Pheromone Synthesis, CXCIV[+]

Synthesis of the Enantiomers of (*Z*)-21-Methyl-8-pentatriacontene, the Major Component of the Female-Produced Contact Sex Pheromone of the Yellow-Spotted Longicorn Beetle, *Psacothea hilaris*

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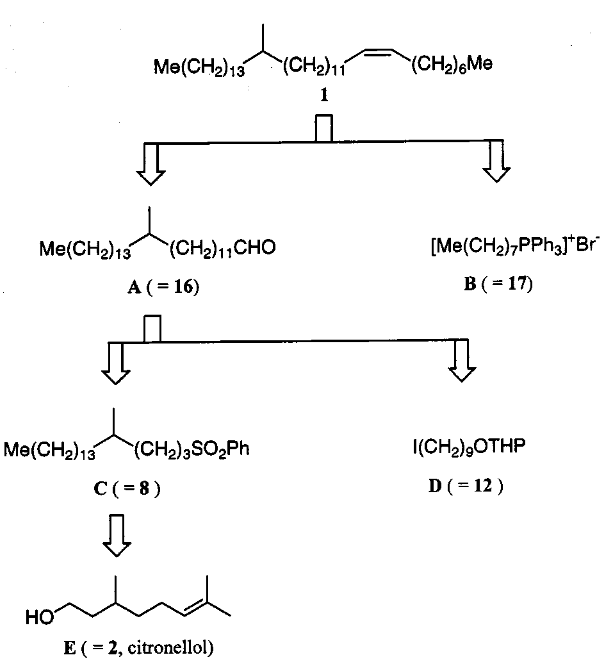
Both the enantiomers of (Z)-21-methyl-8-pentatriacontene (**1**), the major component of the female-produced contact sex pheromone of the yellow-spotted longicorn beetle (*Psacothea hilaris*), were synthesized by starting from the enantiomers of citronellol (**2**)

The yellow-spotted longicorn beetle, *Psacothea hilaris*, is a typical oligophagous insect of moracerous trees, and has damaged mulberry (*Morus bombycis*) plantations in Japan.[1] In 1996 Fukaya and her co-workers isolated and identified the major component of the female-produced contact sex pheromone of *P. hilaris* as (*Z*)-21-methyl-8-pentatriacontene (**1**; Scheme 1) on the basis of its spectroscopic analysis, microchemical reactions and synthesis as the racemate.[2] We became interested in synthesizing both (*R*)- and (*S*)-**1** in order to compare their pheromone activity and also to clarify the absolute configuration of the naturally occurring **1**. While we were working on this project, Fukusaki et al. synthesized (*R*)- and (*S*)-**1**,[3] which were bioassayed by Fukaya et al.[4] No significant difference in pheromone activity was observed between the enantiomers of **1**, and (±)-**1** was as active as the enantiomers.[4] Accordingly, the absolute configuration of the natural **1** could not be determined by the bioassay of (*R*)- and (*S*)-**1**. As shown in Scheme 1, our synthesis of the enantiomers of **1** started from the enantiomers of citronellol (**2**), while that by Fukusaki et al. started from the enantiomers of methyl 3-hydroxy-2-methylpropanoate.[3] The two syntheses are quite different: Fukusaki et al. employed acetylene chemistry to construct the (*Z*) double bond of **1**, while the Wittig reaction (**A** + **B** → **1**) is used in our present synthesis. The aldehyde **A** is prepared from the sulfone **C** and the iodide **D**, the former of which is derived from citronellol (**E** = **2**).

Scheme 2 summarizes the synthesis of the building blocks **C** [= (*R*)-**8**] and **D** (= **12**). Conversion of (*S*)-citronellol (**2**) into the corresponding tosylate **3** was followed by its treatment with 4 equivalents of dodecylmagnesium bromide in the presence of dilithium tetrachlorocuprate[5] to give (*R*)-**4**. Ozonolysis of (*R*)-**4** with a reductive work up furnished, after chromatographic purification, the crystalline alcohol (*R*)-**5** in 94% yield based on **2**. The alcohol (*R*)-**5** was converted into the iodide (*R*)-**7** via the tosylate (*R*)-**6**. Treatment of (*R*)-**7** with sodium benzenesulfinate afforded the crystalline phenylsulfone (*R*)-**8** (= **C**) in 94% yield based on **5**. The building block **D** (= **12**) was prepared in the usual manner from 1,9-nonanediol (**9**) via its monotetrahydropyranyl (mono-THP) ether **10** and the tosylate **11** in 47% yield.



Scheme 1. Retrosynthetic analysis of **1**

Conversion of (*R*)-**8** into one of the target molecules, (*R*)-**1**, is summarized in Scheme 3. Lithiation of (*R*)-**8** with *n*-butyllithium was followed by alkylation with **12** to give **13**,[6] which was reduced with sodium amalgam to give crude (*R*)-**14** contaminated with alkenes generated by β-elimination of the phenylsulfonyl group of **13**. Hydrogenation of the crude (*R*)-**14** on platinum oxide gave pure (*R*)-**14**. Removal of the THP protective group of **14** and subsequent chromatographic purification gave the crystalline

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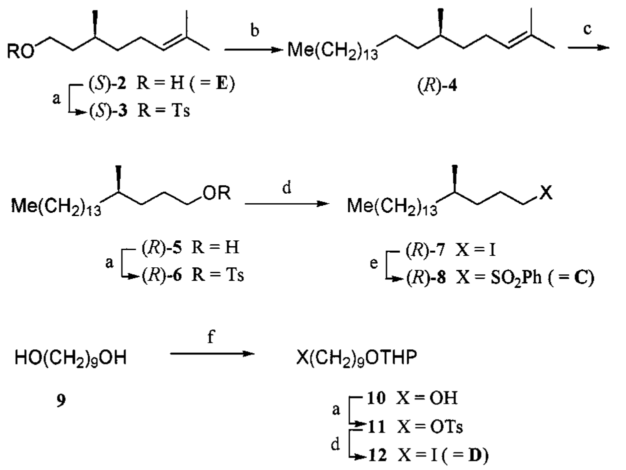
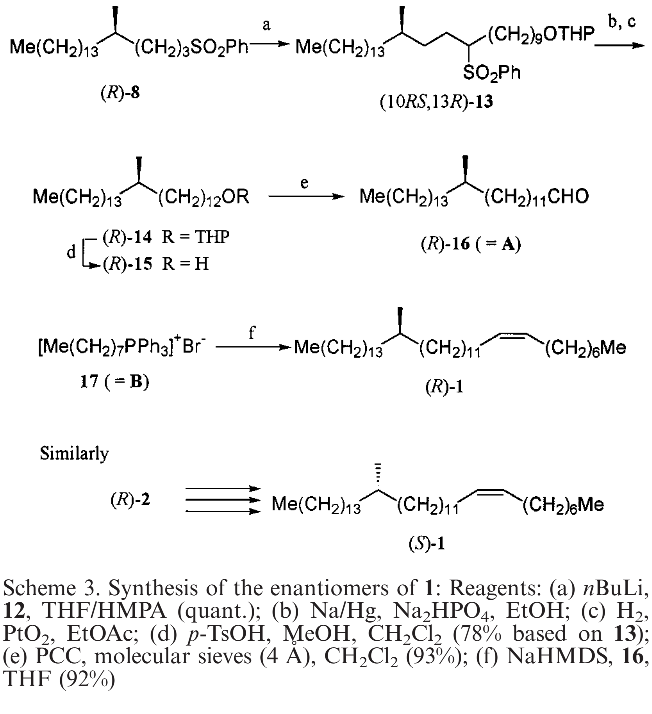


Scheme 2. Synthesis of the building blocks (*R*)-**8** and **12**: Reagents: (a) *p*-TsCl, C_5H_5N (quant.); (b) $Me(CH_2)_{11}MgBr$, Li_2CuCl_4, THF; (c) (i) O_3, $NaHCO_3$, hexane, CH_2Cl_2, MeOH, (ii) $NaBH_4$ (94% based on **2**); (d) NaI, $NaHCO_3$, Me_2CO (quant. for **7**; 92% for **12** based on **10**); (e) $PhSO_2Na$, DMF (94% based on **5**); (f) DHP, *p*-TsOH, CH_2Cl_2, chromatography (52%)

alcohol (*R*)-**15**. Its oxidation with pyridinium chlorochromate (PCC) afforded the aldehyde (*R*)-**16**. Finally, treatment of (*R*)-**16** with the Wittig reagent derived from **17** (= **B**) furnished the final product (*R*,*Z*)-21-methyl-8-pentatriacontene (**1**), $[\alpha]_D^{22} = -0.013$ (*c* = 15.0, $CHCl_3$). The Wittig reaction under the conditions reported by Bestmann et al.[7] and used by us in another pheromone synthesis[8] was highly (*Z*)-selective as manifested by the ^1H-NMR spectrum of the resulting (*R*)-**1**, which showed signals at δ = 2.02 (4 H, 7-H_2, 10-H_2) and 5.34 (m, 2 H, 8-H, 9-H). No signals due to the (*E*) isomer (δ = 1.96 and 5.38[2]) could be observed. Unfortunately, we were unable to determine the (*E*)/(*Z*) ratio by GC analysis of (*R*)-**1** on various stationary phases. Similarly, (*S*)-**1**, $[\alpha]_D^{22} = +0.008$ (*c* = 15.0, $CHCl_3$), was synthesized from (*R*)-citronellol (**2**). The overall yield of (*R*)-**1** was 44% based on (*S*)-**2** (12 steps), and that of (*S*)-**1** was 37% based on (*R*)-**2**. In the synthesis of Fukusaki et al., the overall yield of (*R*)-**1** was 5.8% based on (*S*)-methyl 3-hydroxy-2-methylpropanoate (13 steps), and that of (*S*)-**1** was 4.1% based on the (*R*)-hydroxy ester.



Scheme 3. Synthesis of the enantiomers of **1**: Reagents: (a) *n*BuLi, **12**, THF/HMPA (quant.); (b) Na/Hg, Na_2HPO_4, EtOH; (c) H_2, PtO_2, EtOAc; (d) *p*-TsOH, MeOH, CH_2Cl_2 (78% based on **13**); (e) PCC, molecular sieves (4 Å), CH_2Cl_2 (93%); (f) NaHMDS, **16**, THF (92%)

We were unable to separate the final products (*R*)- and (*S*)-**1** by GC analysis on conventional chiral stationary phases. We therefore assumed them to possess the enantiomeric purity of the starting materials [(*R*)-citronellol (**2**): 97.2% e.e.; (*S*)-**2**: 96.0% e.e.], because there was no step in the synthesis to cause racemization at the stereogenic center. The absolute configuration of the natural **1** remains unknown.

Experimental Section

General: Boiling points and melting points: uncorrected values. – IR: Jasco A-102. – ^1H NMR: Jeol JNM-EX 90A (90 MHz) and Bruker DPX 300 (300 MHz) (TMS at δ = 0.00 or $CHCl_3$ at δ = 7.26 as an internal standard). – ^{13}C NMR: Bruker DPX 300 (75.5 MHz) ($CDCl_3$ at δ = 77.0 as an internal standard). – Optical rotation: Jasco DIP-1000. – MS: Jeol JMS-SX102A and Hitachi M-80B. – M.p.: Yanaco MP.S3. – CC: Merck Kieselgel 60 Art 1.07734. – TLC: 0.25 mm Merck silica gel plates (60F-254).

(*R*)-2,6-Dimethyl-2-icosene [(*R*)-4]: To a stirred and ice-cold solution of (*S*)-**3** (18.0 g, 58.0 mmol) in dry THF (200 mL) was added a solution of dodecylmagnesium bromide in THF (0.3 M, 760 mL, 256 mmol) followed by a solution of dilithium tetrachlorocuprate in THF (0.1 M, 5.0 mL, 0.50 mmol) at −78 °C under argon. The mixture was allowed to warm to room temp. with stirring over 12 h. It was then quenched with a satd. ammonium chloride solution and extracted with *n*-hexane. The organic layer was washed with water, a satd. sodium hydrogen carbonate solution and brine, dried with magnesium sulfate and concentrated in vacuo. The residue was chromatographed on silica gel (180 g; *n*-hexane) to give 35.8 g of crude (*R*)-**4** as a colorless oil. This oil was employed for the next step without further purification.

(*S*)-2,6-Dimethyl-2-icosene [(*S*)-4]: In the same manner as described above, (*R*)-**3** (39.0 g, 128 mmol) was converted into 78.7 g of crude (*S*)-**4**.

(*R*)-4-Methyl-1-octadecanol [(*R*)-5]: Ozone was bubbled into a stirred mixture of (*R*)-**4** (5.86 g) in *n*-hexane/methanol/dichloromethane (1:1:1; 120 mL) for 10 h at −78 °C. After flashing off the excess O_3 with O_2 gas, to the stirred mixture was added $NaBH_4$ (2.87 g, 19 mmol). The mixture was allowed to warm to 0 °C with stirring for 3 h. It was then quenched with 1 M hydrochloric acid and extracted with diethyl ether. The organic layer was washed with water, a satd. sodium hydrogen carbonate solution and brine, dried with magnesium sulfate and concentrated in vacuo. The residue was purified by chromatography on silica gel (120 g; hexane/ethyl acetate, 20:1) to give 5.05 g [94% from (*S*)-**2**] of (*R*)-**5** as colorless fine needles, m.p. 33 °C. – $[\alpha]_D^{21} = +0.91$ (*c* = 0.93, $CHCl_3$). – IR (film): $\tilde{\nu} = 3320\ cm^{-1}$ (s O–H), 1060 (s C–O), 720(C–H). – ^1H NMR (90 MHz, $CDCl_3$): δ = 0.69–0.98 (m, 6 H, 4-Me, 18-H_3), 0.98–1.69 (m, 32 H), 3.63 (t, *J* = 6.4 Hz, 2 H, 1-H_2). – $C_{19}H_{40}O$ (284.51): calcd. C 80.20, H 14.17; found C 79.86, H 13.63.

(*S*)-4-Methyl-1-octadecanol [(*S*)-5]: In the same manner as described above, (*S*)-**4** (5.00 g) was converted into (*S*)-**5** [4.10 g, 89%

from (*R*)-**2**] as colorless fine needles, m.p. 33°C. − $[\alpha]_D^{21} = -1.03$ (c = 0.98, $CHCl_3$). − Its IR and ^{1}H-NMR spectra are identical with those of the (*R*) isomer. − $C_{19}H_{40}O$ (284.51): calcd. C 80.20, H 14.17; found C 79.90, H 13.73.

(*R*)-4-Methyloctadecyl Tosylate [(*R*)-6]: **p**-Toluenesulfonyl chloride (4.96 g, 26.0 mmol) was added to a stirred and ice-cooled solution of (*R*)-**5** (5.69 g, 20.0 mmol) in dry pyridine (30 mL). The mixture was stirred for 12 h at 4°C, then poured into 1 M hydrochloric acid, and extracted with diethyl ether. The ethereal extract was washed with 1 M hydrochloric acid, a satd. cupric sulfate solution, water, a satd. sodium hydrogen carbonate solution and brine, dried with magnesium sulfate and concentrated in vacuo to give 8.60 g (98%) of crude (*R*)-**6**. This compound was employed in the next step without further purification.

(*S*)-4-Methyloctadecyl Tosylate [(*S*)-6]: In the same manner as described above, (*S*)-**5** (5.69 g, 20.0 mmol) was converted into 8.60 g (98%) of (*S*)-**6**. This compound was employed in the next step without further purification.

(*R*)-4-Methyloctadecyl Iodide [(*R*)-7]: Sodium iodide (3.21 g, 21.4 mmol) was added to a solution of crude (*R*)-**6** (6.29 g, 14.3 mmol) in dry acetone (50 mL). The mixture was stirred and heated under reflux for 4 h. To this was added water, and acetone was removed by evaporation. The residue was poured into water, and extracted with diethyl ether. The ethereal extract was washed with water and brine, dried with magnesium sulfate, and concentrated in vacuo. The residue was chromatographed on silica gel (30 g; hexane/ethyl acetate, 200:1) to give 5.51 g (98%) of (*R*)-**7**. − n_D^{25} = 1.4778. − $[\alpha]_D^{21} = -1.52$ (c = 1.12, $CHCl_3$). − IR (film): $\tilde{\nu}$ = 1170 cm^{-1} (m), 720(m). − ^{1}H NMR (90 MHz, $CDCl_3$): δ = 0.78−0.99 (m, 6 H, 4-Me, 18-H_3), 1.15−2.07 (m, 35 H), 3.5 (t, J = 6.4 Hz, 2 H, 1-, H_2). − This compound was employed in the next step without further purification.

(*S*)-4-Methyloctadecyl Iodide [(*S*)-7]: In the same manner as described above, (*S*)-**6** (6.29 g, 14.3 mmol) was converted into 5.41 g (96%) of (*S*)-**7**. − n_D^{25} = 1.4780. − $[\alpha]_D^{21} = +1.72$ (c = 1.26, $CHCl_3$). − Its IR and ^{1}H-NMR spectra are identical with those of (*R*)-**7**. This compound was employed in the next step without further purification.

(*R*)-4-Methyl-1-phenylsulfonyloctadecane [(*R*)-8]: To a stirred solution of (*R*)-**7** (9.00 g, 22.8 mmol) in *N,N*-dimethylformamide (90 mL) was added sodium benzenesulfinate dihydrate (5.94 g, 29.7 mmol). The mixture was stirred at room temp. for about 10 h. It was then poured into brine and extracted with diethyl ether. The ethereal extract was washed with water and brine, dried with magnesium sulfate, and concentrated in vacuo. The residue was purified by chromatography on silica gel (180 g; hexane/ethyl acetate, 50: 1) to give 8.77 g (94%) of (*R*)-**8** as colorless needles, m.p. 35.5°C. − $[\alpha]_D^{22} = -1.81$ (c = 15.0, $CHCl_3$). − IR (film): $\tilde{\nu}$ = 1325 cm^{-1} (s, SO_2), 1158 (s, SO_2), 1095 (s, C−O), 785 (m), 730 (s), 700 (m). − ^{1}H NMR (90 MHz, $CDCl_3$): δ = 0.74−0.99 (m, 6 H, 4-Me, 18-H_3), 0.99−1.47 (m, 29 H), 1.47−1.94 (m, 2 H, 2-H_2), 3.06 (t, J = 7.5 Hz 2 H, 1-H_2), 7.41−8.16 (m, 5 H, Ph). − $C_{25}H_{44}O_2S$ (408.7): calcd. C 73.47, H 10.85; found C 73.32, H 10.85.

(*S*)-4-Methyl-1-phenylsulfonyloctadecane [(*S*)-8]: In the same manner as described above, (*S*)-**7** (5.06 g, 12.8 mmol) was converted into 4.55 g (87%) of (*S*)-**8**. − Its IR and ^{1}H-NMR spectra are identical with those of (*R*)-**8**, m.p. 35.5°C. − $[\alpha]_D^{22} = +2.10$ (c = 5.16, $CHCl_3$). − $C_{25}H_{44}O_2S$ (408.7): calcd. C 73.47, H 10.85; found C 73.16, H 11.27.

9-Tetrahydropyranyloxy-1-nonanol (10): To a stirred solution of diol **9** (5.00 g, 31.2 mmol) and dihydropyran (2.62 g, 31.2 mmol) in dry dichloromethane (100 mL) was added *p*-toluenesulfonic acid monohydrate (593 mg, 3.12 mmol) at room temp. and the mixture was stirred for 2 h. After neutralization with sodium hydrogen carbonate, the mixture was poured into brine and extracted with diethyl ether. The ethereal extract was washed with water and brine, dried with magnesium sulfate and concentrated in vacuo. The residue was purified by chromatography on silica gel (100 g; hexane/ethyl acetate, 10:1−3:1) to give 3.96 g (52%) of **10** as an oil. − n_D^{25} = 1.4559 − IR (film): $\tilde{\nu}$ = 3430 cm^{-1} (s, O−H), 1360 (s), 1120(s), 1080 (s), 1030 (s). − ^{1}H NMR (90 MHz, $CDCl_3$): δ = 1.07−1.91 (m, 19 H), 3.22−3.98 (m, 6 H), 4.56 (br. s, 1 H, 1′-H). − This compound was employed in the next step without further purification.

9-Tetrahydropyranyloxynonyl Tosylate (11): **p**-Toluenesulfonyl chloride (4.25 g, 22.3 mmol) was added to a stirred and ice-cooled solution of **10** (4.00 g, 16.0 mmol) in dry pyridine (20 mL). The mixture was stirred for 12 h at 4°C. It was then poured into 1 M hydrochloric acid and extracted with diethyl ether. The ethereal extract was washed with 1 M hydrochloric acid, a satd. cupric sulfate solution, water, a satd. sodium hydrogen carbonate solution and brine, dried with magnesium sulfate and concentrated in vacuo to give 6.36 g (quant.) of crude **11**. This compound was employed in the next step without further purification.

9-Tetrahydropyranyloxynonyl Iodide (12): Sodium iodide (3.16 g, 20.0 mmol) was added to a mixture of crude **11** (6.36 g, 16.0 mmol) and sodium hydrogen carbonate (1.0 g, 10 mmol) in dry acetone (60 mL). The mixture was stirred and heated under reflux for 4 h. To this was added water and acetone was removed by evaporation. The residue was poured into water, and extracted with diethyl ether. The ethereal extract was washed with water and brine, dried with magnesium sulfate, and concentrated in vacuo. The residue was chromatographed on silica gel (30 g; hexane/ethyl acetate, 200:1) to give 5.67 g (quant.) of **12** as a colorless oil. − n_D^{25} = 1.4587. − IR (film): $\tilde{\nu}$ = 1350 cm^{-1} (s), 1320(s), 1080 (s), 1040 (s, C−O). − ^{1}H NMR (90 MHz, $CDCl_3$): δ = 1.07−1.98 (m, 18 H), 3.25−4.04 (m, 8 H), 3.19 (t, J = 6.8 Hz, 2 H, 1-H_2), 4.57 (br. s, 1 H, 1′-H). − This compound was employed in the next step without further purification.

(10*RS*,13*R*)-13-Methyl-10-phenylsulfonyl-1-tetrahydropyranyloxyheptacosane [(*R*)-13]: A solution of *n*-butyllithium in hexane (1.55 M, 7.15 mL, 11.1 mmol) was added to a stirred and cooled solution of (*R*)-**8** (4.11 g, 10.1 mmol) in dry THF (40 mL) and dry HMPA (80 mL) at −78°C under argon. After the addition, the mixture was stirred at −30°C for 15 min and cooled to −78°C. Then a solution of **12** (4.27 g, 12.0 mmol) in dry tetrahydrofuran (10 mL) was added dropwise to the mixture at −78°C with stirring. The mixture was stirred at ambient temp. for about 10 h. It was then poured into ice and a satd. ammonium chloride solution and extracted with diethyl ether. The ethereal extract was washed with water and brine, dried with magnesium sulfate, and concentrated in vacuo. The residue was chromatographed on silica gel (150 g; hexane/ethyl acetate, 20:1) to give 5.01 g (78%) of crude (*R*)-**13** as an oil. − n_D^{25} = 1.4821. − $[\alpha]_D^{22} = -2.61$ (c = 5.41, $CHCl_3$), . − IR (film): $\tilde{\nu}$ = 1355 cm^{-1} (s, SO_2), 1310 (s), 1150 (s, SO_2), 1090 (s, C−O), 1040 (s, C−O), 765 (m), 735 (s), 700 (s). − ^{1}H NMR (90 MHz, $CDCl_3$): δ = 0.70−1.70 (m, 57 H), 2.68−3.98 (m, 7 H), 4.56 (br., 1 H, 1′-H), 7.40−7.97 (m, 5 H, Ph). − This compound was employed in the next step without further purification.

(10*RS*,13*S*)-13-Methyl-10-phenylsulfonyl-1-tetrahydropyranyloxyheptacosane [(*S*)-13]: In the same manner as described above, (*S*)-**8** (4.37 g, 10.7 mmol) was converted into 5.50 g (81%) of (*S*)-**13** as an oil. − n_D^{25} = 1.4824. − $[\alpha]_D^{22} = +2.50$ (c = 15.0, $CHCl_3$). −

Its IR and ^{1}H-NMR spectra are identical with those of (*R*)-**13**. This compound was employed in the next step without further purification.

(*R*)-13-Methyl-1-tetrahydropyranyloxyheptacosane [(*R*)-14]: A solution of (*R*)-**13** (5.01 g, 7.89 mmol) in dry ethanol (70 mL) was added dropwise to sodium amalgam (5%, 25 g, 54.4 mmol) at 0°C under argon. The mixture was stirred vigorously at room temp. for about 36 h. The mixture was filtered through Celite, and the filter cake was washed several times with diethyl ether. The combined filtrate and washings were concentrated in vacuo. The residue was diluted with water and extracted with diethyl ether. The ethereal extract was washed with water and brine, dried with magnesium sulfate, and concentrated in vacuo. The residue was chromatographed on silica gel (100 g; hexane/ethyl acetate, 30:1), to give 4.7 g of (*R*)-**14**. Then PtO_2 (5 mg) was added to a stirred solution of this compound in ethyl acetate (50 mL) under H_2. The mixture was stirred at room temp. for about 10 h. The mixture was filtered through Celite, and the filter cake was washed several times with diethyl ether. The combined filtrate and washings were concentrated in vacuo to give 4.7 g of crude (*R*)-**14** as a colorless oil. − $n_D^{25} = 1.4587$. − $[\alpha]_D^{21} = +0.51$ ($c = 4.89$, $CHCl_3$). − IR (film): $\tilde{\nu} = 1080$ cm^{-1} (s, C−O), 1040 (s, C−O). − ^{1}H NMR (90 MHz, $CDCl_3$): $\delta = 0.62-1.96$ (m, 58 H), 3.22−3.99 (m, 7 H), 4.57 (br., 1 H, 1′-H), −This compound was employed in the next step without further purification.

(*S*)-13-Methyl-1-tetrahydropyranyoxyheptacosane [(*S*)-14]: In the same manner as described above, (*S*)-**13** (7.28 g, 11.5 mmol) was converted into 6.83 g of (*S*)-**14**. − $n_D^{25} = 1.4593$. − $[\alpha]_D^{21} = -0.39$ ($c = 5.11$, $CHCl_3$). − Its IR and ^{1}H-NMR spectra are identical with those of (*R*)-**14**. This compound was employed in the next step without further purification.

(*R*)-13-Methyl-1-heptacosanol [(*R*)-15]: To a stirred solution of (*R*)-**14** (4.70 g, 9.50 mmol) in methanol (40 mL) was added *p*-toluenesulfonic acid monohydrate (181 mg, 0.95 mmol) at room temp., and the mixture was stirred for 2 h. After neutralization with sodium hydrogen carbonate, the mixture was poured into brine and extracted with diethyl ether. The ethereal extract was washed with water and brine, dried with magnesium sulfate and concentrated in vacuo. The residue was purified by chromatography on silica gel (80 g; hexane/ethyl acetate, 20:1) to give 3.59 g [78% from (*R*)-**13**] of (*R*)-**15** as colorless needles; m.p. 51.5°C. − $[\alpha]_D^{21} = +0.21$ ($c = 6.08$, $CHCl_3$). − IR (film): $\tilde{\nu} = 3360$ cm^{-1} (s, O−H), 1380 (s), 1060 (m, C−O), 720 (m). − ^{1}H NMR (90 MHz, $CDCl_3$): $\delta = 0.68-1.75$ (m, 56 H), 3.64 (t, $J = 6.4$ Hz, 2 H, 1-H_2). − $C_{28}H_{58}O$ (410.8): calcd. C 81.87, H 14.23; found C 81.73, H 14.08.

(*S*)-13-Methyl-1-heptacosanol [(*S*)-15]: In the same manner as described above, (*S*)-**14** (2.14 g, 4.33 mmol) was converted into 1.78 g [74% from (*S*)-**13**] of (*S*)-**15**; m.p. 51.5°C. − $[\alpha]_D^{21} = -0.15$ ($c = 5.88$, $CHCl_3$). − Its IR and ^{1}H-NMR spectra are identical with those of (*R*)-**15**. − $C_{28}H_{58}O$ (410.8): calcd. C 81.87, H 14.23; found C 81.48, H 14.44.

(*R*)-13-Methylheptacosanal [(*R*)-16]: A solution of (*R*)-**15** (2.00 g, 4.87 mmol) in CH_2Cl_2 (20 mL) was added to a stirred suspension of pyridinium chlorochromate (5.46 g, 24.8 mmol) and molecular sieves (4 Å) (0.5 g) in CH_2Cl_2 (50 mL). The mixture was stirred at room temp. for 2 h, then diluted with diethyl ether and filtered through Celite. The filtrate was concentrated in vacuo. The residue was chromatographed on silica gel (40 g). Elution with *n*-hexane gave 1.85 g (93%) of (*R*)-**16** as a white soft wax. − $[\alpha]_D^{21} = +0.11$ ($c = 5.51$, $CHCl_3$). − IR (film): $\tilde{\nu} = 2770$ cm^{-1} (s, m, O=C−H), 1720 (s, C=O), 720(m, C−H). − ^{1}H NMR (90 MHz, $CDCl_3$): $\delta = 0.88$ (t, $J = 6.7$ Hz, 3 H, 27-Me), 1.0−1.8 (m, 47 H), 2.41 (dt, $J = 1.5$, 7.1 Hz, 2 H, 2-H_2), 9.76 (t, $J = 1.8$ Hz, 1 H, 1-H). − This compound was employed in the next step without further purification.

(*S*)-13-Methylheptacosanal [(*S*)-16]: In the same manner as described above, (*S*)-**15** (1.03 g, 2.50 mmol) was converted into 971 mg (95%) of (*S*)-**16**. − $[\alpha]_D^{21} = -0.09$ ($c = 6.21$, $CHCl_3$). − Its IR and ^{1}H-NMR spectra are identical with those of (*R*)-**16**. This compound was employed in the next step without further purification.

(*R*,*Z*)-21-Methyl-8-pentatriacontene [(*R*)-1]: To a solution of the dry phosphonium salt **17** (836 mg, 1.83 mmol) in dry tetrahydrofuran (40 mL) was added sodium bis(trimethylsilyl)amide (1 M, 1.8 mL, 1.8 mmol) at −40°C under argon. After 2 h of stirring at the same temp., the resulting orange solution was added to a solution of (*R*)-**16** (500 mg, 1.22 mmol) in dry tetrahydrofuran (20 mL) at − 78°C under argon. The reaction mixture was then allowed to warm to room temp. with stirring for 12 h, and quenched with a satd. ammonium chloride solution. It was then extracted with diethyl ether. The organic layer was washed with water, satd. sodium hydrogen carbonate solution and brine, dried with magnesium sulfate and concentrated in vacuo. The residue was purified by chromatography on silica gel (10 g, hexane) to give 564 mg (92%) of (*R*)-**1** as a colorless oil; $n_D^{24} = 1.4658$. − $[\alpha]_D^{22} = -0.013$ ($c = 15.0$, $CHCl_3$). − IR (film): $\tilde{\nu} = 2930$ cm^{-1} (s), 1465 (s, C−H), 1380 (s), 723 (m). − ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.84$ (d, $J = 6.4$ Hz, 3 H, 21-Me), 0.88 (t, $J = 6.6$ Hz, 6 H, 1-H_3, 35-H_3), 1.085 (br., 1 H, 21-H), 1.26 (m, 56 H), 2.02 (m, 4 H, 7-H_2, 10-H_2), 5.34 (m, 2 H, 8-H, 9-H). − ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 14.1$, 19.7, 22.7, 27.2, 29.29, 29.33, 29.38, 29.43, 29.63, 29.77, 29.78, 29.83, 30.10, 31.94, 31.99, 32.80, 37.16, 129.90. − $C_{36}H_{72}$ (504.96): calcd. C 85.63, H 14.37; found C 85.96, H 14.53.

(*S*,*Z*)-21-Methyl-8-pentatriacontene [(*S*)-1]: In the same manner as described above, (*S*)-**16** (820 mg, 2.01 mmol) was converted into 906 mg (89%) of (*S*)-**1** as a colorless oil. − $n_D^{24} = 1.4587$. − $[\alpha]_D^{22} = +0.008$ ($c = 15.0$, $CHCl_3$), − Its IR and ^{1}H-, ^{13}C-NMR spectra are identical with those of (*R*)-**1**. − $C_{36}H_{72}$ (504.96): calcd. C 85.63, H 14.37; found C 86.05, H 14.85.

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