Tetrahedron Vol. 38, No. 4, pp. 521 to 525, 1982
Printed in Great Britain.

0040-4020/82/040521-05$03.00/0
Pergamon Press Ltd.

SYNTHESIS OF OPTICALLY ACTIVE FORMS OF (*E*)-6-ISOPROPYL-3,9-DIMETHYL-5,8-DECADIENYL ACETATE, THE PHEROMONE OF THE YELLOW SCALE†

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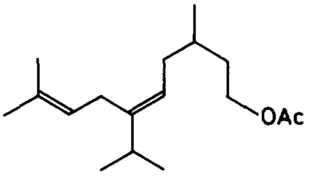
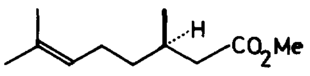
(*Received in Japan* 18 *July* 1981)

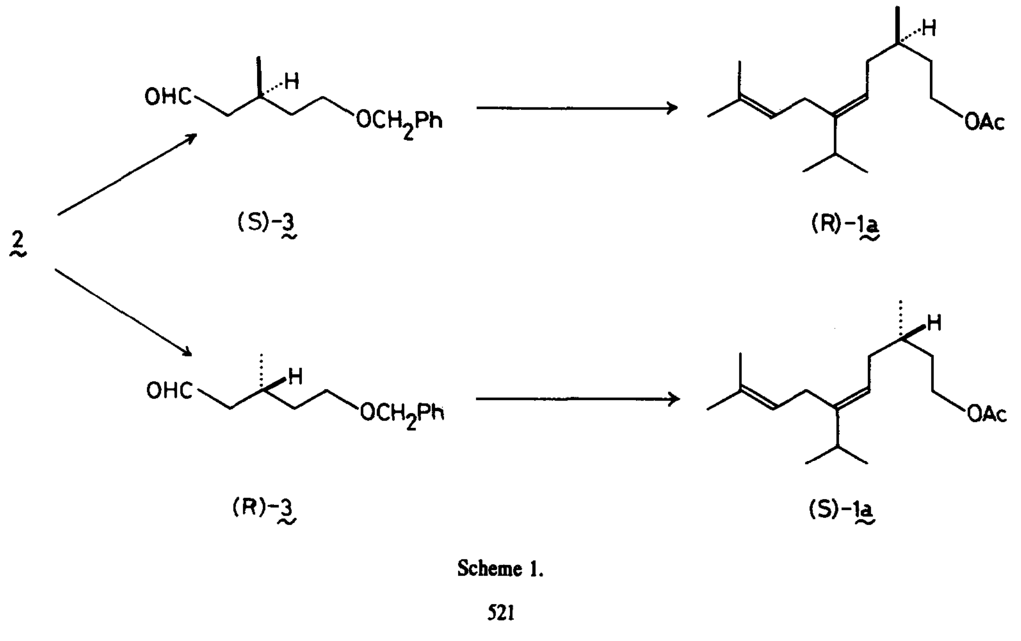
Abstract—Highly optically pure enantiomers of (*E*)-6-isopropyl-3,9-dimethyl-5,8-decadienyl acetate, the sex pheromone of the yellow scale (*Aonidiella citrina*), were stereoselectively synthesized from (*R*)-(+)-citronellic acid. Only the (*s*)-enantiomer was bioactive.

In 1979 Gieselmann *et al.* isolated the sex pheromone of the yellow scale, *Aonidiella citrina* (Coquillett).[1] Their structure assignment as 6-isopropyl-3,9-dimethyl-5,8-decadienyl acetate was soon confirmed by two independent syntheses of its (*E*)- and (*Z*)-isomers as racemates.[2,3] This established the (*E*)-geometry of the natural pheromone as shown in **1a**. In continuation of our recent synthesis of (*S*, *E*)-**1a**,[4] we have now developed an improved stereoselective route to both enantiomers of **1a** starting from a single chiral source, methyl (*R*)-(+)-citronellate **2**. Our synthetic strategy was to employ an aldehyde **3** as a key intermediate (Scheme 1).

The synthesis of both enantiomers of the aldehyde **3** is outlined in Scheme 2. First, the (*S*)-aldehyde **3** was synthesized from highly optically pure methyl (*R*)-(+)-citronellate **2** derived from optically pure (*R*)-(+)-pulegone. The optical purity of our (*R*)-(+)-citronellic acid was proved to be ~100% by the hplc analysis of a derived amide as described previously.[5,6] As no reaction was involved which might cause racemization at the chiral centre, this optical purity was thought to be retained throughout the synthesis. Oxidation of **2** with PhSeOH-t-BuOOH[7] yielded an allylic alcohol **4**. This was ozonized in MeOH. The resulting ozonide was reduced with Me_2S and the crude product was converted to a dimethylacetal **5**. LAH reduction of **5** yielded an alcohol **6**. The OH group of **6** was protected as a benzyl ether and the acetal group of **7** was hydrolyzed to give


1a


2



Scheme 1.

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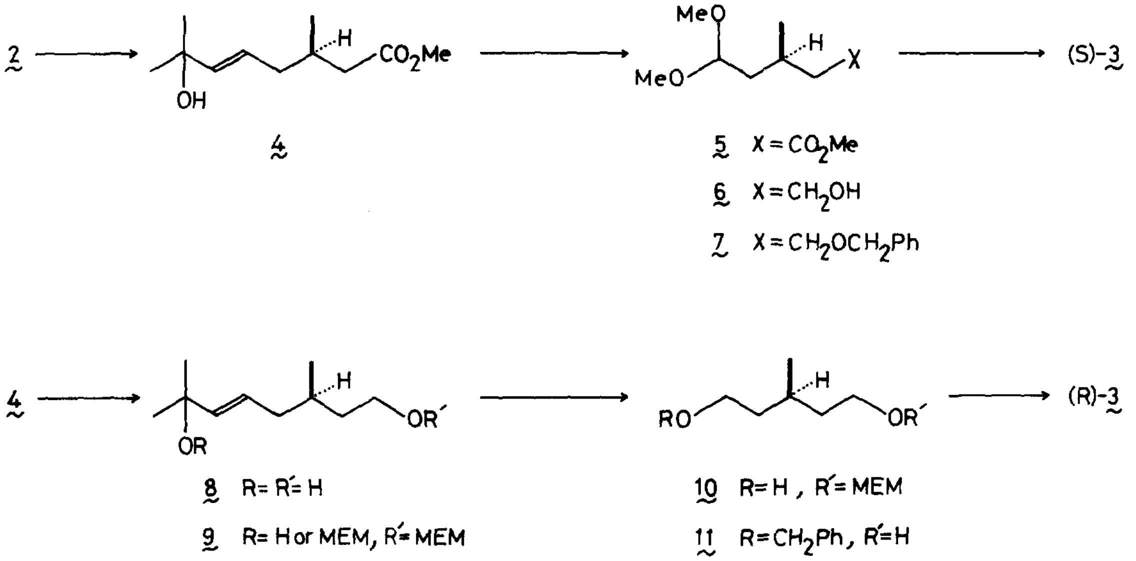
†Pheromone Synthesis-50. Part 49, Y. Miyashita and K. Mori, *Agric. Biol. Chem.* **45**, 2521 (1981). The experimental part of this work was taken from the M.Sc. thesis of S.K. (1982).

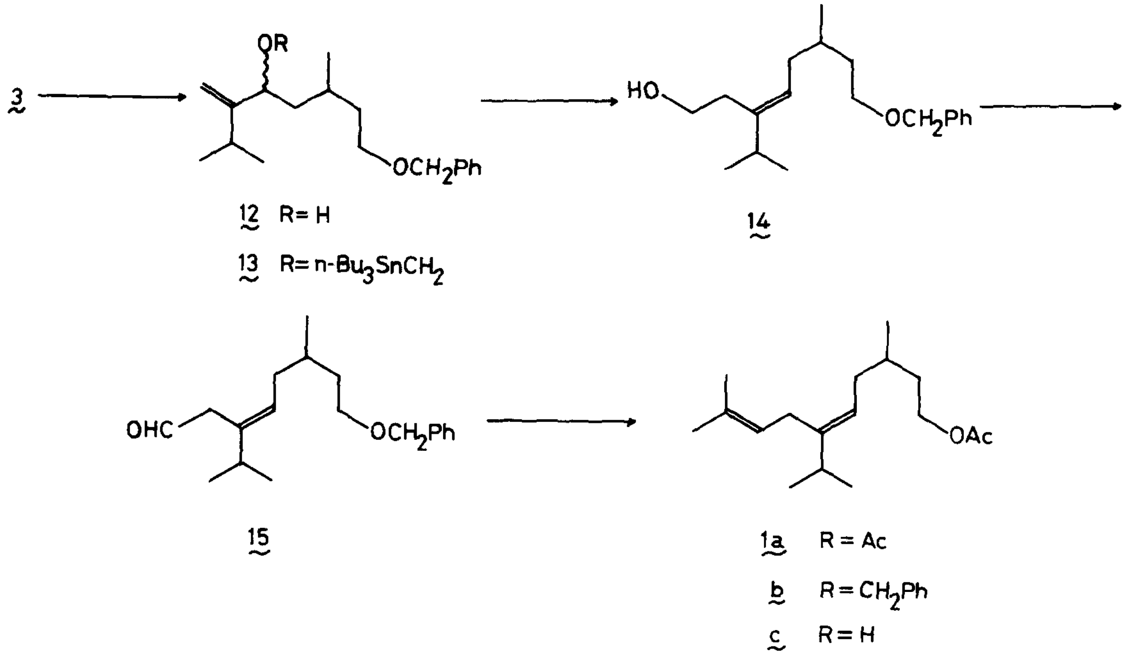
the desired (*S*)-aldehyde **3**. We then turned our attention to the synthesis of (*R*)-**3**. Reduction of **4** with LAH yielded a diol **8**, whose primary OH group was protected as a MEM ether[8] to give **9**. This was, however, a mixture of mono-MEM ether (2/3) and di-MEM ether (1/3). Ozonolysis of **9** followed by LAH reduction gave a diol mono-MEM ether **10**. The free OH group of **10** was benzylated and the MEM protecting group was removed (TsOH/MeOH) to give a diol monobenzyl ether **11**. This was oxidized with $CrO_3 \cdot 2C_5H_5N$ in CH_2Cl_2[9] to give the (*S*)-aldehyde **3**.

The remaining steps to the pheromone itself are shown in Scheme 3. Still's version of a 2,3-sigmatropic Wittig rearrangement reaction[10] was used for the highly stereoselective construction of the tri-substituted (*E*)-double bond, as we had done previously in synthesizing (*S, E*)**1a**.[4] A Grignard reagent prepared from 2-bromo-3-methyl-1-butene[4] was added to the aldyhyde **3** to give an alcohol **12** as a diastereomeric mixture. The allylic alcohol **12** was submitted to the Still procedure.[10] Treatment of **12** with KH and n-Bu_3SnCH_2I[11] gave an allyl stannylmethyl ether **13**. Without isolation this was treated with n-BuLi, which resulted in Sn–Li exchange followed by 2,3-sigmatropic rearrangement to give an (*E*)-homoallylic alcohol **14**.

Oxidation of **14** with $CrO_3 \cdot 2C_5H_5N$ in CH_2Cl_2[9] gave



Scheme 2.



Scheme 3.

an aldehyde **15**. Treatment of **15** with isopropylidene triphenylphosphorane afforded **1b**. The benzyl protective group of **1b** was removed by Birch reduction (Li/NH_3) to give **1c**. Finally this was acetylated to give the pheromone enantiomers **1a**. Thus the (*R*)-enantiomer (*R*)-**1a**, $[\alpha]_D^{22} + 11.5°$ (n-hexane), of the yellow scale pheromone was obtained in 10% overall yield from methyl (*R*)-(+)-citronellate **2** with 96% chemical purity as revealed by glc. Similarly (*S*)-**1a**, $[\alpha]_D^{21.5} - 11.9°$ (n-hexane) (Litt.[4] $[\alpha]_D^{31} - 9.83°$ (n-hexane)), was obtained in 7% overall yield from **2** with 96% purity (glc).

Bioassay of our products was carried out by Prof. W. L. Roelofs, New York State Agricultural Experiment Station. Only (*S*)-**1a** was biologically active.

EXPERIMENTAL

All bps are uncorrected. IR spectra were determined as film on a Jasco A-102 spectrometer. NMR spectra were recorded at 60 MHz as CCl_4 soln with TMS as an internal standard on a Hitachi R-24A spectrometer unless otherwise stated. Optical rotations were measured on a Jasco DIP-4 polarimeter. Glc analyses were performed on a JEOL JGC-20K gas chromatograph.

Methyl (R)-(+)-7-*hydroxy*-3,7-*dimethyl*-5-*octenoate* **4**

35% H_2O_2 (36.0 g) was added to a stirred and ice-cooled soln of PhSeSePh (115.6 g) in CH_2Cl_2 (1050 ml). After the addition, the mixture was stirred for 30 min at 0–5°. Powdered anhyd. $MgSO_4$ (61.73 g) was added to the mixture and stirring was continued for 30 min. The ice-bath was removed and **2** (45.43 g) was added to the mixture. The stirring was continued for 6 hr at room temp. Subsequently 70% t-BuOOH (170.36 g) was added to the stirred and ice-cooled mixture, which was stirred for 20 hr at room temp. The mixture was filtered and the filtrate was concentrated *in vacuo*. The residue was dissolved in ether (1500 ml). The ether soln was washed with 5% Na_2CO_3 soln and water. Then it was added dropwise to a vigorously stirred aq. soln of $FeSO_4$ (10%, 1480 ml). The ether layer was separated, washed with water, sat. $NaHCO_3$ soln, water and brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was distilled to give 40.97 g (83%) of **4**, b.p. 89–96°/0.37 mm Hg. An analytical sample boiled at 76–77°/0.15 mm, $n_D^{22.5}$ 1.4496; $[\alpha]_D^{22.5} + 6.2°$ (c = 5.35, $CHCl_3$); ν_{max} 3450 (m), 2980 (s), 2940 (m), 2890 (m), 2850 (w), 1740 (vs), 1460 (m), 1440 (m), 1370 (m), 1210 (m), 1150 (s), 975 (m) cm^{-1}; δ (CCl_4) 0.93 (3H, d, J = 6 Hz), 1.22 (6H, s), 1.80–2.30 (5H, m), 3.60 (3H, s), 5.40–5.65 (2H, m). (Found: C, 65.85; H, 10.04. Calc. for $C_{11}H_{20}O_3$: C, 65.97; H, 10.07%).

Methyl (R)-(−)-5,5-*dimethoxy*-3-*methylpentanoate* **5**

O_3 was bubbled into a cooled soln of **4** (10.0 g) in MeOH (70 ml) at −50°. When **4** disappeared as checked by tlc, the soln was cooled to −60°. N_2 was bubbled into the soln to remove O_3. Then Me_2S (5 ml) was added dropwise to the stirred soln and the temp. was gradually raised to room temp. After stirring overnight, the mixture was concentrated *in vacuo*. The residue was diluted with water and extracted with ether. The ether soln was washed with water and brine, dried (K_2CO_3) and concentrated *in vacuo* to give 8.32 g of a crude oil. This was dissolved in MeOH (80 ml) containing TsOH (260 mg) and the soln was stirred for 1.5 hr. Then it was concentrated *in vacuo*, diluted with sat. $NaHCO_3$ and extracted with ether. The ether soln was washed with water and brine, dried (K_2CO_3) and concentrated *in vacuo*. The residue was distilled to give 6.98 g (73.5%) of **5**, b.p. 70–76°/5 mm, $n_D^{22.5}$ 1.4215; $[\alpha]_D^{22.5} - 1.54°$ (c = 10.42, $CHCl_3$); ν_{max} 2950 (s), 2830 (m), 1735 (vs), 1435 (m), 1195 (s), 1165 (s), 1125 (s), 1050 (s), 1015 (m) cm^{-1}; δ (CCl_4) 0.95 (3H, d, J = 6 Hz), 1.42 (2H, dd, J_1 = 5 Hz, J_2 = 6 Hz), 1.70–2.40 (3H, m), 3.19 (6H, s), 3.59 (3H, s), 4.34 (1H, t, J = 6 Hz). (Found: C, 56.82; H, 9.54. Calc. for $C_9H_{18}O_4$: C, 56.54; H, 9.50%).

(S)-(+)-5,5-*Dimethoxy*-3-*methyl*-1-*pentanol* **6**

A soln of **5** (6.9 g) in dry ether (20 ml) was added to a stirred and ice-cooled suspension of LAH (2.07 g) in dry ether (80 ml). After the addition, the mixture was stirred for 1 hr. Then it was ice-cooled and the excess LAH was destroyed by the addition of water (2.1 ml), 15% NaOH soln (2.1 ml) and water (6.2 ml). The mixture was stirred for 30 min and filtered. The filtrate was dried (Na_2SO_4) and concentrated *in vacuo*. The residue was distilled to give 5.10 g (86.7%) of **6**, b.p. 91.5–98.5°/6 mm, n_D^{23} 1.4318; $[\alpha]_D^{23} + 5.74°$ (c = 10.7, $CHCl_3$); ν_{max} 3400(s), 2940 (s), 2830 (m), 1455 (m), 1380 (m), 1190 (m), 1125 (s), 1055 (s), 955 (m) cm^{-1}; δ 0.93 (3H, d, J = 6 Hz), 1.2–1.9 (5H, br. m), 3.19 (3H, s), 3.52 (2H, t, J = 6 Hz), 4.34 (1H, t, J = 6 Hz). (Found: C, 58.65; H, 11.27. Calc. for $C_8H_{18}O_3$: C, 59.23; H, 11.18%).

(S)-5,5-*Dimethoxy*-3-*methyl*-1-*pentyl benzyl ether* **7**

50% NaH dispersion (1.74 g) was washed 3 times with n-pentane under Ar and suspended in dry DME (50 ml). A soln of **6** (4.89 g) in dry DME (18 ml) was added dropwise to the stirred suspension and the mixture was stirred for 2 hr at 65–70°, and cooled to room temp. $PhCH_2Br$ (5.70 g) was added dropwise to the mixture. After the addition, the mixture was stirred and heated under reflux for 1 hr and stirred overnight at room temp., diluted with water and extracted with ether. The ether soln was washed with water and brine, dried (K_2CO_3) and concentrated *in vacuo* to give 7.85 g of crude **7**, ν_{max} 3090 (w), 3060 (w), 3030 (w), 2930 (s), 2860 (m), 2840 (m), 1500 (w), 1455 (m), 1365 (m), 1190 (m), 1120 (s), 1070 (s), 1055 (s), 735 (m), 700 (m) cm^{-1}. This was employed for the next step without further purification.

(S)-5-*Benzyloxy*-3-*methylpentanal* (S)-**3**

A mixture of 35% $HClO_4$ (22 ml) and THF (40 ml) was added to a stirred soln of **7** (10.01 g) in THF (10 ml) under ice-cooling. The mixture was stirred for 30 min at room temp., poured into sat. $NaHCO_3$ soln and extracted with ether. The ether soln was washed with water and brine, dried (Na_2SO_4) and concentrated *in vacuo* to give 8.28 g of crude (*S*)-**3**, ν_{max} 3090 (w), 3070 (w), 3040 (m), 2960 (s), 2940 (s), 2870 (s), 1725 (vs), 1500 (m), 1455 (s), 1365 (m), 1100 (s), 735 (s), 700 (s) cm^{-1}. This was used directly for the next step.

(R)-3,7-*Dimethyl*-5-*octene*-1,7-*diol* **8**

A soln of **4** (9.58 g) in dry ether (30 ml) was added dropwise to a stirred and ice-cooled suspension of LAH (3.64 g) in dry ether (140 ml). After the addition, the mixture was stirred for 1 hr at room temp. The excess LAH was destroyed by the addition of water and NaOH soln as usual. Then the mixture was filtered and the filtrate was dried (Na_2SO_4) and concentrated *in vacuo* to give 8.35 g of crude **8**, ν_{max} 3350 (s), 3030 (w), 2970 (s), 2930 (s), 2875 (s), 1460 (m), 1440 (m), 1380 (s), 1365 (m), 1230 (m), 1150 (s), 1060 (s), 1010 (m), 970 (s) cm^{-1}. This was employed for the next step without further purification.

A mixture of (R)-3,7-*dimethyl*-5-*octene*-1,7-*diol mono-MEM ether and di-MEM ether* **9**

50% NaH (5.59 g) was washed 3 times with n-pentane under Ar and suspended in dry THF (70 ml). A soln of **8** (8.35 g) in dry THF (47 ml) was added dropwise to the stirred suspension. After the addition the mixture was stirred and heated under reflux for 1 hr. Then it was ice-cooled. A soln of MEM-Cl (14.65 g) in dry THF (23 ml) was added dropwise to the stirred and ice-cooled mixture. The stirring was continued for 30 min at 0° and 3 hr at room temp. Subsequently the mixture was poured into water and extracted with ether. The ether soln was washed with water and brine, dried (Na_2SO_4) and concentrated *in vacuo* to give 13.44 g of crude **9**, ν_{max} 3490 (m), 2980 (s), 2940 (s), 2890 (s), 1460 (m), 1380 (m), 1365 (m), 1240 (m), 1200 (m), 1115 (s), 1040 (s), 975 (s), 930 (m), 850 (m) cm^{-1}; δ 0.89 (3H, d, J = 6 Hz), 1.22 (6 × 2/3H, s), 1.27 (6 × 1/3 H, s), 1.40–2.15 (5H, m), 3.33 (4H, s), 3.40–3.80 (~7 H, m), 4.62 (2H, s), ~4.67 (1H, s), 5.45–5.75 (2H, m). This was employed for the next step without further purification.

(R)-3-*Methylpentane*-1,5-*diol* 1-*MEM ether* **10**

O_3 was bubbled into a mixture of **9** (13.44 g) and $NaHCO_3$

(2.5 g) in MeOH (75 ml)-CH_2Cl_2 (75 ml) at −50°. After the complete consumption of **9** as checked by tlc, N_2 was bubbled into the mixture to remove excess O_3. Then Me_2S (16 ml) was added and the temp. was gradually raised to room temp. The mixture was stirred overnight at room temp. Subsequently it was concentrated *in vacuo*, diluted with water and extracted with ether. The ether soln was washed with water and brine, dried (Na_2SO_4) and concentrated *in vacuo* to give 9.05 g of crude aldehyde as an oil, ν_{max} 2940 (s), 2880 (s), 2720 (m), 1725 (s), 1440 (m), 1200 (m), 1170 (m), 1115 (s), 1060 (s), 1035 (s), 990 (m), 940 (m), 845 (m) cm^{-1}. This (9.05 g) was dissolved in dry ether (40 ml) and added dropwise to a suspension of LAH (1.71 g) in dry ether (70 ml) with stirring and ice-cooling. After the addition the mixture was stirred for 1 hr at room temp. The excess LAH was destroyed by the addition of water and NaOH soln as usual. The mixture was filtered and the filtrate was dried (Na_2SO_4) and concentrated *in vacuo* to give 8.10 g of crude **10**, ν_{max} 3440 (m), 2940 (s), 2880 (s), 1460 (m), 1380 (m), 1200 (m), 1170 (m), 1115 (s), 1055 (s), 845 (m) cm^{-1}; δ 0.89 (3H, d, J = 6 Hz), 1.15–2.00 (5H, m), 3.24 (3H, s), 3.30–3.95 (10H, m), 4.51 (2H, s). This was employed for the next step without further purification.

(S)-(+)-3-*Methylpentane-1,5-diol 1-benzyl ether* **11**

50% NaH (2.27 g) was washed three times with n-pentane under Ar and suspended in dry DME (70 ml). A soln of **10** (8.10 g) in dry DME (30 ml) was added dropwise to the stirred suspension at room temp. Then the stirring was continued for 1.5 hr at 65–70°. After cooling, $PhCH_2Br$ (8.12 g) was added dropwise. The mixture was stirred and heated under reflux for 1 hr. The stirring was continued for 5 hr at room temp. Subsequently the mixture was poured into water and extracted with ether. The ether soln was washed with water and brine, dried (Na_2SO_4) and concentrated *in vacuo*. The residue was chromatographed over SiO_2 (Mallinckrodt CC-7, 170 g). Elution with n-hexane–ether yielded 8.15 g of the MEM benzyl diether, ν_{max} 3100 (w), 3070 (w), 3040 (w), 2940 (s), 2880 (s), 1500 (w), 1455 (m), 1365 (m), 1200 (m), 1175 (m), 1115 (s), 1100 (s), 1050 (s), 940 (m), 850 (m), 740 (m), 700 (m), cm^{-1}, δ 0.89 (3H, d, J = 6 Hz), 1.10–2.05 (5H, m), 3.20 (3H, s), 3.25–3.70 (8H, m), 4.32 (2H, s), 4.46 (2H, s), 7.08 (5H, s). This (8.10 g) was dissolved in MeOH (80 ml) containing TsOH (500 mg) and the soln was stirred at 40° for 24 hr. Then it was concentrated *in vacuo*, diluted with water and extracted with ether. The ether soln was washed with water, $NaHCO_3$ soln and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed over SiO_2 (75 g). Elution with n-hexane-ether yielded **11**. This was distilled to give 3.58 g (36.2% from **4**) of **11**, b.p. 114.5–115°/0.14 mm, $n_D^{21.5}$ 1.5034; $[\alpha]_D^{21.5}$ +4.57° (c = 4.38, $CHCl_3$); ν_{max} 3400 (m), 3090 (w), 3070 (w), 3040 (m), 2960 (s), 2930 (s), 2870 (s), 1500 (m), 1455 (m), 1365 (m), 1200 (m), 1100 (s), 1075 (s), 1060 (s), 735 (s), 700 (s) cm^{-1}; δ 0.85 (3H, d, J = 6 Hz), 1.08–1.95 (5H, m), 3.35 (2H, t, J = 6 Hz), 3.42 (2H, t, J = 6 Hz), 4.30 (2H, s), 7.05 (5H, s). (Found: C, 74.71; H, 9.64. Calc. for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68%).

(R)-5-*Benzyloxy-3-methylpentanal* (R)-**3**

CrO_3 (12.35 g) was added portionwise to a soln of dry C_5H_5N (19.55 g) in dry CH_2Cl_2 (235 ml) with stirring and ice-cooling. The stirring was continued for 1 hr at room temp. Then a soln of **11** (3.67 g) in dry CH_2Cl_2 (117 ml) was added dropwise to the stirred mixture at room temp. After stirring for 7 hr it was diluted with ether and filtered through a florisil column. The filtrate was washed with sat. $CuSO_4$ soln, water, sat. $NaHCO_3$ soln and brine, dried (Na_2SO_4) and concentrated *in vacuo* to give 3.03 g of crude (*R*)-**3**, ν_{max} 3090 (w), 3070 (w), 3040 (m), 2960 (s), 2940 (s), 2870 (s), 2720 (m), 1725 (vs), 1500 (m), 1455 (s), 1365 (m), 1275 (m), 1205 (m), 1100 (s), 1030 (m), 740 (s), 700 (s) cm^{-1}. This was employed for the next step without further purification.

7-*Benzyloxy - 2 - isopropyl - 5 - methyl - 1 - hepten - 3 - ol* **12**

(a) (3RS, 5S)-(+)-*Isomer*. Grignard reagent was prepared under Ar from 2-bromo-3-methyl-1-butene (11.91 g) and Mg (1.942 g) in dry THF (120 ml). To this was added dropwise a soln of (*S*)-**3** (8.23 g) in dry THF (80 ml) with stirring and water-cooling. The stirring was continued for 6 hr at room temp. Then it was poured into ice-sat. NH_4Cl and extracted with ether. The ether soln was washed with water and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed over SiO_2 (Merck Kieselgel 60, Art. 7734, 150 g). Elution with *n*-hexane–ether gave 7.74 g (72.3% from **6**) of (3RS, 5*S*)-**12**, n_D^{22} 1.4988; $[\alpha]_D^{22}$ +2.0° (c = 6.12, $CHCl_3$); ν_{max} 3440 (m), 3090 (w), 3070 (w), 3040 (w), 2960 (s), 2940 (s), 2870 (s), 1650 (w), 1500 (w), 1455 (m), 1365 (m), 1100 (s), 1025 (m), 900 (m), 735 (m), 700 (m) cm^{-1}; δ 0.90 (3H, d, J = 6 Hz), 1.00 (3H, d, J = 7 Hz), 1.05 (3H, d, J = 7 Hz), 1.20–2.50 (8H, m), 3.40 (2H, t, J = 6 Hz), 3.80–4.20 (1H, m), 4.38 (2H, s), 4.74 (1H, s), 4.91 (1H, s), 7.17 (5H, s); MS; *m/z* 277 (M^+ + 1), 276 (M^+), 233 (M^+ −43).

(b) (3RS, 5R)-(−)-*Isomer*. In the same manner as described above, 3.34 g of (*R*)-**3** yielded 3.43 g (63.9% from **11**) of (3*RS*, 5*R*)-**12**, n_D^{22} 1.4977; $[\alpha]_D^{22}$ −1.92° (c = 6.08, $CHCl_3$). The spectral data (IR, NMR, MS) were identical with those of (3*RS*, 5*S*)-(+)-**12**.

(E)-3-*Isopropyl-6-methyl-3-octene-1,8-diol 8-benzyl ether* **14**

(a) (R)-*Isomer*. 20% KH (4.97 g) was washed three times with n-pentane under Ar and suspended in dry THF (160 ml). To this was added a soln of (3*RS*, 5*S*)-**12** (5.48 g) in dry THF (55 ml) with stirring. The stirring was continued for 1.25 hr at room temp. Then a soln of dicyclohexyl 18-crown-6 (2.29 g) in dry THF (10 ml) was added dropwise followed by a soln of n-Bu_3SnCH_2I (12.82 g) in dry THF (55 ml) under water-cooling. The mixture was stirred for 40 min at room temp. The resulting soln of **13** was cooled to −68° and n-BuLi (1.21N in n-hexane, 32.8 ml) was added dropwise to the stirred and cooled mixture. The stirring was continued for 45 min at −65 ~ −70°. Then the mixture was poured into ice-sat. NH_4Cl soln and extracted with ether. The ether soln was washed with water, sat. $NaHCO_3$ soln and brine, dried (Na_2SO_4) and concentrated *in vacuo*. The residue was chromatographed over SiO_2 (Merck Kieselgel 60, Art. 7734, 365 g). Elution with *n*-hexane–ether yielded 4.34 g (75.4% from (3*RS*, 5*S*)-**12**) of (*R*)-**14**, ν_{max} 3400 (m), 3090 (w), 3070 (w), 3040 (w), 2960 (s), 2940 (s), 2880 (s), 1500 (w), 1455 (m), 1380 (m), 1360 (m), 1100 (s), 1040 (s), 735 (m), 700 (m) cm^{-1}: δ 0.87 (3H, d, J = 6 Hz), 0.97 (6H, d, J = 7 Hz), 1.20–2.30 (8H, m), 3.41 (2H, t, J = 6 Hz), 3.43 (2H, t, J = 7 Hz), 4.39 (2H, s), 5.21 (1H, t, J = 7 Hz), 7.19 (5H, s); MS: *m/z* 291 (M^+ + 1), 290 (M^+), 272 (M^+ −18).

(b) (S)-*Isomer*. In the same manner as described above 2.89 g of (3*RS*, 5*R*)-**12** yielded 2.26 g (74.4%) of (*S*)-**14**, whose spectral data (IR, NMR, MS) coincided with those of (*R*)-**14**.

(E) - 8 - *Benzyloxy - 3 - isopropyl - 6 - methyl - 3 - octenal* **15**

(a) (R)-*Isomer*. CrO_3 (8.02 g) was added portionwise to a stirred and ice-cooled soln of C_5H_5N (12.75 g) in dry CH_2Cl_2 (155 ml). After the addition, the stirring was continued for 1 hr. Then a soln of (*R*)-**14** (3.84 g) in dry CH_2Cl_2 (125 ml) was added dropwise at room temp. The mixture was stirred for 40 min at room temp. Then it was diluted with dry ether and filtered through a florisil column. The filtrate was concentrated *in vacuo* to give 4.07 g of crude (*R*)-**15**, ν_{max} 2710 (w), 1725 (s), 1100 (s), 745 (s), 735 (s), 700 (s) cm^{-1}. This was employed for the next step without further purification.

(b) (S)-*Isomer*. In the same manner 2.23 g of (*S*)-**14** yielded 2.53 g of crude (*S*)-**15**.

Benzyl ether (**1b**) *of* (E) - 6 - *isopropyl* - 3,9 - *dimethyl* - 5,8 - *decadien* - 1 - *ol*

(a) (R)-(+)-*Isomer*. n-BuLi (1.21N in n-hexane, 21 ml) was added dropwise to a stirred and cooled suspension of $Ph_3P(CHMe_2)Br$ (10.19 g) in dry THF (120 ml) at −35 ~ −40° under Ar. The stirring was continued for 30 min at −35° and for another 30 min at room temp. A soln of (*R*)-**15** (4.07 g) in dry THF (60 ml) was added dropwise to the stirred and cooled ylide soln at −60°. The temp. was gradually raised to room temp. during 4.5 hr. Then the mixture was poured into water and extracted with ether. The ether soln was washed with water and brine, dried (Na_2SO_4) and concentrated *in vacuo*. The residue was triturated with n-hexane and the hexane soln was separated. The hexane soln was concentrated *in vacuo*. The residue was chromatographed over SiO_2 (Merck Kieselgel 60, Art. 7734, 150 g). Elution with n-hexane–ether gave 1.93 g (46.4% from (*R*)-**14**) of (*R*)-**1b**, n_D^{21} 1.5048; $[\alpha]_D^{21} +7.29°$ (c = 3.79, $CHCl_3$); ν_{max} 3080 (w), 3050 (w), 3020 (m), 2950 (s), 2915 (s), 2855 (s), 1500 (m), 1455 (s), 1380 (m), 1370 (m), 1105 (s), 1030 (m), 940 (m), 705 (s) cm^{-1}; δ 0.86 (3H, d, J = 6 Hz), 0.97 (6H, d, J = 7 Hz), 1.20–2.45 (6H, m), 1.64 (6H, br. s), 2.67 (2H, d, J = 6 Hz), 3.44 (2H, t, J = 7 Hz), 4.43 (2H, s), 4.80–5.30 (2H, m), 7.27 (5H, s); MS: *m/z* 315 ($M^+ + 1$), 314 (M^+).

(b) (S)-(−)-*Isomer*. In the same manner as described above 2.53 g of (*S*)-**15** yielded 1.56 g (64.6% from (*S*)-**14**) of (*S*)-**1b**, $n_D^{22.5}$ 1.4989; $[\alpha]_D^{22.5}$ −7.25° (c = 3.82, $CHCl_3$). The spectral data (IR, NMR, MS) are identical with those of (*R*)-**1b**.

(E) - 6 - *Isopropyl* - 3,9 - *dimethyl* - 5,8 - *decadien* - 1 - *ol* **1c**

(a) (R)-(+)-*Isomer*. Li wire (600 mg) cut in small pieces was added to stirred liq. NH_3 (540 ml) at −33° under N_2. Li was completely dissolved by stirring for 35 min at −33°. Then a soln of (*R*)-**1b** (1.81 g) in dry THF (36 ml) was added dropwise to the stirred soln. After the addition, the mixture was stirred for 30 min at −33°. Then it was cooled below −50° and the excess Li was destroyed by the addition of solid NH_4Cl. n-Pentane (400 ml) was added and NH_3 was allowed to evaporate. The residue was mixed with sat NH_4Cl soln and extracted with ether. The ether soln was washed with sat. $NaHCO_3$ soln and brine, dried (Na_2SO_4) and concentrated *in vacuo*. The residue was distilled to give 1.08 g (83.6%) of (*R*)-**1c**, b.p. 106–107°/0.13 mm, $n_D^{21.5}$ 1.4715; $[\alpha]_D^{22} + 7.09°$ (c = 1.72, $CHCl_3$); ν_{max} 3330 (m), 2980 (s), 2940 (s), 2890 (s), 1670 (w), 1470 (s), 1390 (m), 1370 (m), 1185 (w), 1115 (m), 1075 (s), 1025 (m), 975 (w), 945 (w), 900 (w), 860 (w), 800 (w) cm^{-1}; δ 0.87 (3H, d, J = 6 Hz), 0.98 (6H, d, J = 7 Hz), 1.64 (6H, br. s), 1.20–2.40 (6H, m), 2.53 (1H, s, –OH), 2.67 (2H, d, J = 6 Hz), 3.57 (2H, t, J = 7 Hz), 4.75–5.25 (2H, m). (Found: C, 80.11; H, 12.61. Calc. for $C_{15}H_{28}O$: C, 80.29; H, 12.58%).

(b) (S)-(−)-*Isomer*. In the same manner as described above 1.53 g of (*S*)-**1b** yielded 0.972 g (89.1%) of (*S*)-**1c**, b.p. 113–114°/0.2 mm, n_D^{22} 1.4716, $[\alpha]_D^{22} - 7.28°$ (c = 1.75, $CHCl_3$). (Found: C, 80.32; H, 12.66. Calc. for $C_{15}H_{28}O$: C, 80.29; H, 12.58%). The IR and NMR data were same as those of (*R*)-(+)-**1c**.

(E) - 6 - *Isopropyl* - 3,9 - *dimethyl* - 5,8 - *decadienyl acetate* (*the yellow scale pheromone*, **1a**)

(a) (R)-(+)-*Isomer*. Ac_2O (3.7 ml) was added to a soln of (*R*)-**1c** (1.05 g) in dry C_5H_5N (4.4 ml) and the mixture was stirred overnight at room temp. Then it was poured into ice-water. After 30 min it was extracted with ether. The ether soln was washed with sat. $NaHCO_3$ soln, water, sat. $CuSO_4$ soln, water, sat, $NaHCO_3$ soln and brine, dried (Na_2SO_4) and concentrated *in vacuo*. The residue was distilled to give 1.12 g (89.9%) of (*R*)-**1a**, b.p. 107–111°/0.13 mm, n_D^{22} 1.4601; $[\alpha]_D^{22} + 11.5°$ (c = 2.98, n-hexane); ν_{max} 2970 (s), 2940 (s), 2880 (m), 1745 (s), 1670 (w), 1460 (m), 1380 (m), 1370 (m), 1240 (s), 1100 (w), 1055 (m), 1035 (m), 960 (w), 840 (w) cm^{-1}; δ (100 MHz, C_6D_6) 0.85 (3H, d, J = 6 Hz), 1.04 (6H, d, J = 7 Hz), 1.62 (3H, s), 1.68 (3H, s), 1.74 (3H, s), 1.20–1.56 (3H, m), 1.84–2.08 (2H, m), 2.08–2.50 (1H, m), 2.80 (2H, d, J = 6 Hz), 4.10 (2H, t, J = 7 Hz), 5.18 (1H, t, J = 7 Hz), 5.25 (1H, t, J = 7 Hz); glc (Column: 3% OV–17, 1.5 m × 2 mm at 152°; Carrier gas: N_2, 0.9 kg/cm^2): Rt 5.6 min (96%); impurities at 2.7, 3.6 and 8.4 min. (Found: C, 76.47; H, 11.23. Calc. for $C_{17}H_{30}O_2$: C, 76.64; H, 11.35%). The NMR spectrum was identical with that of the natural pheromone.[1]

(b) (S)-(−)-*Isomer*. In the same manner as described above 0.932 g of (*S*)-**1c** yielded 0.958 g (86.6%) of (*S*)-**1a**, b.p. 111–113°/0.14 mm, $n_D^{21.5}$ 1.4596; $[\alpha]_D^{21.5} - 11.9°$ (c = 3.00, n-hexane); glc (same conditions as for (*R*)-**1a**): R_t 5.6 min (96%), impurities at 2.6 and 3.5 min. (Found: C, 76.64; H, 11.67. Calc. for $C_{17}H_{30}O_2$: C, 76.64; H, 11.35%). The IR and NMR data were same as those of (*R*)-**1a**.

Acknowledgements—We thank Shiono Perfumery Co., Osaka, for the gift of highly pure (*R*)-(+)-pulegone. This work was supported in part by a Grant-in-Aid for Special Project Research (511608) from the Japanese Ministry of Education, Science and Culture.

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