New Syntheses of (*R*)-(+)-3-Acetoxy-2,6-dimethyl-1,5-heptadiene, the Pheromone of the Comstock Mealybug[†]

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L-Phenylalanine was converted to optically impure (*R*)-(+)-2,6-dimethyl-1,5-heptadien-3-ol **2** (19% *e.e.*). (*R*)-(+)-**2** (96% *e.e.*) was prepared by a kinetic resolution of ($\pm$)-**2**. Acetylation of the pure (*R*)-(+)-**2** gave the pheromone of the Comstock mealybug (*Pseudococcus comstockii* KUWANA) [(*R*)-(+)-**1**].

The Comstock mealybug, *Pseudococcus comstockii* KUWANA, is one of the most important pests against apples, pears and other agricultural crops. In search of a better method to detect its infestation at an early stage, its sex pheromone has been isolated and independently identified as 3-acetoxy-2,6-dimethyl-1,5-heptadiene **1** by two groups.^{1,2)} Synthesis of ($\pm$)-**1** confirmed the correctness of the proposed structure, although the absolute configuration at C-3 remained unknown.^{2,3)} Later, we synthesized both the enantiomers (90~91% *e.e.*) of **1**,⁴⁾ using Sharpless's asymmetric epoxidation.⁵⁾ Consequently, the absolute configuration of the natural and dextrorotatory pheromone was assigned to be *R*,⁴⁾ based on the general rule for the orientation of the introduction of an oxygen atom to a double bond in the course of the asymmetric epoxidation.⁵⁾

Here we report two new syntheses of the optically active pheromone so as to confirm its absolute configuration by relating its stereochemistry to that of a natural product with known absolute configuration and also to synthesize the optically purer pheromone.

One of our syntheses started from L-phenylalanine, which is readily available in optically pure form. The earlier stages of the

conversion of the amino acid to the pheromone followed the path previously developed by Terashima *et al.*⁶⁾ Thus L-phenylalanine yielded a known acetone **3** in 6 steps.⁶⁾ This was oxidized with pyridinium chlorochromate (PCC)⁷⁾ to give an aldehyde **4**. Treatment of **4** with isopropylidenetriphenylphosphorane gave **5**, which was deprotected to give **6a**. The corresponding monomesylate **6b** was treated with potassium carbonate in methanol to afford an epoxide **7**. Ring cleavage of the epoxide **7** with aluminum isopropoxide gave an allylic alcohol (*R*)-(+)-**2**, $[\alpha]_D^{24} +7.8^\circ$ (n-hexane). GLC analysis of its (*S*)- α -methoxy- α -trifluoromethylphenylacetate (MTPA ester)⁸⁾ revealed the optical purity of **2** to be 19%, although we started from optically pure L-phenylalanine. The poor optical purity might be due to racemization in the course of the ring-opening of the epoxide **7**, since this reaction was carried out under a harsh condition (toluene reflux, 16 hr). Conversion of (+)-**2** into the natural (+)-**1** had already been reported.⁴⁾ The present unambiguous synthesis of (*R*)-(+)-**2** from L-phenylalanine therefore confirmed the (*R*)-configuration of the pheromone of the Comstock mealybug, although the optical purity of the product **2** was far from satisfactory.

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Another synthesis of (R)-(+)-1 was then carried out by resolving ($\pm$)-2 to obtain a highly optically pure sample of the pheromone. Recently Sharpless *et al.* have reported that, when a racemic secondary allylic alcohol is oxidized under the asymmetric epoxidation condition, one enantiomer is epoxidized faster than the other.⁹⁾ This phenomenon can be used for a kinetic resolution of the secondary allylic alcohols.⁹⁾ It might be convenient to use this method for the preparation of (R)-(+)-1, because the introduction of the chirality could be in the penultimate step of the synthetic sequence and little possibility of later racemization could be foreseen. Although two syntheses of the racemic alcohol ($\pm$)-2 had been reported,^{2,3)} we developed a new route as described below. This gave purer ($\pm$)-2 than that could be obtained by either of the two existing methods.

Starting from an organolithium compound **8** and an epoxide **9**, an allylic alcohol **10** was obtained as a mixture of the (*E*)- and (*Z*)-isomers according to Normant's procedure.¹⁰⁾ This was epoxidized with *t*-butyl hydroperoxide in the presence of vanadyl acetylacetonate¹¹⁾ to give a diastereomeric mixture of

11a, which was converted into an iodide **12** in the conventional manner *via* **11b**. The key racemic alcohol ($\pm$)-2 was obtained by reductive opening of the epoxide ring of the iodide **12** with zinc in acetic acid. The kinetic resolution of ($\pm$)-2 gave an epoxy alcohol **13** and the desired (R)-(+)-2, $[\alpha]_D^{23} + 31.8^\circ$ (*n*-hexane). GLC analysis of the corresponding (*S*)-MTPA ester revealed the optical purity of the present (+)-2 to be 96%. Our previous sample was of 90% *e.e.*⁴⁾ Finally, acetylation of (R)-(+)-2 yielded the pheromone (R)-(+)-1, $[\alpha]_D^{20} + 4.35^\circ$ (*n*-hexane), whose IR and NMR data were identical with those reported previously.^{4),*1}

In conclusion, we synthesized the natural enantiomer (R)-(+)-1 of the pheromone of the Comstock mealybug in highly optically pure state (96% *e.e.*) and reconfirmed the (*R*)-configuration of the natural pheromone by its derivation from L-phenylalanine.

EXPERIMENTAL

All bps are uncorrected. IR spectra were determined as films on a JASCO A-102 spectrometer. NMR spectra were recorded at 60 MHz with TMS as an internal standard and

*1 The specific rotations in *n*-hexane of the optically pure (R)-2 and (R)-1 were calculated to be $+33.2^\circ$ and $+4.5^\circ$, respectively. Although the specific rotation of the natural pheromone has been reported to be $+6.2^\circ$ and the same value was also observed for our synthetic samples,^{2,4)} it should be referred to too small an amount of sample(s) or to the contamination of some unidentified minor and optically active impurities in the previous samples.

CCl_4 as a solvent on a Hitachi R-24A spectrometer unless otherwise stated. Optical rotations were measured on a JASCO DIP-140 digital polarimeter.

(*S*)-(-)-2-(2,2,4,4-Tetramethyl-1,3-dioxolan-5-yl)-ethanol **3**. According to the reported procedure,⁶⁾ 4.64 g of **3** was prepared from L-phenylalanine. bp $69\sim 70^\circ\text{C}/0.65\text{ mmHg}$, n_D^{24} 1.4383; $[\alpha]_D^{26} -21.0^\circ$ ($c=2.30$, EtOH). Its IR and NMR spectra were identical with those of the reported (*S*)-**3**.⁶⁾

(*S*)-2-(2,2,4,4-Tetramethyl-1,3-dioxolan-5-yl)acetaldehyde **4**. To a suspension of pyridinium chlorochromate (8.33 g) and NaOAc (634 mg) in CH_2Cl_2 (50 ml) was added a solution of **3** (1.41 g) in CH_2Cl_2 (8 ml), and the mixture was stirred at ambient temperature for 2 hr. The mixture was diluted with anhydrous Et_2O (250 ml), the organic solution was decanted, and the residual black solid was washed with anhydrous Et_2O . The combined organic solution was filtered through a pad of florisil, and the filtrate was concentrated *in vacuo* to give 1.3 g of the crude product **4**, which was used in the next step without further purification; IR $\gamma_{\text{max}}\text{ cm}^{-1}$: 2820 (m), 2730 (w), 1730 (s); NMR δ (CDCl_3) 9.77 (1H, aldehyde proton).

(*S*)-(-)-1-(2,2,4,4-Tetramethyl-1,3-dioxolan-5-yl)-3-methyl-2-butene **5**. To a suspension of isopropyltriphenylphosphonium bromide (2.27 g) in THF (110 ml) was added a solution of *n*-BuLi (4.8 ml of 1.43 N solution in *n*-hexane) over a period of 15 min at -75°C under Ar. The phosphorane solution was stirred at -75°C for 30 min and then allowed to warm to -25°C . To the solution was slowly added a solution of **4** (1.3 g) in THF (3 ml) at -25°C . The mixture was stirred at -20°C for 30 min, at 0°C for 1 hr and at ambient temperature for 2 hr. The mixture was poured into water and extracted with ether, and the organic layer was washed with water and brine, and then dried over MgSO_4 . Filtration and concentration gave 1.53 g of the crude product, which was submitted to column chromatography (SiO_2 gel, *n*-hexane–benzene–ether 20:20:1), followed by distillation, to give 546 mg (34% from **3**) of **5** as a colorless oil; bp $57\sim 58^\circ\text{C}/5\text{ mmHg}$, n_D^{24} 1.4336; $[\alpha]_D^{24} -12.3^\circ$ ($n=1.81$, *n*-pentane), IR $\gamma_{\text{max}}\text{ cm}^{-1}$: 2990 (s), 2940 (m), 2870 (m), 1670 (w), 1460 (m), 1450 (m), 1440 (m), 1380 (s), 1370 (s), 1220 (s), 1200 (s), 1125 (m), 1100 (m), 1050 (m), 840 (m), 820 (w); NMR δ 1.02, 1.15, 1.22, 1.30 (12H, four s), 1.60, 1.68 (6H, two s), 2.10 (2H, t, $J=7\text{ Hz}$), 3.55 (1H, t, $J=7\text{ Hz}$), 5.12 (1H, t, $J=7\text{ Hz}$). Anal. Found: C, 72.66; H, 11.19. Calcd. for $\text{C}_{12}\text{H}_{22}\text{O}_2$: C, 72.68, H, 11.18%.

(*S*)-2,6-Dimethyl-2,3-dihydroxy-5-heptene **6a**. A mixture of **5** (1.37 g) in MeOH (27 ml) and 2N HCl aq. (5 ml) was heated at 50°C until no acetone remained. The mixture was cooled in an ice-bath, neutralized with NH_3 aq. and concentrated *in vacuo*. The residue was extracted with EtOAc and the organic solution was concentrated *in*

vacuo. In order to remove water, the residue was dissolved in benzene and the solution was concentrated *in vacuo* to give 1.07 g of the crude product **6a**, which was used in the next step without further purification.

(*S*)-2,6-dimethyl-2-hydroxy-5-hepten-3-yl methanesulfonate **6b**. To a solution of **6a** (500 mg, crude) and Et_3N (485 mg) in CH_2Cl_2 (16 ml) was added MsCl (402 mg) over a period of 10 min at -5 to -10°C . After stirring at -5 to -10°C for 15 min, the mixture was diluted with CH_2Cl_2 , washed with water, 10% HCl aq., sat NaHCO_3 aq. and brine, and dried over Na_2SO_4 . Filtration and concentration *in vacuo* gave 726 mg of crude **6b**, which was used in the next step without further purification.

(*R*)-(+)-2,6-Dimethyl-1,5-heptadien-3-ol **2**. To a solution of **6b** (726 mg, crude) in MeOH (7.5 ml) was added K_2CO_3 (2.15 g) in one portion, and the mixture was stirred at ambient temperature overnight. The mixture was poured into water and extracted with *n*-pentane. The organic solution was washed with water and brine, and dried over Na_2SO_4 . Filtration and concentration under atmospheric pressure gave an oily material, which was submitted to column chromatography (SiO_2 gel, *n*-pentane– Et_2O , 10:1) to give 300 mg of the crude epoxide **7**. This epoxide was dissolved in toluene (2.4 ml) and heated under reflux in the presence of aluminum isopropoxide (300 mg) for 16 hr under Ar. With cooling in an ice-bath, 2N HCl aq. (2.4 ml) was added to the solution, and the organic layer was separated, washed with water and dried over Na_2SO_4 . Filtration and concentration, followed by chromatographic purification (SiO_2 gel, *n*-pentane– Et_2O , 10:1) and distillation gave 90 mg (20% from **5**) of (*R*)-(+)-**2** as a colorless oil: bp $90\sim 100^\circ\text{C}$ (bath temp./17 mmHg), n_D^{24} 1.4577; $[\alpha]_D^{24} +7.81^\circ$ ($c=2.14$, *n*-hexane); IR $\gamma_{\text{max}}\text{ cm}^{-1}$: 3400 (m), 3090 (w), 2990 (s), 2890 (m), 2870 (m), 1650 (m), 1450 (m), 1380 (m), 1110 (m), 1050 (m), 1030 (m), 900 (s); NMR δ 1.60 (3H, s), 1.68 (6H, s), 1.96 (1H, s, D_2O exchangeable), 2.17 (2H, t, $J=7\text{ Hz}$), 3.92 (1H, t, $J=7\text{ Hz}$), 4.74 (1H, broad s), 4.85 (1H, broad s), 5.16 (1H, t, $J=7\text{ Hz}$). Anal. Found: C, 76.30; H, 11.50. Calcd. for $\text{C}_9\text{H}_{16}\text{O}$: C, 77.09; H, 11.50%. The optical purity was determined by GLC analysis of the corresponding (*S*)-MTPA ester, which gave two peaks corresponding to the (*S,S*)- and (*R,S*)-isomer respectively in the ratio of 40.7:59.3. The optical purity of this alcohol was calculated to be 18.6% e.e. GLC: column, SF-65 CR-19 40 m $\times$ 0.28 mm ϕ at $70\sim 220^\circ\text{C}$ ($+3^\circ\text{C}/\text{min}$); N_2 at 1.0 kg/cm²; t_R/min 59.95 (40.7%), 60.17 (59.3%).

2,6-Dimethyl-3,5-heptadien-1-ol **10**. To a mixture of 1,2-epoxy-2-methyl-3-butene **9** (4.21 g) and CuBr (360 mg) in Et_2O (200 ml) was added isobutyryllithium **8** (ca. 0.3 N solution in Et_2O , 200 ml) at -15 to -20°C under Ar. The resulting mixture was stirred at -15 to 20°C for 1.5 hr. To the mixture was added sat. NH_4Cl aq. (100 ml), the organic layer was separated, and the aqueous layer was

extracted with Et₂O. The combined organic layer was washed with 17% NH₃ aq. (100 ml) and brine (100 ml), and dried over MgSO₄. Filtration and concentration *in vacuo* gave an oily material, which was distilled to give 3.51 g (50%) of a 15.6:84.4 mixture of (*Z*)- and (*E*)-**10** (by GLC analysis; 5% PEG-20M, 2.0 mmφ × 150 cm, at 100~200°C (+5°C/min); *t_R* (*Z*)-isomer, 7.17 min, (*E*)-isomer, 7.34 min); bp 101~102°C/7 mmHg (lit.¹⁰) 105°C/15 mmHg), *n*_D²² 1.4716; IR $\gamma_{\max}$ cm⁻¹: 3340 (m), 2980 (m), 2920 (s), 2860 (m), 1670 (w), 1445 (m), 1375 (m), 1010 (m), 825 (w); NMR δ 1.60 (9H, broad s), 2.67 (2H, t, *J*=7 Hz), 2.93 (1H, broad s, D₂O exchangeable), 3.89 (0.8H, s, (*E*)-isomer), 4.05 (0.2H, s, (*Z*)-isomer), 5.10 (1H, t, *J*=7 Hz), 5.35 (1H, t, *J*=7 Hz).

2,3-Epoxy-2,6-dimethyl-5-hepten-1-ol 11a. To a stirred and ice-cooled mixture of **10** (3.51 g) and vanadyl acetylacetonate (103 mg) in benzene (31 ml) was added dropwise a solution of *t*-BuOOH (70% in water, 3.9 ml) at 5~10°C. The resulting greenish yellow solution was stirred at ambient temperature for 1 hr. The mixture was diluted with Et₂O, and washed with Na₂SO₃ aq., sat. NaHCO₃ aq. and brine before being dried over Na₂SO₄. Filtration and concentration *in vacuo* gave 4.48 g of an oily material, which was submitted to column chromatography (SiO₂ 45 g, *n*-hexane-Et₂O, 4:1) to give 2.55 g (65.2%) of **11a** as a pale yellow oil. An analytical sample was obtained by distillation; bp 85°C/0.95 mmHg, IR $\gamma_{\max}$ cm⁻¹: 3450 (m), 2990 (m), 2940 (s), 2760 (m), 1670 (w), 1460 (m), 1450 (m), 1440 (m), 1380 (m), 1075 (m), 1040 (s), 890 (w), 855 (w), 835 (w), 790 (w); NMR δ 1.23 (3H, s), 1.60, 1.69 (6H, two s), 2.17 (2H, dd, *J*=6 Hz, 7 Hz), 2.85 (1H, t, *J*=6 Hz), 2.87 (1H, broad s, D₂O exchangeable), 3.43 (2H, d, *J*=4 Hz), 5.10 (1H, t, *J*=7 Hz). Anal. Found: C, 69.16; H, 10.09. Calcd. for C₉H₁₆O₂: C, 69.19; H, 10.32%.

2,3-Epoxy-2,6-dimethyl-1-tosyloxy-5-heptene 11b. To a stirred and ice-cooled mixture of **11a** (2.55 g) in pyridine (27 ml) was added TsCl (5.74 g) portionwise. The mixture was stirred at ambient temperature for 7 hr. The mixture was poured into ice-cooled water and extracted with Et₂O. The organic layer was washed with water, CuSO₄ aq., water again, sat. NaHCO₃ aq. and brine, and dried over MgSO₄. Filtration and concentration *in vacuo* gave 4.02 g of crude **11b**, which was used in the next step without further purification; IR $\gamma_{\max}$ cm⁻¹: 3040 (w), 2980 (m), 2930 (m), 2880 (m), 2850 (m), 1670 (m), 1600 (m), 1595 (m), 1450 (m), 1440 (m), 1365 (s), 1190 (s), 1180 (s), 1100 (m), 970 (s), 835 (s), 815 (s), 785 (m), 760 (m), 665 (s); NMR δ 1.25 (3H, s), 1.69, 1.79 (6H, two s), 2.10 (2H, dd, *J*=6 Hz, 7 Hz), 2.41 (3H, s), 2.52 (1H, t, *J*=6 Hz), 3.77 (2H, s), 5.02 (1H, t, *J*=7 Hz), 7.22 (2H, d, *J*=9 Hz), 7.63 (2H, d, *J*=9 Hz).

2,3-Epoxy-1-iodo-2,6-dimethyl-5-heptene 12. To a solution of **11b** (14.4 g) in acetone was added NaI (12.26 g) in

one portion. The mixture was heated under reflux for 1.5 hr. After cooling to ambient temperature, the acetone was allowed to evaporate under reduced pressure. The residue was diluted with water and extracted with Et₂O. The combined organic layer was washed with Na₂S₂O₃ aq., sat. NaHCO₃ aq. and brine, and dried over MgSO₄. Filtration and concentration *in vacuo* gave 11.41 g of an oily material, which was submitted to column chromatography (SiO₂ 100 g, *n*-hexane-Et₂O, 50:1) to give 9.72 g (68.8% from **11a**) as a pale yellow oil; IR $\gamma_{\max}$ cm⁻¹: 2980 (m), 2940 (m), 2860 (m), 1670 (w), 1465 (m), 1445 (m), 1440 (m), 1385 (m), 1380 (m), 1225 (m), 1175 (m), 1135 (m), 1065 (m), 865 (m), 835 (m), 785 (s), 760 (m), 700 (m); NMR δ 1.42 (3H, s), 1.63, 1.72 (6H, two s), 2.15 (2H, m), 2.70 (1H, dd, *J*=6 Hz, 7 Hz), 3.00 (1H, d, *J*=9 Hz), 3.27 (1H, d, *J*=9 Hz), 5.15 (1H, t, *J*=7 Hz).

(±)-2,6-Dimethyl-1,5-heptadien-3-ol 2. To a stirred and ice-cooled solution of **12** (9.72 g) in AcOH (60 ml) was added Zn dust (9.63 g) portionwise. The resulting grey suspension was stirred at ambient temperature for 20 min. The mixture was diluted with Et₂O, filtered through a pad of Celite, and the solid was washed with Et₂O. The combined organic solution was washed with water, Na₂S₂O₃ aq., sat. NaHCO₃ aq. and brine, and dried over MgSO₄. Filtration and concentration *in vacuo* gave 4.84 g of an oily material, which was distilled to give 3.88 g (75.8%) of (±)-**2** as a colorless oil; bp 92~93°C/25 mmHg, *n*_D²¹ 1.4608. Anal. Found: C, 76.70; H, 11.46. Calcd. for C₉H₁₆O: C, 77.09; H, 11.50%.

Kinetic resolution of (±)-2. A mixture of Ti(Oi-Pr)₄ (8.3 ml), diisopropyl L-(+)-tartrate (7.39 g) and **2** (3.86 g) was stirred in CH₂Cl₂ (280 ml) at -20°C under Ar. *t*-BuOOH (4.3 ml of 3.94 N solution in CH₂Cl₂) was added to the mixture, and the mixture was left to stand at -20°C for 15 hr. After the addition of dimethyl sulfide (4.5 ml), the mixture was stirred at -20°C for 30 min. The mixture was poured into pre-cooled (-20°C) acetone (560 ml, containing 8.3 ml of water), and was stirred for 2~3 hr at ambient temperature until the filtrate became clear. Filtration and concentration *in vacuo* gave 15.39 g of an oily material, which was diluted with Et₂O (250 ml) and treated with 1 N NaOH aq. (100 ml) at 0°C for 30 min. The organic layer was separated, washed with brine and over MgSO₄. Filtration and concentration *in vacuo* gave 3.57 g of an oily material, which was submitted to column chromatography (SiO₂ 70 g, *n*-hexane-Et₂O, 20:1, then 5:1) to give 2.14 g of an allylic alcohol and 682 mg of the epoxy alcohol **13**. Distillation of the former gave 1.62 g (42.0%) of (*R*)-(+)-**2** as a colorless oil; bp 89°C/22 mmHg, *n*_D²² 1.4606; [α]_D^{21.5} +26.9° (*c*=1.56, *n*-hexane). The optical purity was determined as the (*S*)-MTPA ester by GLC analysis (PEG-20M, 0.25 mmφ × 50 m, at 100~160°C (+0.5°C/min), *t_R*(*S,S*)-isomer 6573sec, (*R,S*)-isomer 6652sec) to be 62.3% e.e. This allylic alcohol (1.17 g) was resolved under the same conditions as described above to

give 611 mg (52.2%) of (*R*)-(+)-**2**; bp 87~91°C/24 mmHg, n_D^{23} 1.4598; $[\alpha]_D^{23}$ +31.8° ($c=5.23$, *n*-hexane). *Anal.* Found: C, 76.89; H, 11.49. Calcd. for $C_9H_{16}O$: C, 77.09; H, 11.50%. The optical purity was determined as the (*S*)-MTPA ester by GLC analysis to be 96% *e.e.*

(*R*)-(+)-3-Acetoxy-3,6-dimethyl-1,5-heptadiene **1**. A mixture of (*R*)-(+)-**2** (600 mg) and acetic anhydride (1.4 ml) in pyridine (2.5 ml) was stirred at ambient temperature overnight. The mixture was poured into ice-cooled water and stirred at ambient temperature for 30 min. The mixture was extracted with Et_2O , and washed with water, $CuSO_4$ aq., water again, sat. $NaHCO_3$ aq. and brine, before being dried over $MgSO_4$. Filtration and concentration *in vacuo* gave an oily material, which was distilled to give 712 mg (91.3%) of (*R*)-(+)-**1** as a colorless oil; bp 100~110°C (bath temp.)/42 mmHg, n_D^{20} 1.4435; $[\alpha]_D^{20}$ +4.35° ($c=2.56$, *n*-hexane); $IR_{\gamma_{max}}$ cm^{-1} : 3140 (w), 3030 (m), 2980 (m), 2920 (m), 2780 (w), 1755 (s), 1690 (w), 1665 (m), 1450 (m), 1380 (m), 1335 (w), 1245 (s), 1185 (w), 1115 (m), 1050 (m), 1025 (m), 990 (m), 960 (m), 940 (w), 905 (m), 840 (w), 760 (w); NMR δ 1.57 (3H, s), 1.66 (6H, s), 1.92 (3H, s), 2.23 (2H, t, $J=7$ Hz), 4.70~5.00 (3H), 5.04 (1H, t, $J=7$ Hz). *Anal.* Found: C, 72.35; H, 10.04. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95%.

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