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Synthesis of the Enantiomers of Some Methyl-branched Cuticular Hydrocarbons of the Ant, *Diacamma* sp.†

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The enantiomers of 3-methylpentacosane, 3-methylheptacosane, 3-methylnonacosane, 13-methylheptacosane, and 5-methylheptacosane were synthesized by starting from the enantiomers of 2-methylbutyl bromide or citronellol. These methyl-branched alkanes are the characteristic components of the cuticular hydrocarbons of queen of the ant, *Diacamma* sp.

Key words: methyl-branched alkane; optically active alkane; queen of ant; *Diacamma* sp.; cuticular hydrocarbon

Lipids, including hydrocarbons, play an important role in protecting the surface of living organisms. The cuticular hydrocarbons of such insects as flies and ants have been studied and analyzed since the advent of the gas chromatographic method. Their role in chemical communication, however, remained unknown until the mid 1970s. Since then, a number of pheromone hydrocarbons have been isolated, identified, and synthesized.[1] Assignment of the absolute configuration of minute amounts of methyl-branched hydrocarbons, however, still remains as an unsolved challenge, because the stereoisomers of chiral hydrocarbon cannot be separated even by the modern technique of gas chromatographic analysis. The only solution at present is to synthesize and bioassay all the possible stereoisomers of the pheromone to discover the bioactive one. Our 1983 synthesis of the stereoisomers of 13,23-dimethylpentatriacontane,[2] the tsetse fly pheromone, enabled McDowell *et al.* to find only its *meso*-isomer to be bioactive.[3] More recently, in 1999, we synthesized all the stereoisomers of 7-methylheptadecane and 7,11-dimethylheptadecane,[4] the pheromone of the spring hemlock looper, and their subsequent bioassay revealed only the (*S*)-isomer of the former and the *meso*-isomer of the latter to be bioactive.

As to the cuticular hydrocarbons of social insects such as honeybees and ants, their importance in species, colony and queen recognition has been known for many years. But even by the mid 1980s, clarification of the role of these hydrocarbons seemed to be very difficult as noted by Bradshaw and Howse: "These odours are probably complex, and are therefore difficult to study after extraction".[5] In 1990, in their seminal paper on queen recognition by ants, Yamaoka and Kubo reported that the common cuticular hydrocarbon profile among *Formica* workers depended on the queen: workers experimentally deprived of their queen showed considerable differences in their main cuticular hydrocarbon levels.[6] Clement and his co-workers also noticed the importance of cuticular hydrocarbons whereby *Messor barbarus* ant workers discriminate between monogynous and polygynous colonies.[7]

In connection with his study on queen recognition by the ant of *Diacamma* sp. (togé-ôhariari in Japanese), Yamaoka requested Mori to synthesize the hydrocarbons as shown in Fig. 1. These hydrocarbons **1**–**8** are the characteristic components of the cuticular hydrocarbons of the queen of *Diacamma* sp. In this paper, we describe the synthesis of monomethyl-branched hydrocarbons **1**–**5**. So as to clarify the chiral recognition of the ant, pure enantiomers (≥97% e.e.) of **1**–**5** were synthesized by starting from known chiral building blocks. Hydrocarbons are often regarded as simple synthetic targets, because they lack functionality. The synthesis of enantiomerically pure methyl-branched alkanes, however, is not at all an easy business. There are two problems to be solved: i) choice of the proper starting materials of high enantiomeric purity, and ii) choice of the proper functional groups as the connective pivot for constructing the whole carbon skeleton from intermediates with fewer carbon atoms.

Scheme 1 summarizes our synthesis of the enantiomers of 3-methylpentacosane (**1**), 3-methylheptacosane (**2**) and 3-methylnonacosane (**3**). The common chiral building blocks employed for the synthesis were (*R*)- and (*S*)-2-methylbutyl bromide (**9**) which have been popular building blocks of high

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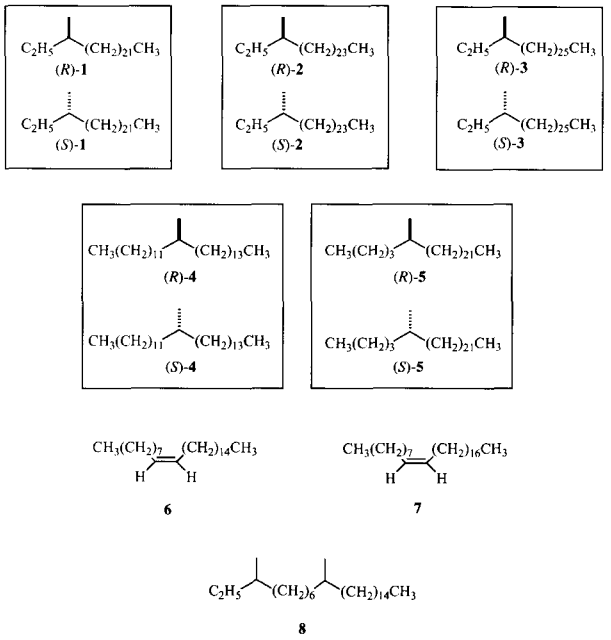
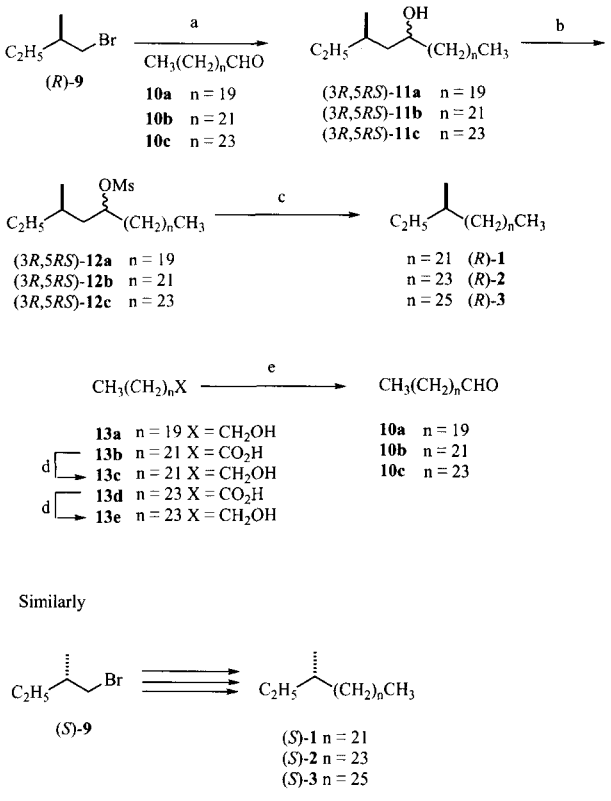
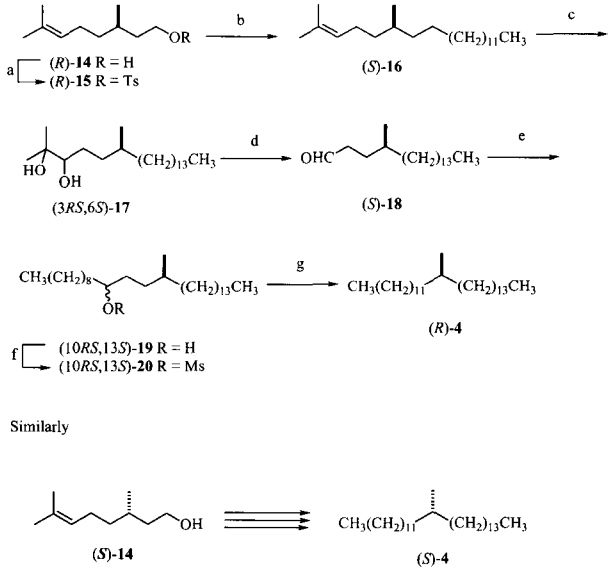


Fig. 1. Structures of the Cuticular Hydrocarbons of the Ant *Dicamma* sp.



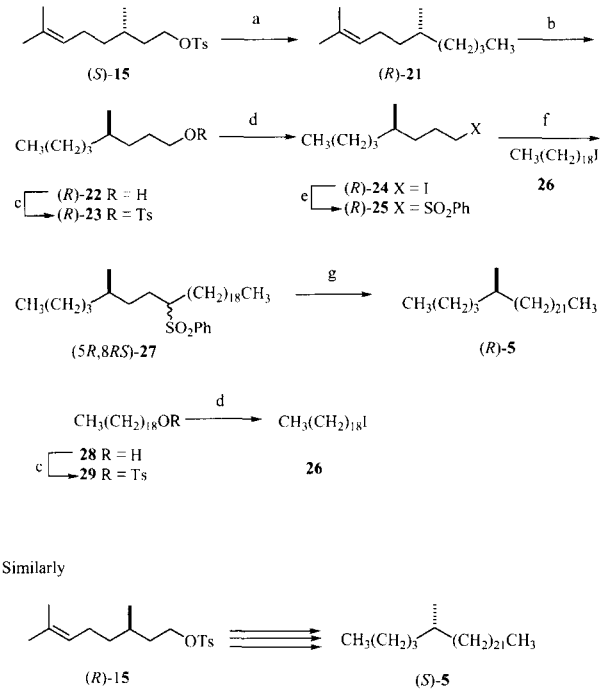
Scheme 1. Synthesis of the Enantiomers of **1**, **2** and **3**.
Reagents: (a) Mg, THF (80–90%). (b) MsCl, C_5H_5N. (c) $LiB(C_2H_5)_3H$, THF [2 steps 70–90% based on **11**]. (d) $LiAlH_4$, $(C_2H_5)_2O$ (70–97%). (e) PCC, mol. sieves 4A, CH_2Cl_2 (80–90%).



Scheme 2. Synthesis of the Enantiomers of **4**.
Reagents: (a) TsCl, C_5H_5N. (b) $CH_3(CH_2)_{11}MgBr$, Li_2CuCl_4, THF. (c) OsO_4, NMO, t-$C_4H_9OH/(CH_3)_2CO/H_2O$ [3 steps, 82% based on (*R*)-**14**]. (d) $HIO_4 \cdot 2H_2O$, THF (98%). (e) $CH_3(CH_2)_8MgBr$, THF (55%). (f) MsCl, C_5H_5N. (g) $LiB(C_2H_5)_3H$, THF [2 steps, 83% based on (*S*)-**19**].

enantiomeric purity (>99% e.e.) and often been used in pheromone synthesis since the 1970s.[8,9] For the synthesis of (*R*)-3-methylpentacosane (**1**), treatment of henicosanal (**10a**) with the Grignard reagent prepared from (*R*)-**9** afforded alcohol **11a**, whose mesylate **12a** was reduced with lithium triethylborohydride (Super-hydride®) to give (*R*)-**1** in a 61% overall yield based on (*R*)-**9** (3 steps). By employing tricosanal (**10b**) and pentacosanal (**10c**) instead of henicosanal (**10a**), (*R*)-**2** and (*R*)-**3** were respectively obtained in the same manner. The opposite enantiomers, (*S*)-**1**, **2** and **3**, were similarly prepared, starting from (*S*)-bromide **9**. It should be added that aldehydes **10a–c** were synthesized from commercially available alcohol **13a** or carboxylic acids **13b** and **13d** by the conventional routes as shown in Scheme 1.

Synthesis of the enantiomers of 13-methylheptacosane (**4**) employed the enantiomers of citronellol (**14**, 97% e.e.)[4] as the starting materials (Scheme 2). To prepare (*R*)-**4**, (*R*)-citronellyl tosylate (**15**) was treated with dodecylmagnesium bromide in the presence of dilithium tetrachlorocuprate[10] to give (*S*)-**16** contaminated with some hydrocarbon by-products. Dihydroxylation of alkene (*S*)-**16** with osmium tetroxide and *N*-methylmorpholine *N*-oxide (NMO)[11] was followed by chromatographic purification to remove the hydrocarbon by-products. Desired diol (3*RS*,6*S*)-**17** was obtained in an 82% overall yield based on (*R*)-**14**. Cleavage of the 1,2-glycol system of **17** with periodic acid yielded aldehyde (*S*)-**18**, whose treatment with nonylmagnesium bromide afforded alcohol (10*RS*,13*S*)-**19**. Finally, corresponding mesylate (10*RS*,13*S*)-**20** was reduced with lithium triethylborohydride to give (*R*)-13-



Scheme 3. Synthesis of the Enantiomers of **5**.
Reagents: (a) C_2H_5MgBr, Li_2CuCl_4, THF (86%). (b) (i) O_3, CH_2Cl_2/CH_3OH; (ii) $NaBH_4$ (65%). (c) TsCl, C_5H_5N. (d) NaI, $NaHCO_3$, $(CH_3)_2CO$ [2 steps, 99% for (*R*)-**24** based on (*R*)-**22**; 87% for **26** based on **28**]. (e) $PhSO_2Na \cdot 2H_2O$, DMF (89%). (f) (i) n-C_4H_9Li, THF; (ii) **26** (50%). (g) Na-Hg, C_2H_5OH (91%).

methylheptacosane (**4**). The overall yield of (*R*)-**4** was 37% based on (*R*)-**14** (7 steps). Similarly, (*S*)-**4** was prepared from (*S*)-citronellol (**14**).

Synthesis of the enantiomers of 5-methylheptacosane (**5**) was achieved as shown in Scheme 3. Again we used the enantiomers of **14** as the starting materials. Chain-elongation of (*S*)-citronellyl tosylate **15** with ethylmagnesium bromide under Schlosser conditions[10] furnished alkene (*R*)-**21**.[11] Ozonolysis of (*R*)-**21** with a reductive workup gave alcohol (*R*)-**22**. We first attempted to couple corresponding tosylate (*R*)-**23** with nonadecylmagnesium bromide under Schlosser conditions.[10] It turned out, however, that a Grignard reagent with such a long alkyl chain as C_{19} was difficult to efficiently prepare. Accordingly, tosylate (*R*)-**23** was converted to phenylsulfone (*R*)-**25** via iodide (*R*)-**24**, and chain-elongation was successfully achieved to give (5*R*,8*RS*)-**27** by alkylating the anion derived from (*R*)-**25** with nonadecyl iodide (**26**), which had been prepared from commercially available 1-nonadecanol (**28**) via corresponding tosylate **29**. Finally, the phenylsulfonyl group of **27** was removed by reducting with sodium amalgam to furnish (*R*)-5-methylheptacosane (**5**). The overall yield of (*R*)-**5** was 22% based on (*S*)-citronellol (**14**) through 8 steps. Similarly, (*S*)-**5** was prepared from (*R*)-**15**.

In conclusion, seven cuticular hydrocarbons characteristic of the queen of *Diacamma* sp. were synthesized in both enantiomeric forms. These fourteen samples will be bioassayed in Prof. Yamaoka's laboratory, and the results will be reported in due course. We are now synthesizing remaining hydrocarbons **6**, **7** and **8**.

Experimental

Boiling point (bp) data are uncorrected. Melting point (mp) data were measured with a Yanaco MP-S3 instrument and are uncorrected. IR data were measured with a Jasco A-102 spectrometer. ^{1}H-NMR data were measured with a Jeol JNM-EX90A (90 MHz), Jeol JNM-LA400 (400 MHz) or Jeol JNM-LA500 (500 MHz) spectrometer (TMS at $\delta_H = 0.00$ or $CHCl_3$ at $\delta_H = 7.26$ was used as the internal standard). Optical rotation data were measured with a Jasco DIP-1000 spectrometer, and MS data were measured with a Jeol JMS-AX 505 HA spectrometer.

(3R,5RS)-3-Methylpentacosan-5-ol [(R)-11a]. To a stirred and ice-cooled solution of **10a** (1.37 g, 4.41 mmol) in dry THF (15 ml) was added a solution of the Grignard reagent prepared from (*R*)-**9** in THF (0.4 M, 26 ml, 10.0 mmol) at 0°C under argon. The mixture was allowed to warm to room temperature while stirring for 2 h. It was then quenched with a saturated aqueous ammonium chloride solution, and the mixture was extracted with hexane. The organic phase was successively washed with water and a saturated aqueous ammonium chloride solution, dried with magnesium sulfate, and concentrated *in vacuo*. The residue was chromatographed on silica gel (35 g; hexane/ethyl acetate, 50:1) to give 1.15 g of (*R*)-**11a** (68%) as a colorless solid, mp 48.5–49.5°C. $[\alpha]_D^{22}$ −3.7° (*c* 1.04, $CHCl_3$). IR ν_{max} (KBr) cm^{-1}: 3350 (s, O-H), 1130 (m, C-O). NMR δ_H (90 MHz, $CDCl_3$): 0.85–1.00 (9H, m, 1-H, 13-Me, 25-H), 1.05–1.60 (44H, m, 2-H, 3-H, 4-H, 6-H, 7-H, 8-H, 9-H, 10-H, 11-H, 12-H, 13-H, 14-H, 15-H, 16-H, 17-H, 18-H, 19-H, 20-H, 21-H, 22-H, 23-H, 24-H, 5-OH), 3.50–3.80 (1H, m, 5-H). *Anal.* Found: C, 81.30; H, 14.59%. Calcd. for $C_{26}H_{54}O$: C, 81.60; H, 14.22%.

(3S,5RS)-3-Methylpentacosan-5-ol [(S)-11a]. In the same manner as that just described, **10a** (1.24 g, 3.99 mmol) was converted into 0.74 g (48%) of (*S*)-**11a** as a colorless solid, mp 49.5–50.0°C. $[\alpha]_D^{22}$ +4.2° (*c* 1.12, $CHCl_3$). Its IR and ^{1}H-NMR spectra are identical with those of (*R*)-**11a**. *Anal.* Found: C, 81.66; H, 14.50%. Calcd. for $C_{26}H_{54}O$: C, 81.60; H, 14.22%.

(3R,5RS)-3-Methylheptacosan-5-ol [(R)-11b]. In the same manner as that just described, **10b** (546 mg, 1.62 mmol) was converted into 549 mg (83%) of (*R*)-**11b** as a colorless solid, mp 52–53°C. $[\alpha]_D^{28}$ −3.8° (*c* 2.12, $CHCl_3$). Its IR and ^{1}H-NMR spectra are similar

to those of (*R*)-**11a**. *Anal.* Found: C, 81.53; H, 14.54%. Calcd. for $C_{28}H_{58}O$: C, 81.87; H, 14.23%.

(3S,5RS)-3-Methylheptacosan-5-ol [(S)-11b]. In the same manner as that just described, **10b** (503 mg, 1.49 mmol) was converted into 530 mg (87%) of (*S*)-**11b** as a colorless solid, mp 51.5–52.5°C. $[\alpha]_D^{22}$ +1.5° (*c* 5.55, $CHCl_3$). Its IR and ^{1}H-NMR spectra are identical with those of (*R*)-**11b**. *Anal.* Found: C, 81.68; H, 14.46%. Calcd. for $C_{28}H_{58}O$: C, 81.87; H, 14.23%.

(3R,5RS)-3-Methylnonacosan-5-ol [(R)-11c]. In the same manner as that just described, **10c** (400 mg, 1.08 mmol) was converted into 340 mg (72%) of (*R*)-**11c** as a colorless solid, mp 59.5–62.0°C. $[\alpha]_D^{26}$ −4.1° (*c* 1.10, $CHCl_3$). Its IR and ^{1}H-NMR spectra are similar to those of (*R*)-**11a**. *Anal.* Found: C, 81.65; H, 14.64%. Calcd. for $C_{30}H_{62}O$: C, 82.11; H, 14.24%.

(3S,5RS)-3-Methylnonacosan-5-ol [(S)-11c]. In the same manner as that just described, **10c** (1.00 g, 2.70 mmol) was converted into 810 mg (68%) of (*S*)-**11c** as a colorless solid, mp 59.0–61.5°C. $[\alpha]_D^{26}$ +3.76° (*c* 1.03, $CHCl_3$). Its IR and ^{1}H-NMR spectra are identical with those of (*R*)-**11c**. *Anal.* Found: C, 81.67; H, 14.47%. Calcd. for $C_{30}H_{62}O$: C, 82.11; H, 14.24%.

Henicosanal (10a). To a suspension of PCC (6.06 g, 28.1 mmol) and powdered molecular sieves 4A (5.00 g) in dry CH_2Cl_2 (50 ml) was added a solution of **13a** (4.39 g, 14.0 mmol) in dry CH_2Cl_2 (20 ml) at room temperature, and the mixture was stirred for 3 h at room temperature. The mixture was filtered through SiO_2, and the resulting filter-cake was washed with diethyl ether. The combined filtrate and washings were concentrated *in vacuo* to give 4.01 g (92%) of crude **10a** as a colorless solid. IR ν_{max} (nujol) cm^{-1}: 2780 (w, CHO), 1720 (s, C=O). NMR δ_H (90 MHz, $CDCl_3$): 0.85–1.00 (3H, m, 21-H), 1.00–1.90 (36H, m, 3-H, 4-H, 5-H, 6-H, 7-H, 8-H, 9-H, 10-H, 11-H, 12-H, 13-H, 14-H, 15-H, 16-H, 17-H, 18-H, 19-H, 20-H), 2.41 (2H, t, J=7.2 Hz, 2-H), 9.76 (1H, t, J=2.0 Hz, CHO). This compound was employed in the next step without further purification.

Tricosanal 10b. In the same manner as that just described, **13c** (1.59 g, 4.68 mmol) was converted into 1.37 g (87%) of crude **10b** as a colorless solid, mp 52–53°C. Its IR and ^{1}H-NMR spectra are similar to those of **10a**. This compound was employed in the next step without further purification.

Pentacosanal 10c. In the same manner, **13e** (1.50 g, 4.07 mmol) was converted into 1.50 g (quant.) of crude **10c** as a colorless solid, mp 56–57°C. Its IR and ^{1}H-NMR spectra are similar to those of **10a**. This compound was employed in the next step without further purification.

(3R,5RS)-5-Methanesulfonyloxy-3-methylpentacosane [(R)-12a]. To a stirred and ice-cooled solution of (*R*)-**11a** (301 mg, 0.786 mmol) in dichloromethane (15 ml) and dry pyridine (2 ml) was added methanesulfonyl chloride (0.15 ml, 1.3 mmol). After stirring for 8 h at room temperature, the mixture was poured into water and extracted with distilled hexane. The organic phase was successively washed with 1 M HCl, water, a saturated sodium hydrogen carbonate solution and brine, dried with magnesium sulfate, and concentrated *in vacuo* to give 358 mg (96%) of crude (*R*)-**12a**. IR ν_{max} (film) cm^{-1}: 1340 (s, SO_2), 1170 (s, SO_2), 900 (s), 780 (w, C–S). NMR δ_H (90 MHz, $CDCl_3$): 0.80–1.00 (9H, m, 1-H, 3-Me, 25-H), 1.00–1.80 (43H, m, 2-H, 3-H, 4-H, 6-H, 7-H, 8-H, 9-H, 10-H, 11-H, 12-H, 13-H, 14-H, 15-H, 16-H, 17-H, 18-H, 19-H, 20-H, 21-H, 22-H, 23-H, 24-H), 2.99 (3H, s, CH_3–SO_2–), 4.62–4.90 (1H, m, 5-H). This compound was employed in the next step without further purification.

(3S,5RS)-5-Methanesulfonyloxy-3-methylpentacosane [(S)-12a]. In the same manner, (*S*)-**11a** (650 mg, 1.70 mmol) was converted into 810 mg (quant.) of crude (*S*)-**12a**. Its IR and ^{1}H-NMR spectra are identical with those of (*R*)-**12a**. This compound was employed in the next step without further purification.

(3R,5RS)-5-Methanesulfonyloxy-3-methylheptacosane [(R)-12b]. In the same manner, (*R*)-**11b** (273 mg, 0.665 mmol) was converted into 327 mg (98%) of crude (*R*)-**12b**. Its IR and ^{1}H-NMR spectra are similar to those of (*R*)-**12a**. This compound was employed in the next step without further purification.

(3S,5RS)-5-Methanesulfonyloxy-3-methylpentacosane [(S)-12b]. In the same manner, (*S*)-**11b** (500 mg, 1.22 mmol) was converted into 604 mg (99%) of crude (*S*)-**12b**. Its IR and ^{1}H-NMR spectra are identical with those of (*R*)-**12b**. This compound was employed in the next step without further purification.

(3R,5RS)-5-Methanesulfonyloxy-3-methylnonacosane [(R)-12c]. In the same manner, (*R*)-**11c** (250 mg, 0.567 mmol) was converted into 302 mg (quant.) of crude (*R*)-**12c**. Its IR and ^{1}H-NMR spectra are similar to those of (*R*)-**12a**. This compound was employed in the next step without further purification.

(3S,5RS)-5-Methanesulfonyloxy-3-methylnonacosane [(S)-12c]. In the same manner, (*S*)-**11c** (601 mg, 1.37 mmol) was converted into 696 mg (98%) of crude (*S*)-**12c**. Its IR and ^{1}H-NMR spectra are identical with those of (*R*)-**12c**. This compound was em-

ployed in the next step without further purification.

(R)-13-Methylpentacosane [(R)-1]. To a solution of crude (*R*)-**12a** (358 mg) in dry THF (20 ml) was added Super-hydride® (a 1.0 M solution in THF, 20 ml, 20 mmol) at 0°C under argon. After stirring for 12 h at room temperature, the mixture was poured into water and extracted with distilled hexane. The organic phase was successively washed with a saturated aqueous ammonium chloride solution, water, a satd. aqueous sodium hydrogen carbonate solution and brine, dried with magnesium sulfate, and concentrated *in vacuo* to give a mixture of (*R*)-**1** and inseparable olefinic by-product(s). To a solution of this mixture in distilled hexane (10 ml) was added *m*-chloroperbenzoic acid (MCPBA, 70% purity, 192 mg, 0.78 mmol) at 0°C. The resulting mixture was stirred for 12 h at room temperature. Aqueous sodium thiosulfate was added to the reaction mixture to destroy the unreacted MCPBA, and it was then stirred for 1 h and extracted with distilled hexane. The organic phase was successively washed with a saturated aqueous sodium hydrogen carbonate solution and brine, dried with magnesium sulfate, and concentrated *in vacuo*. The residue was choromatographed on silica gel (2 g, distilled hexane) to give 259 mg [2 steps, 90% based on (*R*)-**11a**] of (*R*)-**1** as a colorless solid. The resulting solid was recrystallized from distilled ethanol to afford 242 mg [2 steps, 84% based on (*R*)-**11a**] of pure (*R*)-**1** as a colorless crystalline solid, mp 36°C. $[\alpha]_D^{24}$ −4.1° (*c* 0.98, $CHCl_3$). IR ν_{max} (KBr) cm^{-1}: 2920 (s, C–H), 2850 (s, C–H), 1460 (m), 1380 (m), 720 (m, CH_2). NMR δ_H (400 MHz, $CDCl_3$): 0.84 (3H, d, J=6.1 Hz, 3-Me), 0.86 (3H, t, J=7.6 Hz, 25-H), 0.88 (3H, t, J=6.6 Hz), 1.06–1.33 (45H, m, 2-H, 3-H, 4-H, 5-H, 6-H, 7-H, 8-H, 9-H, 10-H, 11-H, 12-H, 13-H, 14-H, 15-H, 16-H, 17-H, 18-H, 19-H, 20-H, 21-H, 22-H, 23-H, 24-H). MS (EI) *m/z* (relative intensity): 57 (100), 309 (3.0), 337 (28.0), 366 (M^+, 0.4). *Anal.* Found: C, 85.20; H, 14.93%. Calcd. for $C_{26}H_{54}$: C, 85.25; H, 14.75%. GC [TC-WAX column (0.53 mm × 15 m), 120 to 200°C, +3.0°C/min; He carrier gas at 1.0 kg/cm²] t_R=15.1 min (**1**, >99%).

(S)-3-Methylpentacosane [(S)-1]. In the same manner, crude (*S*)-**12a** (810 mg) was converted into 438 mg [2 steps, 70% based on (*S*)-**11a**] of (*S*)-**1** as a colorless solid. The product was recrystallized from distilled ethanol to afford 370 mg [2 steps, 60% based on (*S*)-**11a**] of pure (*S*)-**1** as a colorless crystalline solid, mp 36°C. $[\alpha]_D^{27}$ +4.2° (*c* 0.98, $CHCl_3$). Its IR and ^{1}H-NMR spectra are identical with those of (*R*)-**1**. MS (EI) *m/z* (relative intensity): 57 (100), 309 (1.8), 337 (20.7), 366 (M^+, 0.2). *Anal.* Found: C, 85.01; H, 15.05%. Calcd. for $C_{26}H_{54}$: C, 85.25; H, 14.75%. GC [TC-WAX column (0.53 mm × 15 m), 120 to 200°C, +3.0°C/min; He carrier gas at 1.0 kg/cm²] t_R=14.3 min (**1**, >97%).

(R)-3-Methylheptacosane [(R)-2]. In the same manner, crude (*R*)-**12b** (327 mg) was converted into 270 mg [2 steps, quant. based on (*R*)-**11b**] of (*R*)-**2** as a colorless solid. The product was recrystallized from distilled ethanol to afford 212 mg [2 steps, 81% based on (*R*)-**11b**] of pure (*R*)-**2** as a colorless crystalline solid, mp 43°C. $[\alpha]_D^{26}$ −3.6° (*c* 1.06, $CHCl_3$). Its IR and ^{1}H-NMR spectra are similar to those of (*R*)-**1**. MS (EI) *m/z* (relative intensity): 57 (100), 337 (2.5), 365 (26.6), 395 (M^+, 0.4). *Anal.* Found: C, 85.45; H, 14.81%. Calcd. for $C_{28}H_{58}$: C, 85.19; H, 14.81%. GC [TC-WAX column (0.53 mm × 15 m), 120 to 200°C, +3.0°C/min; He carrier gas at 1.0 kg/cm²] t_R=19.2 min (**2**, >97%).

(S)-3-Methylheptacosane [(S)-2]. In the same manner, crude (*S*)-**12b** (604 mg) was converted into 402 mg [2 steps, 83% based on (*S*)-**11b**] of (*S*)-**2** as a colorless solid. The product was recrystallized from distilled ethanol to afford 362 mg [2 steps, 75% based on (*S*)-**11b**] of pure (*S*)-**2** as a colorless crystalline solid, mp 43°C. $[\alpha]_D^{24}$ +3.7° (*c* 0.95, $CHCl_3$). Its IR and ^{1}H-NMR spectra are identical with those of (*R*)-**2**. MS (EI) *m/z* (relative intensity): 57 (100), 337 (1.9), 365 (21.1), 394 (M^+, 0.2). *Anal.* Found: C, 85.19; H, 14.92%. Calcd. for $C_{28}H_{58}$: C, 85.19; H, 14.81%. GC [TC-WAX column (0.53 mm × 15 m), 120 to 200°C, +3.0°C/min; He carrier gas at 1.0 kg/cm²] t_R=19.1 min (**2**, >97%).

(R)-3-Methylnonacosane [(R)-3]. In the same manner as described above, crude (*R*)-**12c** (302 mg) was converted into 270 mg [2 steps, quant. based on (*R*)-**11c**] of (*R*)-**3** as a colorless solid. The product was recrystallized from distilled ethanol to afford 178 mg [2 steps, 74% based on (*R*)-**11c**] of pure (*R*)-**3** as a colorless crystalline solid, mp 49.5°C. $[\alpha]_D^{26}$ −3.6° (*c* 0.99, $CHCl_3$). Its IR and ^{1}H-NMR spectra are similar to those of (*R*)-**1**. MS (EI) *m/z* (relative intensity): 57 (100), 365 (1.1), 393 (11.9), 422 (M^+, 0.1). *Anal.* Found: C, 84.92; H, 14.97%. Calcd. for $C_{30}H_{62}$: C, 85.22; H, 14.78%. GC [TC-WAX column (0.53 mm × 15 m), 120 to 200°C, +3.0°C/min; He carrier gas at 1.0 kg/cm²] t_R=24.6 min (**3**, >97%).

(S)-3-Methylnonacosane [(S)-3]. In the same manner, crude (*S*)-**12c** (692 mg) was converted into 512 mg [2 steps, 90% based on (*S*)-**11c**] of (*S*)-**3** as a colorless solid. The product was recrystallized from distilled ethanol to afford 469 mg [2 steps, 83% based on (*S*)-**11c**] of pure (*S*)-**3** as a colorless crystalline solid, mp 50°C. $[\alpha]_D^{24}$ +3.5° (*c* 0.98, $CHCl_3$). Its IR and ^{1}H-NMR spectra are identical with those of (*R*)-**3**. MS (EI) *m/z* (relative intensity): 57 (100), 365 (3.9), 393 (39.2), 422 (M^+, 0.3). *Anal.* Found: C, 85.12; H, 14.76%. Calcd. for $C_{30}H_{62}$: C, 85.22; H,

14.78%. GC [TC-WAX column (0.53 mm × 15 m), 120 to 200°C, +3.0°C/min; He carrier gas at 1.0 kg/cm^2] t_R = 24.9 min (**3**, >97%).

(S)-2,6-Dimethyl-2-icosene [(S)-16]. To a stirred and ice-cooled solution of (*R*)-**15** (8.14 g, 26.2 mmol) in dry THF (100 ml) were successively added a solution of dodecylmagnesium bromide in THF (0.93 M, 150 ml, 140 mmol) and a solution of dilithium tetrachlorocuprate in THF (0.32 M, 4.0 ml, 1.3 mmol) at −78°C under argon. The mixture was allowed to warm to 4°C while stirring over 12 h, before being quenched with a saturated aqueous ammonium chloride solution and extracted with hexane. The organic phase was successively washed with water, a saturated aqueous ammonium chloride solution and brine, dried with magnesium sulfate, and concentrated *in vacuo*. The residue was chromatographed on silica gel (100 g, hexane) to give 24.8 g of crude (*S*)-**16** as a colorless oil. This was employed in the next step without further purification.

(R)-2,6-Dimethyl-2-icosene [(R)-16]. In the same manner, (*S*)-**15** (10.0 g, 32.2 mmol) was converted into 30.5 g of crude (*R*)-**16** as a colorless oil. This was employed in the next step without further purification.

(3RS,6S)-2,6-Dimethylicosane-2,3-diol [(S)-17]. To a stirred solution of (*S*)-**16** (*ca.* 24.8 g) in *t*-BuOH (100 ml), acetone (240 ml) and water (60 ml) were added *N*-methylmorpholine *N*-oxide (50% water, 25.0 g, 107 mmol) and osmium (VIII) oxide (1 g/100 ml of solution in *t*-BuOH, 12 ml, 0.78 mmol) at room temperature. The mixture was stirred for 72 h at room temperature. Sodium sulfite heptahydrate (14.8 g, 58.7 mmol) was added to the reaction mixture to destroy the unreacted *N*-methylmorpholine *N*-oxide. After stirring for 30 min, the mixture was extracted with ethyl acetate. The organic phase was washed with brine, dried with magnesium sulfate and concentrated *in vacuo*. The residue was chromatographed on silica gel (480 g; hexane/ethyl acetate, 10:1) to give 5.10 g [3 steps, 82% based on (*R*)-**14**] of (*S*)-**17** as a colorless waxy solid, mp 50–51°C. $[\alpha]_D^{20}$ +1.3° (±0.1) (*c* 1.00, $CHCl_3$). IR ν_{max} (nujol) cm^{-1}: 3360 (s, O-H), 1080 (m, C-O). NMR δ_H (90 MHz, $CDCl_3$): 0.80–1.10 (6H, m, 6-Me, 20-H), 1.16 (3H, s, C*H*$_3$-C-OH), 1.22 (3H, s, C*H*$_3$-C-OH), 1.23–2.10 (33H, m, 4-H, 5-H, 6-H, 7-H, 8-H, 9-H, 10-H, 11-H, 12-H, 13-H, 14-H, 15-H, 16-H, 17-H, 18-H, 19-H, 2-OH, 3-OH), 3.20–3.45 (1H, m, 3-H). *Anal.* Found: C, 77.15; H, 13.83%. Calcd. for $C_{22}H_{46}O_2$: C, 77.13; H, 13.53%.

(3RS,6R)-2,6-Dimethylicosane-2,3-diol [(R)-17]. In the same manner, crude (*R*)-**16** (*ca.* 10 g) was converted into 1.23 g [3 steps, 46% based on (*S*)-**14**] of (*R*)-**17** as a colorless waxy solid, mp 51–52°C. $[\alpha]_D^{20}$ −2.0° (±0.1) (*c* 1.00, $CHCl_3$). Its IR and ^{1}H-NMR spectra are identical with those of (*S*)-**17**. *Anal.* Found: C, 77.02; H, 13.90%. Calcd. for $C_{22}H_{46}O_2$: C, 77.13; H, 13.53%.

(S)-4-Methyloctadecanal [(S)-18]. A solution of (*S*)-**17** (1.01 g, 2.95 mmol) in dry diethyl ether (30 ml) was added dropwise to a solution of periodic acid dihydrate (750 mg, 3.10 mmol) in THF (30 ml) at 0°C under argon. The mixture was stirred at room temperature for 45 min, before it was diluted with water and extracted with diethyl ether. The organic phase was successively washed with water, a saturated aqueous sodium hydrogen carbonate solution and brine, dried with magnesium sulfate, and concentrated *in vacuo* to give 840 mg (98%) of crude (*S*)-**18** as a colorless oil. IR ν_{max} (film) cm^{-1}: 2730 (m, CHO), 1730 (s, C=O). NMR δ_H (90 MHz, $CDCl_3$): 0.80–1.00 (6H, m, 4-Me, 18-H), 1.01–1.80 (29H, m, 3-H, 4-H, 5-H, 6-H, 7-H, 8-H, 9-H, 10-H, 11-H, 12-H, 13-H, 14-H, 15-H, 16-H, 17-H), 2.43 (2H, t, *J* = 7.9 Hz, 2-H), 9.77 (1H, t, *J* = 2.0 Hz, CHO). This compound was employed in the next step without further purification.

(R)-4-Methyloctadecanal [(R)-18]. In the same manner, (*R*)-**17** (600 mg, 1.76 mmol) was converted into 520 mg (quant.) of crude (*R*)-**18**. Its IR and ^{1}H-NMR spectra are identical with those of (*S*)-**18**. This compound was employed in the next step without further purification.

(10RS,13S)-13-Methylheptacosan-10-ol [(S)-19]. To a stirred and ice-cooled solution of (*S*)-**18** (720 mg, 2.50 mmol) in dry THF (9 ml) was added a solution of nonylmagnesium bromide in THF (0.9 M, 15 ml, 13.5 mmol) at −78°C under argon. The mixture was allowed to warm to room temperature while stirring for 2 h. It was then quenched with a saturated aqueous ammonium chloride solution, and the mixture was extracted with hexane. The organic phase was successively washed with water and a saturated aqueous ammonium chloride solution, dried with magnesium sulfate, and concentrated *in vacuo*. The residue was chromatographed on silica gel (70 g; hexane/ethyl acetate, 10:1) to give 1.05 g of (*S*)-**19** (55%) as a colorless solid, mp 36–37°C. $[\alpha]_D^{22}$ +1.2° (±0.3) (*c* 0.24, $CHCl_3$). IR ν_{max} (nujol) cm^{-1}: 3360 (s, O-H), 1135 (m, C-O). NMR δ_H (500 MHz, $CDCl_3$): 0.83–0.93 (9H, m, 1-H, 13-Me, 27-H), 1.05–1.60 (48H, m, 2-H, 3-H, 4-H, 5-H, 6-H, 7-H, 8-H, 9-H, 11-H, 12-H, 13-H, 14-H, 15-H, 16-H, 17-H, 18-H, 19-H, 20-H, 21-H, 22-H, 23-H, 24-H, 25-H, 26-H, 10-OH), 3.50–3.65 (1H, m, 10-H). *Anal.* Found: C, 81.99; H, 14.55%. Calcd. for $C_{28}H_{58}O$: C, 81.87; H, 14.23%.

(10RS,13R)-13-Methylheptacosan-10-ol [(R)-19]. In the same manner, (*R*)-**18** (150 mg, 0.500 mmol) was converted into 162 mg (77%) of (*R*)-**19** as a colorless solid, mp 37–38°C. $[\alpha]_D^{22}$ −0.1° (±0.01) (*c* 2.48, $CHCl_3$). Its IR and ^{1}H-NMR spectra are identical with those of (*S*)-**19**. *Anal.* Found: C, 81.52; H, 14.02%. Calcd. for $C_{28}H_{58}O$: C, 81.87; H, 14.23%.

(10RS,13S)-10-Methanesulfonyloxy-13-methylheptacosane [(S)-20]. To a stirred and ice-cooled solution of (*S*)-**19** (206 mg, 0.487 mmol) in dichloromethane (10 ml) and dry pyridine (3 ml) was added methanesulfonyl chloride (0.10 ml, 1.3 mmol). After stirring for 8 h at room temperature, the mixture was poured into water and extracted with distilled hexane. The organic phase was successively washed with 1 M HCl, water, a saturated sodium hydrogen carbonate solution and brine, dried with magnesium sulfate, and concentrated *in vacuo* to give 340 mg (quant.) of crude (*S*)-**20**. IR ν_{max} (film) cm^{-1}: 1350 (s, SO_2), 1170 (s, SO_2), 900 (s), 770 (w, C–S). NMR δ_H (90 MHz, $CDCl_3$): 0.77–1.04 (9H, m, 1-H, 13-Me, 27-H), 1.06–1.84 (47H, m, 2-H, 3-H, 4-H, 5-H, 6-H, 7-H, 8-H, 9-H, 11-H, 12-H, 13-H, 14-H, 15-H, 16-H, 17-H, 18-H, 19-H, 20-H, 21-H, 22-H, 23-H, 24-H, 25-H, 26-H), 2.99 (3H, s, CH_3–SO_2–), 4.62–4.82 (1H, m, 10-H). This compound was employed in the next step without further purification.

(10RS,13R)-10-Methanesulfonyloxy-13-methylheptacosane [(R)-20]. In the same manner, (*R*)-**19** (61 mg, 0.142 mmol) was converted into 60 mg (84%) of crude (*R*)-**20**. Its IR and ^{1}H-NMR spectra are identical with those of (*S*)-**20**. This compound was employed in the next step without further purification.

(R)-13-Methylheptacosane [(R)-4]. To a solution of crude (*S*)-**20** (0.34 g) in dry THF (20 ml) was added Super-hydride® (a 1.0 M solution in THF, 10 ml, 10 mmol) at 0°C under argon. After stirring for 12 h at room temperature, the mixture was poured into water and extracted with distilled hexane. The organic phase was successively washed with a saturated aqueous ammonium chloride solution, water, a saturated aqueous sodium hydrogen carbonate solution and brine, dried with magnesium sulfate, and concentrated *in vacuo* to give a mixture of (*R*)-**4** and inseparable olefinic by-product(s). To a solution of this mixture in distilled hexane (10 ml) was added *m*-chloroperbenzoic acid (MCPBA, 70% purity, 14.2 mg, 57.6 mmol) at 0°C. The resulting mixture was stirred for 12 h at room temperature, before aqueous sodium thiosulfate was added to destroy the unreacted MCPBA. The mixture was then stirred for 1 h and extracted with distilled hexane. The organic phase was successively washed with a saturated aqueous sodium hydrogen carbonate solution and brine, dried with magnesium sulfate, and concentrated *in vacuo*. The residue was choromatographed on silica gel (2 g, distilled hexane) to give 160 mg [2 steps, 83% based on (*S*)-**19**] of (*R*)-**4** as a colorless solid. The resulting solid was recrystallized from distilled ethanol to afford 97 mg [2 steps, 51% based on (*S*)-**19**] of pure (*R*)-**4** as a colorless crystalline solid, mp 31–32°C. $[\alpha]_D^{22}$ −0.10° (±0.012) (*c* 10.6, $CHCl_3$). IR ν_{max} (KBr) cm^{-1}: 2920 (s, C–H), 2950 (s, C–H), 1470 (m), 1380 (m), 730 (m, CH_2). NMR δ_H (400 MHz, $CDCl_3$): 0.83 (3H, d, J=6.5 Hz, 13-Me), 0.88 (6H, t, J=7.1 Hz, 1-H, 27-H), 1.00–1.45 (49H, m, 2-H, 3-H, 4-H, 5-H, 6-H, 7-H, 8-H, 9-H, 10-H, 11-H, 12-H, 13-H, 14-H, 15-H, 16-H, 17-H, 18-H, 19-H, 20-H, 21-H, 22-H, 23-H, 24-H, 25-H, 26-H). MS (EI) *m/z* (relative intensity): 196 (100), 225 (73.8), 395 (M^+, 29.1). *Anal.* Found: C, 85.16; H, 14.87%. Calcd. for $C_{28}H_{58}$: C, 85.19; H, 14.81%. GC [TC-WAX column (0.53 mm × 15 m), 120 to 200°C, +3.0°C/min; He carrier gas at 1.0 kg/cm^2] t_R=19.1 min (**4**, >99%).

(S)-13-Methylheptacosane [(S)-4]. In the same manner, crude (*R*)-**20** (5 mg, 0.11 mmol) was converted into 50 mg [2 steps, 89% based on (*R*)-**19**] of (*S*)-**4** as a colorless solid. The product was recrystallized from distilled ethanol to afford 39 mg [2 steps, 70% based on (*R*)-**19**] of pure (*S*)-**4** as a colorless crystalline solid, mp 31–32°C. $[\alpha]_D^{22}$ +0.45° (±0.17) (*c* 1.80, $CHCl_3$). Its IR and ^{1}H-NMR spectra are identical with those of (*R*)-**4**. MS (EI) *m/z* (relative intensity): 196 (100), 225 (83.8), 395 (M^+, 41.5). *Anal.* Found: C, 85.43; H, 15.10%. Calcd. for $C_{28}H_{58}$: C, 85.19; H, 14.81%. GC [TC-WAX column (0.53 mm × 15 m), 120 to 200°C, +3.0°C/min; He carrier gas at 1.0 kg/cm^2] t_R=19.0 min (**4**, >98%).

(R)-2,6-Dimethyl-2-decene [(R)-21]. To a stirred and ice-cooled solution of crude (*S*)-**15** (12 g, 39 mmol) in dry THF (100 ml) were added a solution of ethylmagnesium bromide in THF (1.0 M, 260 ml, 260 mmol) and then a solution of dilithium tetrachlorocuprate in THF (0.32 M, 5.0 ml, 1.0 mmol) at −78°C under argon. The mixture was allowed to warm to 4°C while stirring for 12 h. It was then quenched with a saturated aqueous ammonium chloride solution, and the mixture was extracted with hexane. The organic phase was successively washed with water and a saturated aqueous ammonium chloride solution, dried with magnesium sulfate, and concentrated *in vacuo*. The residue was chromatographed on silica gel (100 g; hexane) and distilled to give 4.59 g [2 steps, 86% based on (*S*)-**14**] of (*R*)-**21** as a colorless oil, bp 77–79°C at 10 Torr. n_D^{23} 1.4355. $[\alpha]_D^{22}$ −1.0° (±0.04) (*c* 1.03, $CHCl_3$). $[\alpha]_D^{28}$ −0.55° (±0.014) (*c* 1.46, hexane). [lit.[12] n_D^{23} 1.4362, $[\alpha]_D^{22}$ +0.068° (±0.044) (*c* 1.61, hexane).] IR ν_{max} (film) cm^{-1}: 2900 (s, C–H), 1460 (m). NMR δ_H (90 MHz,

$CDCl_3$): 0.80–1.00 (6H, m, 6-Me, 10-H), 1.01–1.42 (9H, m, 5-H, 6-H, 7-H, 8-H, 9-H), 1.60 (3H, s, CH_3-C=C), 1.69 (3H, s, CH_3-C=C), 1.75–2.20 (2H, m, 4-H), 5.10 (1H, t, J=6.5 Hz, 3-H).

(S)-2,6-Dimethyl-2-decene [(S)-21]. In the same manner, crude (*R*)-**15** (14 g, 45 mmol) was converted into 3.85 g [2 steps, 71% based on (*R*)-**14**] of (*S*)-**21** as a colorless oil, bp 78–80°C at 10 Torr. n_D^{24} 1.4351. $[\alpha]_D^{22}$ +0.98° (±0.04) (*c* 1.10, $CHCl_3$). $[\alpha]_D^{28}$ +0.61° (±0.025) (*c* 2.36, hexane). [lit.[12] n_D^{24} 1.4369, $[\alpha]_D^{26}$ +0.022° (±0.029) (*c* 2.83, hexane).] Its IR and ^{1}H-NMR spectra are identical with those of (*R*)-**21**.

(R)-4-Methyloctan-1-ol [(R)-22]. Ozone was bubbled into a stirred solution of (*R*)-**21** (2.92 g, 17.4 mmol) in methanol (10 ml) and dichloromethane (5 ml) for 6 h at −78°C. After flashing off the excess O_3 with O_2 gas, to the stirred mixture was slowly added $NaBH_4$ (1.32 g, 34.5 mmol) at −78°C. The mixture was allowed to warm to 0°C while stirring for 3 h, before being quenched with 1 M hydrochloric acid and extracted with diethyl ether. The organic phase was successively washed with water, a saturated aqueous sodium hydrogen carbonate solution and brine, dried with magnesium sulfate, and concentrated *in vacuo*. The residue was purified by chromatography on silica gel (50 g; hexane/ethyl acetate, 10:1) and distilled to give 1.64 g (65%) of (*R*)-**22** as a colorless oil, bp 98–100°C at 16 Torr. n_D^{23} 1.4339. $[\alpha]_D^{22}$ +0.47° (±0.040) (*c* 1.10, $CHCl_3$). $[\alpha]_D^{28}$ +0.55° (±0.03) (*c* 1.60, MeOH). [lit.[12] n_D^{27} 1.4320, $[\alpha]_D^{23}$ +0.22° (±0.16) (*c* 1.44, MeOH).] IR ν_{max} (film) cm^{-1}: 3330 (s, O-H), 1060 (s, C-O). NMR δ_H (90 MHz, $CDCl_3$): 0.80–1.00 (6H, m, 4-Me, 8-H), 1.01–1.80 (12H, m, 2-H, 3-H, 4-H, 5-H, 6-H, 7-H, 1-OH), 3.63 (2H, t, J=6.5 Hz, 1-H).

(S)-4-Methyloctan-1-ol [(S)-22]. In the same manner, (*S*)-**21** (3.07 g, 18.3 mmol) was converted into 2.17 g (83%) of (*S*)-**22** as a colorless oil, bp 92–94°C at 11 Torr. n_D^{24} 1.4332. $[\alpha]_D^{23}$ −0.34° (±0.04) (*c* 1.00, $CHCl_3$). $[\alpha]_D^{28}$ −0.48° (±0.023) (*c* 1.77, MeOH). [lit.[12] n_D^{27} 1.4320, $[\alpha]_D^{23}$ −0.91° (±0.05) (*c* 2.48, MeOH).] Its IR and ^{1}H-NMR spectra are identical with those of (*R*)-**22**.

(R)-4-Methyloctyl Tosylate [(R)-23]. To a stirred and ice-cooled solution of (*R*)-**22** (1.52 g, 10.5 mmol) in chloroform (18 ml) and dry pyridine (4 ml) was added *p*-toluenesulfonyl chloride (2.51 g, 13.2 mmol). The solution was stirred for 12 h at 4°C, before being poured into water and extracted with diethyl ether. The ethereal extract was successively washed with water, a saturated cupric sulfate solution, water, a saturated sodium hydrogen carbonate solution and brine, dried with magnesium sulfate, and concentrated *in vacuo* to give 4.26 g (quant.) of crude (*R*)-**23**. IR ν_{max} (film) cm^{-1}: 1600 (m, aromatic), 1360 (s, SO_2), 1190 (s, SO_2), 1180 (s, SO_2), 965 (m, aromatic), 920 (m), 790 (m, C-S). NMR δ_H (90 MHz, $CDCl_3$): 0.70–1.00 (6H, m, 4-Me, 8-H), 1.01–1.80 (11H, m, 2-H, 3-H, 4-H, 5-H, 6-H, 7-H), 2.45 (3H, s, Ar-CH_3), 4.01 (2H, t, J=6.5 Hz, 1-H), 7.32 (2H, d, J=8.4 Hz, aromatic), 7.78 (2H, d, J=8.4 Hz, aromatic). This compound was employed in the next step without further purification.

(S)-4-Methyloctyl Tosylate [(S)-23]. In the same manner, (*S*)-**22** (1.50 g, 10.4 mmol) was converted into 4.22 g (quant.) of (*S*)-**23** as a colorless oil. Its IR and ^{1}H-NMR spectra are identical with those of (*R*)-**23**. This compound was employed in the next step without further purification.

(R)-4-Methyloctyl Iodide [(R)-24]. To a solution of crude (*R*)-**23** (*ca.* 4.26 g) in dry acetone (40 ml) were added sodium iodide (2.40 g, 16.0 mmol) and sodium hydrogen carbonate (2.50 g, 29.8 mmol). 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 successively washed with water and brine, dried with magnesium sulfate, and concentrated *in vacuo*. The residue was chromatographed on silica gel (40 g, hexane) to give 2.65 g [2 steps, 99% based on (*R*)-**22**] of (*R*)-**24** as a colorless oil. n_D^{25} 1.4849. $[\alpha]_D^{23}$ −4.2° (*c* 0.82, $CHCl_3$). $[\alpha]_D^{26}$ −4.7° (*c* 2.53, hexane). [lit.[12] n_D^{26} 1.4861, $[\alpha]_D^{26}$ −4.5° (*c* 2.14, hexane).] IR ν_{max} (film) cm^{-1}: 1170 (m). NMR δ_H (90 MHz, $CDCl_3$): 0.80–1.00 (6H, m, 4-Me, 8-H) 1.01–2.00 (11H, m, 2-H, 3-H, 4-H, 5-H, 6-H, 7-H), 3.18 (2H, t, J=7.2 Hz, 1-H). This compound was employed in the next step without further purification.

(S)-4-Methyloctyl Iodide [(S)-24]. In the same manner, (*S*)-**23** (3.51 g, 10.4 mmol) was converted into 2.42 g [2 steps, 92% based on (*S*)-**22**] of (*S*)-**24** as a colorless oil. n_D^{25} 1.4865. $[\alpha]_D^{20}$ +4.6° (*c* 1.10, $CHCl_3$). $[\alpha]_D^{26}$ +4.5° (*c* 2.66, hexane). [lit.[12] n_D^{26} 1.4870, $[\alpha]_D^{26}$ +5.33° (*c* 2.48, hexane).] Its IR and ^{1}H-NMR spectra are identical with those of (*R*)-**24**. This compound was employed in the next step without further purification.

(R)-4-Methyl-1-phenylsulfonyloctane [(R)-25]. To a stirred solution of (*R*)-**24** (2.65 g, 10.4 mmol) in *N*,*N*-dimethylformamide (50 ml) was added sodium benzenesulfinate dihydrate (2.37 g, 14.4 mmol). The mixture was stirred at room temperature for 12 h, before being poured into brine and extracted with diethyl ether. The ethereal extract was successively washed with water and brine, dried with magnesium sulfate, and concentrated *in vacuo*. The residue was purified by chromatography on silica gel (60 g;

hexane/ethyl acetate, 20:1) to give 2.48 g (89%) of (*R*)-**25** as a colorless oil. n_D^{25} 1.5048. $[\alpha]_D^{23}$ −2.4° (± 0.05) (*c* 1.10, $CHCl_3$). IR ν_{max} (film) cm^{-1}: 1590 (m, aromatic), 1310 (s, SO_2), 1185 (m), 1150 (s, SO_2), 780 (m, C-S). NMR δ_H (90 MHz, $CDCl_3$): 0.70–1.00 (6H, m, 4-Me, 8-H), 1.01–2.00 (11H, m, 2-H, 3-H, 4-H, 5-H, 6-H, 7-H), 2.97–3.18 (2H, m, 1-H), 7.40–7.98 (5H, m, aromatic). *Anal.* Found: C, 67.38; H, 9.02%. Calcd. for $C_{15}H_{24}SO_2$: C, 67.12; H, 9.01%.

(S)-4-Methyl-1-phenylsulfonyloctane [(S)-25]. In the same manner, (*S*)-**24** (2.35 g, 9.30 mmol) was converted into 1.94 g (78%) of (*S*)-**25** as a colorless oil. n_D^{24} 1.5062. $[\alpha]_D^{23}$ +2.4° (±0.03) (*c* 1.10, $CHCl_3$). Its IR and ^{1}H-NMR spectra are identical with those of (*R*)-**25**. *Anal.* Found: C, 67.48; H, 9.32%. Calcd. for $C_{15}H_{24}SO_2$: C, 67.12; H, 9.01%.

Nonadecyl Tosylate (29). To a stirred and ice-cooled solution of nonadecan-1-ol (3.50 g, 12.3 mmol) in chloroform (20 ml) and dry pyridine (22 ml) was added *p*-toluenesulfonyl chloride (2.51 g, 13.2 mmol). The mixture was stirred for 12 h at 4°C, before being poured into water and extracted with diethyl ether. The ethereal extract was successively washed with water, a saturated aqueous cupric sulfate solution, water, a saturated aqueous sodium hydrogen carbonate solution and brine, dried with magnesium sulfate, and concentrated *in vacuo* to give 5.36 g (99%) of crude **29**. IR ν_{max} (film) cm^{-1}: 1600 (m, aromatic), 1360 (s, SO_2), 1180 (s, SO_2), 965 (m, aromatic). NMR δ_H (90 MHz, $CDCl_3$): 0.79–1.02 (3H, m, 19-H), 1.07–1.80 (34H, m, 2-H, 3-H, 4-H, 5-H, 6-H, 7-H, 8-H, 9-H, 10-H, 11-H, 12-H, 13-H, 14-H, 15-H, 16-H, 17-H, 18-H), 2.45 (3H, s, Ar-CH_3), 3.99–4.30 (2H, m, 1-H), 7.34 (2H, d, J=8.2 Hz, aromatic), 7.80 (2H, d, J=8.4 Hz, aromatic). This compound was employed in the next step without further purification.

Nonadecyl Iodide (26). To a solution of crude **29** (*ca.* 5.4 g) in dry acetone (40 ml) were added sodium iodide (2.74 g, 18.3 mmol) and sodium hydrogen carbonate (3.03 g, 36.1 mmol). The mixture was stirred and heated under reflux for 2 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 successively washed with water and brine, dried with magnesium sulfate, and concentrated *in vacuo*. The residue was chromatographed on silica gel (40 g, hexane) to give 4.42 g (88%) of **26** as colorless needles, mp 39–40°C. IR ν_{max} (film) cm^{-1}: 1165 (m). NMR δ_H (90 MHz, $CDCl_3$): 0.75–1.00 (3H, m, 19-H), 1.10–2.00 (34H, m, 2-H, 3-H, 4-H, 5-H, 6-H, 7-H, 8-H, 9-H, 10-H, 11-H, 12-H, 13-H, 14-H, 15-H, 16-H, 17-H, 18-H), 3.19 (2H, t, J=7.0 Hz, 1-H). This compound was employed in the next step without further purification.

(5R,8RS)-5-Methyl-8-phenylsulfonylheptacosane [(R)-27]. To a stirred and cooled solution of (*R*)-**25** (1.60 g, 5.96 mmol) in dry THF (20 ml) and dry hexamethylphosphoramide (HMPA, 5 ml), *n*-butyllithium in hexane (1.6 M, 4.3 ml, 6.6 mmol) was added at −78°C under argon. The solution was stirred at −30°C for 15 min and then cooled to −78°C. A solution of **26** (*ca.* 2.5 g) in dry THF (15 ml) was next added dropwise to the mixture at −78°C while stirring. The mixture was stirred at ambient temperature for 12 h, before being poured into a saturated aqueous ammonium chloride solution at 0°C and extracted with diethyl ether. The ethereal extract was successively washed with water and brine, dried with magnesium sulfate, and concentrated *in vacuo*. The residue was chromatographed on silica gel (66 g; hexane/ethyl acetate, 40:1) to give 1.58 g (50%) of (*R*)-**27** as a colorless solid, mp 43–44°C. $[\alpha]_D^{23}$ −1.4° (±0.1) (*c* 1.20, $CHCl_3$). IR ν_{max} (nujol) cm^{-1}: 1580 (w, aromatic), 1300 (s, SO_2), 1140 (s, SO_2). NMR δ_H (90 MHz, $CDCl_3$): 0.75–1.00 (9H, m, 1-H, 5-Me, 27-H), 1.01–1.80 (47H, m, 2-H, 3-H, 4-H, 5-H, 6-H, 7-H, 9-H, 10-H, 11-H, 12-H, 13-H, 14-H, 15-H, 16-H, 17-H, 18-H, 19-H, 20-H, 21-H, 22-H, 23-H, 24-H, 25-H, 26-H), 2.86 (1H, m, 8-H), 7.40–8.00 (5H, m, aromatic). *Anal.* Found: C, 75.93; H, 11.99%. Calcd. for $C_{34}H_{62}SO_2$: C, 76.34; H, 11.68%.

(5S,8RS)-5-Methyl-8-phenylsulfonylheptacosane [(S)-27]. In the same manner, (*S*)-**25** (304 mg, 1.13 mmol) was converted into 300 mg (50%) of (*S*)-**27**. n_D^{24} 1.5062. $[\alpha]_D^{22}$ +1.4° (±0.05) (*c* 1.10, $CHCl_3$). Its IR and ^{1}H-NMR spectra are identical with those of (*R*)-**27**. *Anal.* Found: C, 75.80; H, 12.00%. Calcd. for $C_{34}H_{62}SO_2$: C, 76.34; H,11.68%.

(R)-5-Methylheptacosane [(R)-5]. A solution of (*R*)-**27** (1.56 g, 2.84 mmol) in dry ethanol (50 ml) was added dropwise to sodium amalgam (5%, 25.0 g, 54.4 mmol) at 0°C under argon. The mixture was stirred vigorously at room temperature for 48 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 successively washed with water and brine, dried with magnesium sulfate, and concentrated *in vacuo*. The residue was chromatographed on silica gel (9 g, distilled hexane) to give a mixture of (*R*)-**5** and inseparable olefinic by-product(s). To a solution of this mixture in distilled hexane (15 ml) was added MCPBA (70% purity, 160 mg, 0.650 mmol) at 0°C. The resulting mixture was stirred for 12 h at room

temperature, before aqueous sodium thiosulfate was added to destroy the unreacted MCPBA. It was then stirred for 1 h and extracted with distilled hexane. The organic phase was successively washed with a saturated aqueous sodium hydrogen carbonate solution and brine, dried with magnesium sulfate, and concentrated *in vacuo*. The residue was choromatographed on silica gel (5 g, distilled hexane) to give 1.00 g (91%) of (*R*)-**5** as a colorless solid. This solid was recrystallized from distilled ethanol to afford 828 mg (75%) of pure (*R*)-**5** as a colorless crystalline solid, mp 37–38°C. $[\alpha]_D^{22}$ −0.72° (±0.040) (*c* 1.10, $CHCl_3$). IR ν_{max} (KBr) cm^{-1}: 2920 (s, C-H), 2950 (s, C-H), 1475 (m), 1380 (m), 730 (m, CH_2). NMR δ_H (500 MHz, $CDCl_3$): 0.84 (3H, d, J=6.8 Hz, 5-Me), 0.86–0.95 (6H, m, 1-H, 27-H), 1.05–1.58 (49H, m, 2-H, 3-H, 4-H, 5-H, 6-H, 7-H, 8-H, 9-H, 10-H, 11-H, 12-H, 13-H, 14-H, 15-H, 16-H, 17-H, 18-H, 19-H, 20-H, 21-H, 22-H, 23-H, 24-H, 25-H, 26-H). MS (EI) *m/z* (relative intensity): 57.1 (22.5), 84.1 (100), 309 (23.0), 338 (87.3), 395 (M^+, 34.7). *Anal.* Found: C, 85.03; H, 15.08%. Calcd. for $C_{28}H_{58}$: C, 85.19; H, 14.81%. GC [TC-WAX column (0.53 mm × 15 m), 120 to 200°C, +3.0°C/min; He carrier gas at 1.0 kg/cm²] t_R = 21.1 min (**5**, >99%).

(S)-5-Methylheptacosane [(S)-5]. In the same manner, (*S*)-**27** (930 mg, 1.69 mmol) was converted into 610 mg (91%) of (*S*)-**5** as a colorless solid. The product was recrystallized from distilled ethanol to afford 480 mg (72%) of pure (*S*)-**5** as a colorless crystalline solid, mp 36–37°C. $[\alpha]_D^{22}$ +0.70° (±0.06) (*c* 1.00, $CHCl_3$). Its IR and ^{1}H-NMR spectra are identical with those of (*R*)-**5**. MS (EI) *m/z* (relative intensity): 57.1 (76.5), 84.1 (100), 309 (19.0), 338 (85.5), 395 (M^+, 36.9). *Anal.* Found: C, 84.96; H, 15.09%. Calcd. for $C_{28}H_{58}$: C, 85.19; H, 14.81%. GC [TC-WAX column (0.53 mm × 15 m), 120 to 200°C, +3.0°C/min; He carrier gas at 1.0 kg/cm²] t_R = 20.2 min (**5**, >99%).

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