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SYNTHESIS OF (2*S*,3*S*)-2,3-OCTANEDIOL AND (*S*)-2-HYDROXY-3-OCTANONE, THE MALE SEX PHEROMONE OF THE GRAPE BORER *XYLOTRECHUS PYRRHODERUS*†

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Abstract—(2*S*,3*S*)-2,3-Octanediol and (*S*)-2-hydroxy-3-octanone, the pheromone of the grape borer, were synthesized from (±)-1-octen-3-ol employing the Sharpless asymmetric epoxidation as the starting step.

The grape borer, *Xylotrechus pyrrhoderus* Bates, is known as a major pest of grapevines in Japan. Recently Sakai *et al.* isolated the sex pheromone produced by the male grape borer and identified it as a mixture of (2*S*,3*S*)-2,3-octanediol **1a** and (*S*)-2-hydroxy-3-octanone **2a** by synthesizing them from D-tartaric and L-lactic acids, respectively.[1] Herein we report an asymmetric synthesis of both (2*S*,3*S*)-**1a** and (*S*)-**2a** employing the Sharpless asymmetric epoxidation.[2]

Our synthetic route is straightforward as shown in Scheme 1. The first step was the kinetic resolution of the commercially available (±)-1-octen-3-ol **3** by enantioselective epoxidation.[3] Employing diisopropyl D-(−)-tartrate as the chiral source and interrupting the reaction after 14.5 hr at −20° in the presence of t-BuOOH and $Ti(i\text{-}PrO)_4$, an optically active epoxy alcohol (2*S*,3*R*)-**4a**, $[\alpha]_D^{20} - 21.0^\circ$ ($CHCl_3$), was obtained in 83.5% yield based on (*R*)-**3**. The optical purity of (2*S*,3*R*)-**4a** was shown to be 91.0–93.6% by the HPLC analysis of the corresponding α-methoxy-α-trifluoromethylphenylacetate (MTPA ester[4]) **4b**. To establish the correct *S*-configuration at C-3 of **1a** and **2a**, **4a** was submitted to the Walden inversion under the Mitsunobu condition.[5] Treatment of **4a** with Ph_3P, 3,5-dinitrobenzoic acid[6] and diethyl azodicarboxylate yielded (2*S*,3*S*)-**5a**. Alkaline hydrolysis of **5a** afforded (2*S*,3*S*)-**5b**, whose optical purity was estimated to be 92.0% by the HPLC analysis of the corresponding MTPA ester **5c**. Protection of the OH group of **5b** by treatment with ethyl vinyl ether and *p*-TsOH gave an ethoxyethyl (EE) ether **5d**. This was reduced with LAH to give **1b**. Removal of the EE protective group of **1b** with acid yielded (2*S*,3*S*)-2,3-octanediol **1a**, $[\alpha]_D^{21} - 18.5^\circ$ ($CHCl_3$) [lit.[1] $[\alpha]_D^{23} - 19.2^\circ$ ($CHCl_3$)], whose IR and ^1H-NMR spectra were identical with those of the natural product. The overall yield of **1a** from (*R*)-**3** was 38.4% in six steps. The stereochemical homogeneity of **1a** was manifested in its ^{13}C-NMR spectrum which showed only eight signals disproving the possible contamination of **1a** with either (2*R*,3*S*)- or (2*S*,3*R*)-isomers. The optical purity of **1a** was assumed to be 92.0%, since the intermediate **5b** was of 92% e.e. None of the subsequent steps leading to **1a** was thought to have caused racemization.

For the synthesis of (*S*)-2-hydroxy-3-octanone **2a**, the epoxy alcohol **4a** was first converted to the corresponding EE ether **4c**. LAH reduction of **4c** gave **6a**, which was benzylated with $PhCH_2Cl$ and NaH in DMF to give **6b**. Treatment of **6b** with dil HCl removed the EE protective group to yield **6c**. This was oxidized with the Jones CrO_3 to give **2b**. Hydrogenolytic removal (H_2/Pd–C) of the benzyl group of **2b** yielded the desired (*S*)-**2a**, $[\alpha]_D^{20} + 66.8^\circ$ ($CHCl_3$), whose IR and ^1H-NMR spectra coincided with the authentic spectra. The overall yield of **2a** from (*R*)-**3a** was 20.2% in 7 steps. ^1H- as well as ^{13}C-NMR spectra of our **2a** supported its regiochemical homogeneity. It should be noted that **2a** was reported to be readily isomerizable to 3-hydroxy-2-octanone upon GLC purification.[1] The optical purity of (*S*)-**2a** was shown to be 91.8–93.9% by the HPLC analysis of the corresponding MTPA ester **2c**.

In summary we completed a short and enantioselective synthesis of (2*S*,3*S*)-2,3-octanediol and also an enantioselective synthesis of (*S*)-2-hydroxy-3-octanone starting from a readily available racemic material.

EXPERIMENTAL

All b.ps were uncorrected. IR spectra were recorded on a Jasco A-102 spectrometer as a film. NMR spectra were measured on a Hitachi R-24A spectrometer at 60 MHz with TMS as an internal standard unless otherwise stated. Optical rotations were measured on a Jasco DIP-140 automatic polarimeter.

(2S,3R)-1,2-*Epoxy*-3-*octanol* **4a**

To stirred and cooled (dry ice–CCl_4 bath) dry CH_2Cl_2 (500 ml) at −20° under Ar were added $Ti(i\text{-}PrO)_4$ (19.3 ml, 64.8 mmol) and diisopropyl D-(−)-tartrate (16.2 ml, 77.8 mmol). After stirring for 5 min, (±)-**3** (8.30 g, 64.8 mmol) and t-BuOOH (7.3 M in CH_2Cl_2, 18.1 ml, 132.5 mmol) were added to the mixture at −20°. The mixture was left to stand for 14.5 hr at −20° in a freezer. It was then cooled with a dry ice–CCl_4 bath. To the stirred and cooled soln was added 10% aq soln of L-(+)-tartaric acid. The stirring was continued for 30 min at −20° and for 2 hr at room temp. The organic layer was separated, washed with water, dried (Na_2SO_4) and concentrated *in vacuo*. The residue was diluted with ether (480 ml) and stirred with 1 N NaOH (200 ml) at 0° for 40 min. The ether soln was separated, washed with brine, dried (Na_2SO_4) and concentrated *in vacuo*. The residue was chromatographed over SiO_2 (Merck Kieselgel 60, 400 g). Elution with 12–20% (v/v) EtOAc in n-hexane gave 4.14 g [94.2% from (*R*)-**3**] of **4a**. This was distilled to give 3.90 g [83.5% from (*R*)-**3**] of **4a**, b.p. 58–60°/0.2 mm, n_D^{20} 1.4385; $[\alpha]_D^{20} - 21.6^\circ$ ($c = 1.43$, $CHCl_3$); ν_{max}: 3350 (s), 3075 (w), 1255 (s), 1070 (s), 945 (s), 850 (s), 830 (s) cm^{-1}; ^1H-NMR δ ($CDCl_3$) 0.88 (3H, t, J = 7 Hz), 1.05–1.75 (8H, m), 2.50 (1H, d, J = 2 Hz), 2.55–2.83 (2H, m), 2.83–3.08 (1H, m), 3.70 (1H, m).

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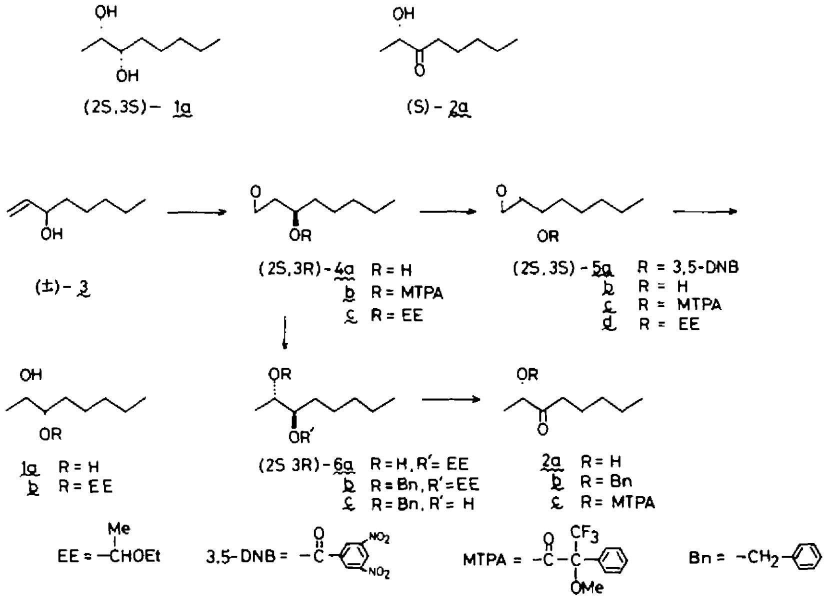
† Pheromone Synthesis—72. Part 71, K. Mori and T. Otsuka, *Tetrahedron* **41**, 547 (1985).



Scheme 1.

(Found: C, 66.51; H, 11.05. Calc for $C_8H_{16}O_2$: C, 66.63; H, 11.18%.)

The HPLC analysis of **4b** *to determine the optical purity of* **4a**

Acylation of **4a** with MTPA-Cl prepared from either (*R*)-MTPA or (*S*)-MTPA gave two diasteromers of **4b** in the usual manner. HPLC analysis of **4b** (column, Nucleosil 50-5, 25 cm × 4.6 mm; solvent, n-hexane–$ClCH_2CH_2Cl$ (7:3); press, 50 kg/cm^2; flow rate, 0.95 ml/min): R_t 19.46 min [(*R*)-MTPA ester], 22.23 min [(*S*)-MTPA ester]. Two batches of **4a** were analyzed: **4a** with $[\alpha]_D^{20} -21.6°$ (*c* = 1.43, $CHCl_3$) was of 91.0% e.e., while **4a** with $[\alpha]_D^{21} -22.3°$ (*c* = 1.30, $CHCl_3$) was of 93.6% e.e.

(2S,3S)-1,2-*Epoxy-3-octanol 3,5-dinitrobenzoate* **5a**

To a stirred soln of Ph_3P (9.44 g, 36.0 mmol), 3,5-dinitrobenzoic acid (7.63 g, 36.0 mmol) and **4a** (5.19 g, 36.0 mmol) in THF (90 ml) was added dropwise over 30 min a soln of diethyl azodicarboxylate (6.27 g, 36.0 mmol) in THF (30 ml) at room temp. After stirring for 15 hr at room temp, the mixture was concentrated *in vacuo*. The residual brown oil was chromatographed over SiO_2 (Merck Kieselgel 60, 300 g). Elution with $CHCl_3$ gave 12.75 g of crude **5a** as an oil. This was rechromatographed over SiO_2 (Merck Kieselgel 60, 300 g). Elution with 5–6.5% (v/v) EtOAc–n-hexane gave 10.7 g (87.7%) of **5a** as a light yellow oil, n_D^{21} 1.5188, $[\alpha]_D^{21} +4.1°$ (*c* = 2.58, $CHCl_3$); ν_{max}: 3100 (m), 1730 (s), 1630 (m), 1595 (w), 1545 (s), 1340 (s), 1270 (s), 1165 (s), 730 (s), 720 (s) cm^{-1}; ^{1}H-NMR δ ($CDCl_3$): 0.88 (3H, deformed t, J = 7 Hz), 1.08–1.60 (6H, m), 1.65–2.05 (2H, m), 2.70 (1H, dd, J_1 = 3 Hz, J_2 = 7 Hz), 2.90 (1H, dd, J_1 = 4 Hz, J_2 = 7 Hz), ~ 3.25 (1H, m), 4.95 (1H, dt, J_1 = 7 Hz, J_2 = 7 Hz), 9.18 (3H, s). (Found: C, 53.43; H, 5.50; N, 8.08. Calc. for $C_{15}H_{18}O_7N_2$: C, 53.25; H, 5.36; N, 8.28%.)

(2S,3S)-1,2-*Epoxy-3-octanol* **5b**

A soln of **5a** (10.0 g, 29.6 mmol) in THF (60 ml) was added dropwise over 10 min to the stirred and ice-cooled mixture of 1 N KOH (33 ml) and MeOH (40 ml). The stirring was continued for 30 min at room temp. The mixture was extracted with CH_2Cl_2. The CH_2Cl_2 soln was washed with $NaHCO_3$ aq and brine, dried (Na_2SO_4) and concentrated *in vacuo*. The residue was chromatographed over SiO_2 (Merck Kieselgel 60, 50 g). Elution with 20% (v/v) EtOAc–n-hexane gave an oil. This was distilled to give 3.36 g (78.9%) of **5b**, b.p. 54–56°/0.32 mm, $n_D^{20.5}$ 1.4382; $[\alpha]_D^{21} +4.40°$ (*c* = 1.66, $CHCl_3$); ν_{max}: 3450 (s), 3050 (w), 1250 (m), 1080 (m), 1050 (m), 1030 (m), 910 (m) cm^{-1}; ^{1}H-NMR δ ($CDCl_3$): 0.88 (3H, deformed t, J = 7 Hz), 1.05–1.85 (8H, m), 2.70 (2H, m), 2.92 (2H, m), ~ 3.35 (1H, m). (Found: C, 66.37; H, 11.15. Calc for $C_{18}H_{16}O_2$: C, 66.63; H, 11.18%.)

The HPLC analysis of **5c** *to determine the optical purity of* **5b**

Acylation of **5b** with MTPA-Cl prepared from either (*R*)-MTPA or (*S*)-MTPA gave two diastereomers of **5c** in the usual manner. HPLC analysis of **5c** (column, Partisil-5, 25 cm × 4.6 mm; solvent, n-hexane–$ClCH_2CH_2Cl$ (5:2); press, 45 kg/cm^2; flow rate, 1.6 ml/min): R_t 13.46 min [(*S*)-MTPA ester], 16.38 min [(*R*)-MTPA ester]. The optical purity of **5b** was estimated to be 92.0%.

(2S,3S)-1,2-*Epoxy-3-octanol* EE *ether* **5d**

A trace amount of *p*-TsOH was added to a stirred soln of **5b** (3.04 g, 14.1 mmol) in ethyl vinyl ether (20 ml). The stirring was continued for 7 hr at room temp. The mixture was then diluted with ether. The ether soln was washed with $NaHCO_3$ aq and brine, dried (Na_2SO_4) and concentrated *in vacuo*. The residue was chromatographed over SiO_2 (Merck Kieselgel 60, 50 g). Elution with EtOAc–n-hexane gave **5d**, which was distilled over K_2CO_3 to give 4.12 g (90.4%) of pure **5d**, b.p. 73–76°/0.18 mm, $n_D^{20.5}$ 1.4267; $[\alpha]_D^{20.5} -28.9°$ (*c* = 1.22, $CHCl_3$); ν_{max}: 3050 (w), 1130 (s), 1080 (s), 1055 (s) cm^{-1}; ^{1}H-NMR δ ($CDCl_3$): 0.89 (3H, deformed t, J = 6 Hz), 1.03–1.80 (14H, m), ~ 2.53 (1H, m), ~ 2.78 (1H, m), 2.88–3.40 (2H, m), 3.40–3.95 (2H, m), 4.70–5.12 (1H, m). (Found: C, 66.65; H, 11.25. Calc for $C_{12}H_{24}O_3$: C, 66.63; H, 11.18%.)

(2S,3S)-2,3-*Octanediol* 3-EE *ether* **1b**

A soln of **5d** (3.88 g, 17.9 mmol) in dry ether (50 ml) was added over 30 min to a stirred and ice-cooled suspension of LAH (680 mg, 17.9 mmol) in dry ether (50 ml). The stirring was continued overnight at room temp. The excess LAH was destroyed by the successive addition of water (0.68 ml), 15% NaOH aq (0.68 ml) and water (2 ml) to the stirred and ice-cooled mixture. The precipitate was filtered off and the filter-cake was washed with THF. The combined filtrate and washings were dried (Na_2SO_4) and concentrated *in vacuo*. The residue was distilled over K_2CO_3 to give 3.74 g (95.4%) of **1b**, b.p. 72–73°/0.18 mm, n_D^{21} 1.4287; $[\alpha]_D^{21}$ + 18.6° (c = 1.22, $CHCl_3$); ν_{max}: 3450 (m), 1125 (s), 1080 (s), 1050 (s), 1025 (m) cm^{-1}; ^{1}H-NMR δ ($CDCl_3$): 0.89 (3H, deformed t, J = 6 Hz), 1.00–1.80 (17H, m), ~ 2.83 (1H, d, J = 4 Hz, OH), 3.15–4.00 (4H, m), 4.50–4.95 (1H, m). (Found: C, 65.77; H, 12.05. Calc for $C_{12}H_{26}O_3$: C, 66.01; H, 12.00%.)

(2S,3S)-2,3-*Octanediol* **1a**

35% $HClO_4$ (1.5 ml) was added to a soln of **1b** (250 mg, 1.71 mmol) in THF (2.5 ml). The mixture was stirred and heated under reflux for 24 hr. It was then poured into ice-cooled sat $NaHCO_3$ aq (25 ml) and extracted with CH_2Cl_2. The extract was dried (Na_2SO_4) and concentrated *in vacuo*. The residue was chromatographed over SiO_2 (Merck Kieselgel 60, 3.5 g). Elution with 25–50% (v/v) ether–n-hexane gave **1a**, which was distilled to give 129 mg (77.2%) of pure **1a**, b.p. 85–87°/4 mm, n_D^{21} 1.4396; $[\alpha]_D^{21}$ − 18.5° (c = 1.14, $CHCl_3$) [lit.[1] $[\alpha]_D^{23}$ − 19.2° (c = 0.48, $CHCl_3$)]; ν_{max}: 3380 (vs), 2980 (sh), 2940 (vs), 2870 (s), 1460 (s), 1400 (m), 1375 (s), ~ 1270 (m), 1190 (w), 1150 (m), 1120 (m), 1060 (vs), 1025 (s), 990 (m), 940 (m), 905 (m), 860 (w), 720 (w) cm^{-1}; ^{1}H-NMR δ (100 MHz, $CDCl_3$): 0.89 (3H, deformed t, J = 7 Hz), 1.16 (3H, d, J = 6 Hz), 1.10–1.70 (8H, m), ~ 2.32 (2H, br, OH), ~ 3.33 (1H, m), ~ 3.58 (1H, m); ^{13}C-NMR δ (25 MHz, $CDCl_3$): 14.06, 19.47, 22.64, 25.34, 31.95, 33.31, 70.94, 76.25. The IR and ^{1}H-NMR spectra were identical with the authentic spectra. (Found: C, 65.74; H, 12.50. Calc for $C_8H_{18}O_2$: C, 65.71; H, 12.41%.)

(2S,3R)-1,2-*Epoxy-3-octanol* EE *ether* **4c**

A trace amount of *p*-TsOH was added to a soln of **4a** (4.28 g, 29.7 mmol) in ethyl vinyl ether (25 ml). The mixture was stirred overnight at room temp and diluted with ether. The ether soln was washed with sat $NaHCO_3$ aq and brine, dried (Na_2SO_4) and concentrated *in vacuo*. The residue was chromatographed over SiO_2 (Merck Kieselgel 60, 100 g). Elution with 10% (v/v) EtOAc–n-hexane gave an oil, which was distilled to give 5.37 g (83.6%) of **4c**, b.p. 68–70°/0.2 mm, n_D^{22} 1.4248; $[\alpha]_D^{22}$ + 8.5° (c = 1.72, $CHCl_3$); ν_{max}: 3050 (w), 1130 (s), 1080 (s), 1055 (s), 1030 (s), 960 (s) cm^{-1}; ^{1}H-NMR δ (CCl_4): 0.70–1.05 (6H, m), 1.05–1.70 (11H, m), 2.40–2.80 (3H, m), 2.95–3.65 (3H, m), ~ 4.62 (1H, m). (Found: C, 66.75; H, 11.08, Calc. for $C_{12}H_{24}O_3$: C, 66.63; H, 11.18%.)

(2S,3R)-2,3-*Octanediol* 3-EE *ether* **6a**

A soln of **4c** (2.50 g, 11.6 mmol) in dry ether (30 ml) was added dropwise over 20 min at 0–5° to a stirred and ice-cooled suspension of LAH (440 mg, 11.6 mmol) in dry ether (20 ml). The stirring was continued for 6 hr at room temp. The excess LAH was destroyed by the successive addition of water (0.45 ml), 15% NaOH aq (0.45 ml) and water (1.35 ml) to the stirred and ice-cooled mixture. The precipitate was filtered off and the filter-cake was washed with THF. The combined filtrate and washings were dried (Na_2SO_4) and concentrated *in vacuo*. The residue was distilled over K_2CO_3 to give 2.41 g (95.6%) of **6a**, b.p. 79–80°/0.55 mm, n_D^{20} 1.4286; $[\alpha]_D^{20.5}$ − 6.9° (c = 1.48, $CHCl_3$); ν_{max}: 3450 (m), 1120 (s), 1080 (s), 1050 (s) cm^{-1}; ^{1}H-NMR δ (CCl_4): 0.70–1.03 (6H, m), 1.03–1.65 (14H, m), 2.65 (1H, d, J = 4 Hz), 3.18–3.90 (4H, m), 4.35–4.90 (1H, m). (Found: C, 65.97; H, 12.03. Calc for $C_{12}H_{26}O_3$: C, 66.01; H, 12.00%.)

(2S,3R)-2,3-*Octanediol 2-benzyl*-3-EE *ether* **6b**

A soln of **6a** (2.00 g, 9.16 mmol) in dry DMF (20 ml) was added dropwise to a stirred suspension of NaH (60% suspension in mineral oil, 440 mg, 11.0 mmol, washed with pentane to remove mineral oil) under Ar. The mixture was stirred for 1 hr at 60–65° until it became a clear yellow soln. It was then cooled to 40°. To this was added $PhCH_2Cl$ (1.39 g, 11.0 mmol). The mixture was stirred for 2 days at 55°. After cooling, it was diluted with water and extracted with n-pentane. The extract was dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed over SiO_2 (Merck Kieselgel 60, 100 g). Elution with 10% (v/v) EtOAc–n-hexane gave an oil. This was distilled over K_2CO_3 to give 1.88 g (67.9%) of **6b**, b.p. 123–125°/0.12 mm, $n_D^{20.5}$ 1.4696; $[\alpha]_D^{20}$ + 22.0° (c = 1.96, $CHCl_3$); ν_{max}: 1605 (vw), 1495 (w), 1120 (s), 1085 (s), 1060 (sh), 730 (m), 690 (m) cm^{-1}. (Found: C, 74.09; H, 10.49. Calc for $C_{19}H_{32}O_3$: C, 73.98; H, 10.46%.)

(2S,3R)-2,3-*Octanediol 2-benzyl ether* **6c**

1 N HCl (2 ml) was added to a stirred soln of **6b** (1.80 g, 5.84 mmol) in THF (15 ml). The stirring was continued for 2 hr at room temp. The mixture was diluted with water and extracted with ether. The ether soln was washed with sat $NaHCO_3$ aq and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed over SiO_2 (Merck Kieselgel 60, 100 g). Elution with 10% (v/v) EtOAc–n-hexane gave 1.40 g of an oil. This was distilled to give 1.26 g (91.3%) of **6c**, b.p. 112–113°/0.15 mm, $n_D^{20.5}$ 1.4904; $[\alpha]_D^{20.5}$ + 22.8° (c = 1.49, $CHCl_3$); ν_{max}: 3460 (m), 3075 (w), 3040 (w), 1600 (vw), 1495 (w), 1080 (s), 1070 (s), 730 (s), 695 (s) cm^{-1}; ^{1}H-NMR δ (CCl_4): 0.89 (3H, deformed t, J = 6 Hz), 1.08 (3H, d, J = 6 Hz), 1.00–1.60 (8H, m), 2.25 (1H, br s, OH), 3.13–3.75 (2H, m), 4.45 (2H, s), 7.23 (5H, s). (Found: C, 76.08; H, 10.38. Calc for $C_{15}H_{24}O_2$: C, 76.22; H, 10.24%.)

(S)-2-*Benzyloxy-3-octanone* **2b**

Jones CrO_3 (8 N, 2.5 ml) was added dropwise to a stirred and ice-cooled soln of **6c** (1.23 g, 5.20 mmol) in acetone (15 ml) at 0–5°. The mixture was stirred for 15 min at 0–10° and diluted with ether (200 ml). The ether soln was washed with $NaHCO_3$ aq and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatogrphaed over SiO_2 (Merch Kieselgel 60, 60 g). Elution with 5% (v/v) EtOAc–n-hexane gave 1.01 g (82.8%) of **2b**. A portion of it was distilled to give an analytical sample, b.p. 97–98°/0.07 mm, $n_D^{19.5}$ 1.4849; $[\alpha]_D^{19.5}$ − 37.9° (c = 2.96, $CHCl_3$); ν_{max}: 3070 (w), 3040 (w), 1715 (s), 1600 (w), 1585 (w), 1495 (m), 1110 (vs), 1070 (sh), 1020 (m), 730 (s), 690 (s) cm^{-1}; ^{1}H-NMR δ (CCl_4): 0.88 (3H, deformed t, J = 6 Hz), 1.25 (3H, d, J = 7 Hz), 1.05–1.75 (6H, m), 2.47 (2H, t, J = 7 Hz), 3.75 (1H, q, J = 7 Hz), 4.43 (2H, s), 7.27 (5H, s). (Found: C, 76.40; H, 9.23. Calc for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46%.)

(S)-2-*Hydroxy-3-octanone* **2a**

10% Pd–C (260 mg) was added to a soln of **2b** (752 mg, 3.2 mmol) in 95% EtOH (20 ml) and the mixture was shaken under H_2. At the time when the theoretical amount of H_2 (76.9 ml) was absorbed, the mixture was filtered to remove the catalyst. The filtrate was concentrated *in vacuo*. The residue was chromatographed over SiO_2 (Merck Kieselgel 60, 40 g). Elution with EtOAc–n-hexane gave 273 mg (59.2%) of **2a**, n_D^{21} 1.4298, $[\alpha]_D^{20}$ + 66.8° (c = 1.82, $CHCl_3$); ν_{max}: 3450 (s), 2960 (s), 2930 (s), 2870 (s), 1710 (s), 1460 (m), 1405 (m), 1370 (m), 1310 (m), 1250 (m), 1150 (m), 1120 (s), 1050 (s), 1025 (m), 965 (w), 905 (m), 840 (w), 760 (w), 725 (w) cm^{-1}; ^{1}H-NMR δ (60 MHz, $CDCl_3$): 0.89 (3H, t, J = 6 Hz), 1.28 (3H, d, J = 7 Hz), 1.05–1.95 (6H, m), 2.25–2.60 (2H, m), 3.36 (1H, d, J = 4 Hz), 3.80–4.40 (1H, m); ^{13}C-NMR δ (25 MHz, $CDCl_3$): 13.87, 19.83, 22.41, 23.31, 31.42, 37.50, 72.63, 212.77. The IR and ^{1}H-NMR spectra were identical with the authentic spectra. MS m/z 144 (M^+, 3%), 99 [M^+ − CH(OH)Me, 100%], 71 (99 − CO, 60%), 45 [MeCH(OH), 73%]. (Found: C, 66.28; H, 11.06. Calc for $C_8H_{16}O_2$: C, 66.03; H, 11.18%.)

The HPLC analysis of **2c** *to determine the optical purity of* **2a**

Acylation of **2a** with MTPA Cl prepared from either (*R*)-MTPA or (*S*)-MTPA gave two diastereomers of **2c** in the usual manner. HPLC analysis of **2c** (column, Nucleosil 50-5, 25 cm × 4.6 mm; solvent, n-hexane–$ClCH_2CH_2Cl$ (7:3); press, 48 kg/cm^2; flow rate 0.90 ml/min): R_t 14.93 min [(*S*)-MTPA ester], 16.71 min [(*R*)-MTPA ester]. The optical purity of **2a** was estimated to be 91.8–93.9% (average: 92.7%).

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