spectra were recorded in $CDCl_3$ with a JEOL JNM EX-90 or Bruker AC 300, or in $C_6D_6$ with a JEOL JNM GSX-500 NMR spectrometer, using $CHCl_3$ ($\delta_H$ = 7.26 ppm), $C_6D_5H$ ($\delta_H$ = 7.15 ppm), $CDCl_3$ ($\delta_C$ = 77.0 ppm), or $C_6D_6$ ($\delta_C$ = 128.0 ppm) as the internal reference. Refractive indexes were measured with an Atago 1T refractometer. Gas chromatography was performed with Shimadzu GC-14A instruments, using a Neutrabond-1 capillary column (0.25 mm × 15 m, GL Sciences Inc.) and helium as the carrier gas (1.0 kg/cm$^{-2}$). Column chromatography was performed on Merck Kieselgel 60, Art.-Nr. 7734. All boiling point data are uncorrected.

*4-Methyl-2,5-heptadien-4-ol* (**6**). To magnesium turnings (7.80 g, 321 mmol) was added a portion (20 ml) of a solution of 1-bromopropene (25.0 ml, 292 mmol) and 1,2-dibromoethane (0.40 ml, 5.7 mmol) in anhydrous THF (300 ml) under argon, before 1,2-dibromoethane (0.40 ml, 5.7 mmol) was subsequently added to the mixture. When reaction started, the remaining solution of the bromides was slowly added while stirring over an 80-min period. The resulting solution of Grignard reagents was cooled to room temperature in a water bath, and EtOAc (11.4 ml, 117 mmol) was then added dropwise. After 1 h, the mixture was poured into ice-cooled saturated $NH_4Cl$ and extracted twice with ether. The organic layer was successively washed with aq. $Na_2S_2O_3$, saturated $NaHCO_3$ and brine, dried with $K_2CO_3$ and $Na_2SO_4$, and concentrated *in vacuo*. The residue was distilled to give 14.0 g of **6** (95%) as a mixture of isomers; bp 59–65°C at 19 Torr. IR $\nu_{max}$ (film) cm$^{-1}$: 3429 (s, O–H), 3016 (s, =C–H), 1712 (s, C=O), 1651 (m, C=C), 1109 (s, C–O), 970 (s), 912 (s), 715 (s). $^1$H-NMR (90 MHz, $CDCl_3$) $\delta$: 1.48–1.59 (3H, s × 3, 4-Me), 1.65–2.00 (7H, m, 1-H, 7-H, OH), 5.20–6.00 (4H, m, 2-H, 3-H, 5-H, 6-H) [for 4-methyl-5-hepten-2-one: 1.11 (3H, d, $J$ = 6.6 Hz, 4-Me), 1.65–2.00 (4H, m, 4-H, 7-H), 2.26 (3H, s, 1-H), 2.52 (2H, d, $J$ = 7.1 Hz, 3-H), 5.20–6.00 (2H, m, 5-H, 6-H)]. *Anal.* Found: C, 75.95; H, 11.06%. Calcd. for $C_8H_{14}O$: C, 76.14; H, 11.18%.

*(3E,5E)-2,4-Dimethyl-3,5-heptadienenitrile* (**7**) *and (3Z,5E)-2,4-dimethyl-3,5-heptadienenitrile* (**7′**). To a stirred solution of $Me_3SiCN$ (3.17 ml, 23.8 mmol) and $Me_3SiOTf$ (0.46 ml, 2.38 mmol) in anhydrous $CH_2Cl_2$ (20 ml) was added dropwise a solution of **6** (3.00 g, 23.8 mmol) and $Me_3SiCN$ (6.34 ml, 47.6 mmol) in anhydrous $CH_2Cl_2$ (40 ml) at −30 ~ −35°C during a 20-min period under argon. After 30 min, $Et_3N$ (0.7 ml, 5 mmol) and saturated $NaHCO_3$ were added, and the reaction mixture was allowed to warm to room temperature. The mixture was extracted with hexane, and the organic layer was washed with brine, dried with $MgSO_4$, and concentrated *in vacuo*. A GLC analysis was carried out at this stage (oven temperature, 100°C; $t_R$ 2.48 min for **7′** and 2.83 min for **7**), and the ratio of **7** : **7′** was estimated to be 5.3 : 1. The crude product was roughly chromatographed on $SiO_2$ (60 g, hexane/EtOAc = 50 : 1) to give 1.80 g of a mixture of **7** and **7′** (56%) as a colorless oil. These two isomers could be separated by further careful chromatography. **7**: bp 62°C at 1.0 Torr, $n_D^{20}$ = 1.4852. IR $\nu_{max}$ (film) cm$^{-1}$: 3032 (s, =C–H), 2239 (s, C≡N), 1626 (m, C=C), 964 (s). $^1$H-NMR (300 MHz, $CDCl_3$) $\delta$: 1.40 (3H, d, $J$ = 7.1 Hz, 2-Me), 1.78 (3H, dd, $J$ = 6.4, 1.4 Hz, 7-H), 1.78 (3H, d, $J$ = 1.1 Hz, 4-Me), 3.54 (1H, dq, $J$ = 8.6, 7.2 Hz, 2-H), 5.24 (1H, br. d, $J$ = 8.7 Hz, 3-H), 5.76 (1H, dq, $J$ = 15.5, 6.7, 6-H), 6.04 (1H, dq, $J$ = 15.6, 1.2 Hz, 5-H). *Anal.* Found: C, 79.73; H, 9.74; N, 9.93%. Calcd. for $C_9H_{13}N$: C, 79.95; H, 9.69; N, 10.35%. **7′**: $n_D^{23}$ = 1.4820. IR $\nu_{max}$ (film) cm$^{-1}$: 3039 (s, =C–H), 2239 (s, C≡N), 1657 (m, C=C), 960 (s), 931 (s). $^1$H-NMR (300 MHz, $CDCl_3$) $\delta$: 1.39 (3H, d, $J$ = 7.1 Hz, 2-Me), 1.83 (3H, dd, $J$ = 6.5, 1.5 Hz, 7-H), 1.83 (3H, d, $J$ = 1.3 Hz, 4-Me), 3.67 (1H, dq, $J$ = 8.9, 7.1 Hz, 2-H), 5.12 (1H, br. d, $J$ = 9.1 Hz, 3-H), 5.87 (1H, dq, $J$ = 14.8, 6.8, 6-H), 6.28 (1H, br. d, $J$ = 15.3 Hz, 5-H). *Anal.* Found: C, 79.71; H, 9.72; N, 10.07%. Calcd. for $C_9H_{13}N$: C, 79.95; H, 9.69; N, 10.35%.

*(±)-1-Iodo-3,5-dimethylhexane.* To a stirred and ice-cooled solution of (±)-3,5-dimethyl-1-hexanol[15] (2.60 g, 20.0 mmol), imidazole (2.17 g, 31.9 mmol), and triphenylphosphine (7.33 g, 27.9 mmol) in $CH_2Cl_2$ (60 ml) was added portionwise iodine (8.11 g, 31.9 mmol). After 1 h, saturated $NaHCO_3$ (20 ml) and saturated $Na_2SO_3$ (20 ml) were added, and the reaction mixture was extracted with hexane. The organic layer was successively washed with water and brine, dried with $MgSO_4$, and concentrated *in vacuo*. The residue was filtered through a pad of silica gel with hexane and concentrated *in vacuo* to give the crude product, which was distilled at a reduced pressure to give 3.14 g of (±)-1-iodo-3,5-dimethylhexane (65%) as a colorless oil, bp 52–53°C at 3.0 Torr, $n_D^{24}$ = 1.4882. IR $\nu_{max}$ (film) cm$^{-1}$: 2956 (s, C–H), 2925 (s, C–H), 2904 (s, C–H), 2870 (s, C–H), 1466 (s, C–H), 1385 (s, C–H), 1365 (m, C–H), 1227 (s, C–H), 1176 (s, C–H). $^1$H-NMR (90 MHz, $CDCl_3$) $\delta$: 0.86 (6H, d,

$J$=6.2 Hz, 6-H, 5-Me), 0.88 (3H, d, $J$=6.2 Hz, 3-Me), 1.00–1.20 (2H, m, 4-H), 1.35–2.05 (4H, m, 2-H, 3-H, 5-H), 3.20 (2H, m, 1-H). *Anal.* Found: C, 39.99; H, 7.04%. Calcd. for $C_8H_{17}I$: C, 40.02; H, 7.14%.

*(2E,4E)-4,6,10,12-Tetramethyl-2,4-tridecadien-7-one* (**1'**). To a stirred solution of (±)-1-iodo-3,5-dimethylhexane (266 mg, 1.11 mmol) in anhydrous ether (1.5 ml) was added dropwise *t*-butyllithium (1.6 M in pentane, 1.29 ml, 2.06 mmol) over a 5-min period at −78°C under argon, and the mixture was allowed to warm gradually to −10°C. To this reaction mixture was then added a solution of **7** (100 mg, 0.740 mmol) in anhydrous ether (1 ml). After 10 min, the reaction was quenched with saturated $NaHCO_3$ (2 ml), and the mixture was extracted with ether. The extract was successively washed with saturated $Na_2SO_3$ and saturated $NaHCO_3$. The ethereal solution was treated with 2 ml of 3 N $H_2SO_4$ at 0°C and allowed to warm gradually to room temperature while stirring during a 90-min period. The mixture was extracted with hexane, successively washed with saturated $Na_2SO_3$, saturated $NaHCO_3$ and brine, dried with $MgSO_4$ and concentrated *in vacuo*. The residue was chromatographed on $SiO_2$ (7 g, hexane/EtOAc = 100 : 1) to give 130 mg of **1'** (70%) as a colorless oil. $n_D^{21}$ = 1.4779. IR $\nu_{max}$ (film) $cm^{-1}$: 3028 (s, =C–H), 1714 (s, C=O), 1620 (w, C=C), 962 (s). $^1$H-NMR (500 MHz, $C_6D_6$) $\delta$: 0.75 (3H, d, $J$=6.0 Hz, 10-Me), 0.81 (3H, d×2, $J$=6.5 Hz, 13-H), 0.85 (3H, d×2, $J$=6.5 Hz, 12-Me), 0.92 (1H, m, 11-$H_1$), 1.03 (1H, ddd, $J$=13.5, 8.0, 5.5 Hz, 11-$H_1$), 1.14 (3H, d×2, $J$=6.8 Hz, 6-Me), 1.32–1.43 (2H, m, 9-$H_1$, 10-H), 1.51–1.63 (1H, m, 12-H), 1.60 (3H, br. d, $J$=7.0 Hz, 1-H), 1.63–1.72 (1H, m, 9-$H_1$), 1.67 (3H, d×2, $J$=1.0 Hz, 4-Me), 2.13 (0.5H, ddd, $J$=16.8, 8.5, 6.0 Hz, 8-$H_1$ of 6,10-*anti* isomer), 2.18 (0.5H, ddd, $J$=17.0, 9.5, 5.5 Hz, 8-$H_1$ of 6,10-*syn* isomer), 2.28 (0.5H, ddd, $J$=18.0, 8.5, 6.5 Hz, 8-$H_1$ of 6,10-*syn* isomer), 2.32 (0.5H, ddd, $J$=17.0, 9.0, 5.5 Hz, 8-$H_1$ of 6,10-*anti* isomer), 3.29 (0.5H, dq, $J$=10.0, 6.5 Hz, 6-H), 3.30 (0.5H, dq, $J$=10.0, 6.5 Hz, 6-H), 5.25 (1H, br. d, $J$=10.0 Hz, 5-H), 5.49 (1H, dq, $J$=15.5, 6.5, 2-H), 6.01 (1H, br. d, $J$=15.5 Hz, 3-H). The integration of the very small peak at $\delta$ 6.50 ppm [doublet, 3-H of the (2*E*,4*Z*)-isomer] indicated its *ca.* 1.6% contamination. $^{13}$C-NMR (125 MHz, $C_6D_6$) $\delta$: 12.9, 16.7, 18.2, (19.6, 19.7), (22.4), (23.4, 23.5), 25.4, 30.1, 31.3, (38.4), (46.6), (46.7, 46.9), 123.7, 129.5, 135.5, 136.1, 209.5. *Anal.* Found: C, 81.53; H, 11.98%. Calcd. for $C_{17}H_{30}O$: C, 81.60; H, 12.08%.

*(8E,10E)-3,7,9-Trimethyl-8,10-dodecadien-6-one* (**2'**). To a stirred solution of (±)-1-iodo-3-methylpentane[16] (1.18 g, 5.56 mmol) in anhydrous ether (10 ml) was added dropwise *t*-butyllithium (1.6 M in pentane, 6.47 ml, 10.4 mmol) over a 10-min period at −78°C under argon, and the mixture was allowed to warm gradually to −10°C. To the reaction mixture was then added a solution of **7** (500 mg, 3.70 mmol) in anhydrous ether (4 ml). After 20 min, the reaction was quenched with saturated $NaHCO_3$ (5 ml), the mixture was extracted twice with ether, and the combined organic layer was successively washed with saturated $Na_2SO_3$ and saturated $NaHCO_3$. The ethereal solution was then treated with 6 ml of 3 N $H_2SO_4$ at 0°C, before it was allowed to warm gradually to room temperature while stirring during a 90-min period. The organic layer was separated, successively washed with saturated $Na_2SO_3$, saturated $NaHCO_3$ and brine, dried with $MgSO_4$ and concentrated *in vacuo*. The residue was chromatographed on $SiO_2$ (15 g, hexane/EtOAc = 100 : 1) to give 601 mg of **2'** (73%) as a colorless oil. It contained *ca.* 1.9% of the (8*Z*,10*E*)-isomer, which was determined by 500 MHz $^1$H-NMR (a small doublet was observed at $\delta$ 6.48 ppm) and GLC [oven temperature, 150°C; $t_R$ 3.48 min for the (8*Z*,10*E*)-isomer and 4.23 min for **2'**]. $n_D^{21}$ = 1.4820. IR $\nu_{max}$ (film) $cm^{-1}$: 3028 (s, =C–H), 1714 (s, C=O), 1620 (w, C=C), 962 (s). $^1$H-NMR (500 MHz, $C_6D_6$) $\delta$: 0.75 (3H, d, $J$=6.5 Hz, 3-Me), 0.80 (3H, t, $J$=7.3 Hz, 1-H), 1.03 (1H, m, 2-$H_1$), 1.13 (3H, d×2, $J$=6.8 Hz, 7-Me), 1.15–1.27 (2H, m, 2-$H_1$, 3-H), 1.39 (1H, m, 4-$H_1$), 1.60 (3H, dd, $J$=11.3, 1.5 Hz, 12-H), 1.60–1.71 (1H, m, 4-$H_1$), 1.66 (3H, d, $J$=1.5 Hz, 9-Me), 2.12 (0.5H, ddd, $J$=16.5, 9.0, 6.0 Hz, 5-$H_1$ of the 3,7-*anti* isomer), 2.15 (0.5H, ddd. $J$=17.5, 9.5, 6.0 Hz, 5-$H_1$ of the 3,7-*syn* isomer), 2.27 (0.5H, ddd, $J$=16.9, 9.1, 6.6 Hz, 5-$H_1$ of the 3,7-*syn* isomer), 2.29 (0.5H, ddd, $J$=16.9, 9.1, 5.9 Hz, 5-$H_1$ of the 3,7-*anti* isomer), 3.28 (1H, dq, $J$=9.8, 6.8 Hz, 7-H), 5.24 (1H, d, $J$=9.5 Hz, 8-H), 5.49 (1H, dq, $J$=15.5, 6.5, 11-H), 6.02 (1H, dq, $J$=15.5, 1.0 Hz, 10-H). $^{13}$C-NMR (125 MHz, $C_6D_6$) $\delta$: 11.5, (12.9), 16.7, (18.2, 18.3), 19.1, (29.5, 29.6), 30.7, 34.3, 38.5, 46.6, 123.7, 129.5, 135.5, 136.0, 209.5. *Anal.* Found: C, 81.20; H, 11.64%. Calcd. for $C_{15}H_{26}O$: C, 81.02; H, 11.79%.

*(2E,6E,8E)-5,7-Dimethyl-2,6,8-decatrien-4-ol* (**9**). To a stirred solution of **7** (100 mg, 0.740 mmol) in pentane (2 ml) was added diissobutylaluminium hydride (0.95 M in hexane, 0.934 ml, 0.887 mmol) at −20°C under argon. After 30 min, the mixture was treated with 1 N tartaric acid (4 ml) and allowed to warm gradually to room temperature while vigorously stirring during a 2-h period. The mixture was then extracted with hexane, and the organic layer was successively washed with water, saturated $NaHCO_3$, water and brine, dried with $Na_2SO_4$ and concentrated *in vacuo* to give crude aldehyde **8** as a pale yellow oil. This crude product was used in the next step without further purification. To a stirred solution of (*E*)-1-(tributylstannyl)propene[17] (367 mg, 1.11 mmol) in anhydrous THF (2 ml) was added *n*-butyllithium (1.6 M in hexane, 0.601 ml, 0.962 mmol) at −78°C under argon. After 10 min, the mixture was warmed to −5°C, stirred for 15 min at the same temperature, and then cooled to −78°C again. A solution of **8** in THF (0.5 ml × 2) was added to the mixture, which was warmed gradually to room temperature. The reaction mixture was treated with saturated $NH_4Cl$ and extracted twice with ether, before the combined organic layer was successively washed with water, saturated $NaHCO_3$ and brine, dried with $MgSO_4$ and concentrated *in vacuo*. The residue was chromatographed on $SiO_2$ (8 g, hexane/EtOAc = 10 : 1) to give 89.9 mg of **9** (67%) as a diastereomeric mixture. $n_D^{23}$ = 1.5018. IR $\nu_{max}$ (film) $cm^{-1}$: 3390 (s, O–H), 3028 (s, =C–H), 1670 (m, C=C), 1626 (m, C=C), 1088 (m, C–O), 1009 (s), 962 (s), 926 (s). $^1$H-NMR for the major 4,5-*syn*-isomer (90 MHz, $CDCl_3$) $\delta$: 0.98 (3H, d, $J$=7.1 Hz, 5-Me), 1.40–1.90 (10H, m, 1-H, 10-H, 7-Me, OH), 2.60 (1H, m, 5-H), 3.80 (1H, m, 4-H), 5.19 (1H, br. d, $J$=10.2 Hz, 6-H), 5.30–5.90 (3H, m, 2-H, 3-H, 9-H), 6.10 (1H, d, $J$=15.5 Hz, 8-H). *Anal.* Found: C, 79.79; H, 11.02%. Calcd. for $C_{12}H_{20}O$: C, 79.84; H, 11.18%.

*(2E,6E,8E)-5,7-Dimethyl-2,6,8-decatrien-4-one* ((±)-**3**). To a stirred solution of **9** (72.3 mg, 0.401 mmol) in DMF (2 ml) was added pyridinium dichromate (PDC; 302 mg, 0.803 mmol) in one portion at 0°C. The mixture was gradually warmed to room temperature during a 90-min period, more PDC (76.0 mg, 0.202 mmol) was then added, and the mixture was stirred for 1 h. The mixture was diluted with hexane, successively washed with brine, water, *dil* HCl, water, saturated $NaHCO_3$ and brine, dried with $MgSO_4$ and concentrated *in vacuo*. The residue was chromatographed on $SiO_2$ (8 g, hexane/EtOAc = 100 : 1) to give 35.0 mg of (±)-**3** (49%) as a colorless oil, $n_D^{22}$ = 1.5092. IR $\nu_{max}$ (film) $cm^{-1}$: 3028 (s, =C–H), 1697 (s, C=O), 1672 (s, C=C), 1631 (s, C=C), 964 (s). $^1$H-NMR (300 MHz, $CDCl_3$) $\delta$: 1.17 (3H, d, $J$=6.6 Hz, 5-Me), 1.77 (3H, dd, $J$=6.6, 1.4 Hz, 10-H), 1.81 (3H, d, $J$=1.1 Hz, 7-Me), 1.86 (3H, dd, $J$=6.9, 1.7 Hz, 1-H), 3.61 (1H, dq, $J$=9.7, 6.8 Hz, 5-H), 5.24 (1H, br. d, $J$=9.8 Hz, 6-H), 5.67 (1H, dq, $J$=15.5, 6.6 Hz, 9-H), 6.08 (1H, dq, $J$=15.0, 1.7 Hz, 8-H), 6.16 (1H, dq, $J$=15.5, 1.6 Hz, 3-H), 6.89 (1H, dq, $J$=15.5, 6.9 Hz, 2-H). $^{13}$C-NMR (75 MHz, $CDCl_3$) $\delta$: 12.9, 16.6, 18.21, 18.24, 44.6, 124.0, 128.5, 129.8, 135.5, 135.6, 142.5, 200.4. *Anal.* Found: C, 80.70; H, 10.00%. Calcd. for $C_{12}H_{18}O$: C, 80.85; H, 10.18%.

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