Pheromone Synthesis, CXCII[+]

Synthesis of All the Stereoisomers of 10,14-Dimethyloctadec-1-ene, 5,9-Dimethyloctadecane and 5,9-Dimethylheptadecane, the Sex Pheromone Components of the Apple Leafminer, *Lyonetia prunifoliella*

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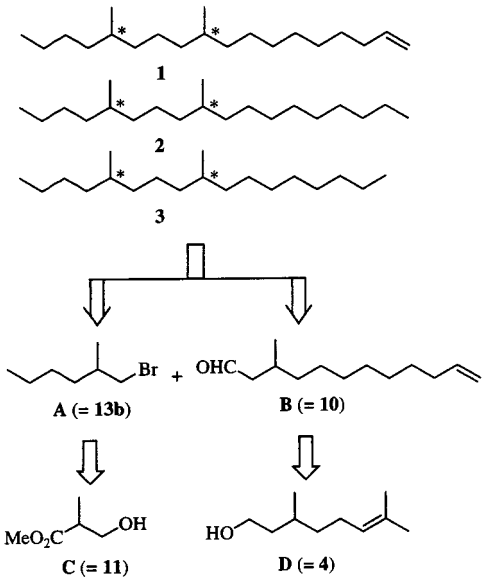
All of the stereoisomers of 10,14-dimethyloctadec-1-ene (**1**), 5,9-dimethyloctadecane (2) and 5,9-dimethylheptadecane (**3**), the sex pheromone components of the apple leafminer (*Lyonetia prunifoliella*), were synthesized by starting from the enantiomers of citronellol (**4**) and methyl 3-hydroxy-2-methylpropanoate (**11**).

The apple leafminer (*Lyonetia prunifoliella*) is a pest in apple orchards in eastern North America. In 1997 Gries et al. identified three methyl-branched hydrocarbons, 10,14-dimethyloctadec-1-ene (**1**, Scheme 1), 5,9-dimethyloctadecane (**2**) and 5,9-dimethylheptadecane (**3**) as its synergistic female-produced pheromone components.[1] Structural assignment of **1**, **2** and **3** was carried out by comparing natural products with the corresponding synthetic hydrocarbons obtained as stereoisomeric mixtures. In field trapping experiments, **1**, **2** and **3** singly were unattractive to males, but as ternary mixture attracted numerous male moths. The importance of **1** in the pheromone communication of *L. prunifoliella* was revealed by the fact that no attraction of males to the pheromone lure was observed without **1**.[1]

Each of the hydrocarbons **1**, **2** and **3** has two stereogenic centers, and therefore possesses four stereoisomers. The enantiomeric composition of the naturally occurring **1**, **2** and **3** is not determined yet, but may be clarified by testing the pheromone activity of every stereoisomer of **1**, **2** and **3**. In order to achieve this aim, we decided to synthesize all the stereoisomers of **1**, **2** and **3** according to the plan shown in Scheme 1. The carbon skeleton of **1** can be constructed by connecting the chiral and non-racemic building blocks **A** and **B**, which in turn are to be derived from **C** and **D**. Both the enantiomers of methyl 3-hydroxy-2-methylpropanoate (**C**) as well as those of citronellol (**D**) are commercially available, and previously employed by us for the synthesis of the stereoisomers of 3,13-dimethylheptadecane, the pheromone of the western false hemlock looper.[2] The stereoisomers of **1** can be converted into the stereoisomers of **2** and **3**.

Scheme 2 summarizes the preparation of the building blocks **10** (= **B**) and **13b** (= **A**). (*S*)-Citronellol (**4**, 97% e.e.)



Scheme 1. Sex pheromone components of *Lyonetia prunifoliella* and their retrosynthetic analysis

was converted into (*S*)-**5a** in 86% yield as reported by Mori and Kato.[3] The corresponding tosylate (*S*)-**5b** was treated with 5-hexenylmagnesium bromide in the presence of $Li_2CuBr_2{\cdot}SMe_2{\cdot}SPh$[4] to give a 7:3 mixture of the desired (*S*)-**6** and the by-product (*S*)-**7**, which presumably was generated by a cyclization process such as conversion of **E** into **F**. This type of cyclization had been recorded in the cases of the Grignard reaction in general[5] and in the case of 5-hexenylmagnesium chloride in particular.[6] The mixture of the acetates (*S*)-**6** and (*S*)-**7** was then hydrolyzed with potassium hydroxide to give a mixture of the alcohols (*S*)-**8** and (*S*)-**9**, which was separated by chromatography on silica gel impregnated with silver nitrate to give the pure alcohol (*S*)-**8**. Oxidation of (*S*)-**8** with pyridinium chlorochromate (PCC) furnished the desired aldehyde (*S*)-**10** in 35% overall yield based on (*S*)-citronellol (**4**, 6 steps). Similarly, (*R*)-citronellol (**4**) afforded crude (*R*)-**10** in 44% overall yield. In

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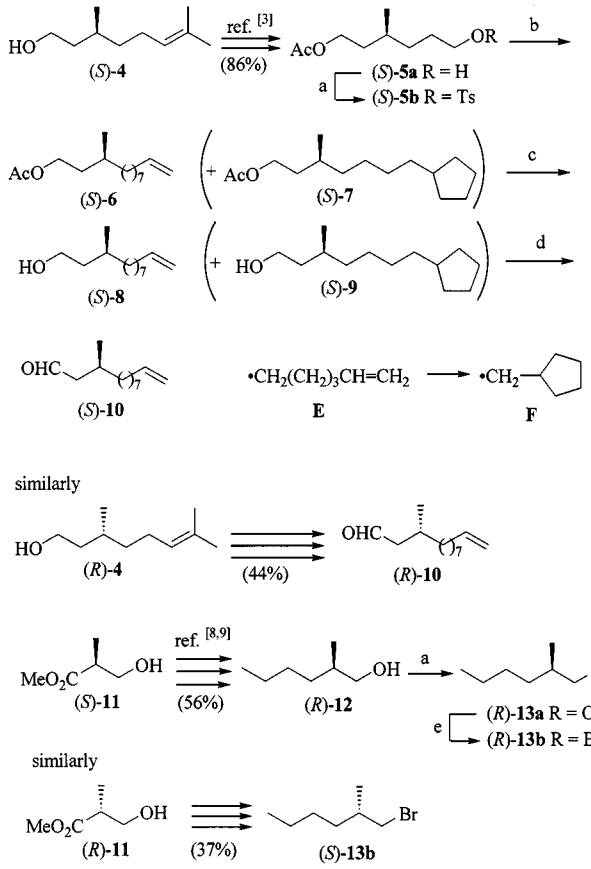
this case, unfortunately, we overlooked the contamination of (*R*)-**6** with 12% of (*R*)-**7**, and therefore the crude (*R*)-**10** contained 12% of the aldehyde resulting from (*R*)-**9**. The contaminating cyclopentyl derivatives could be removed at the final purification stage of the synthesis to give pure (10*R*,14*R*)- and (10*R*,14*S*)-**1** after chromatography on silica gel impregnated with silver nitrate. The enantiomers of the building block **13b**[7] were prepared from the enantiomers of methyl 3-hydroxy-2-methylpropanoate (**11**) via the

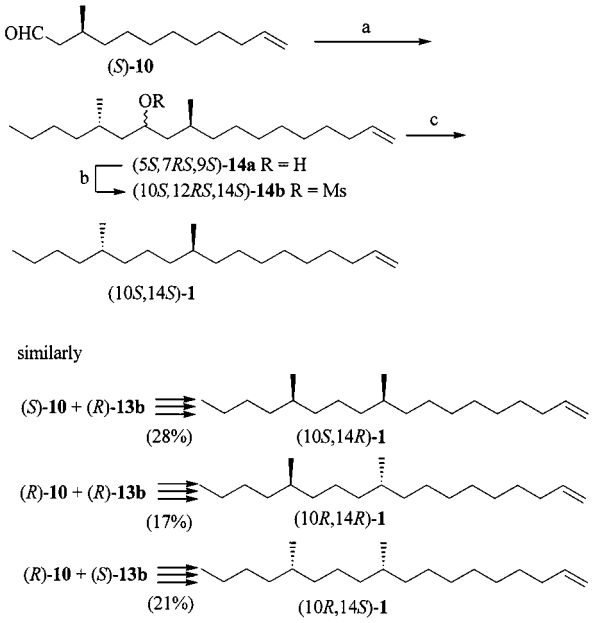


Scheme 2. Synthesis of intermediates **10** and **13b**: reagents: (a) TsCl, C_5H_5N; (b) $H_2C{=}CH(CH_2)_4MgBr$, $Li_2CuBr_2{\cdot}SMe_2{\cdot}SPh$, HMPA, THF [73%, based on (*S*)-**5a**]; (c) KOH, MeOH, then $SiO_2{\cdot}AgNO_3$ chromatography (63%); (d) PCC, CH_2Cl_2 (89%); (e) LiBr, acetone [71% based on (*R*)-**12**]

known alcohol **12** and the corresponding tosylate **13a**.[8][9]

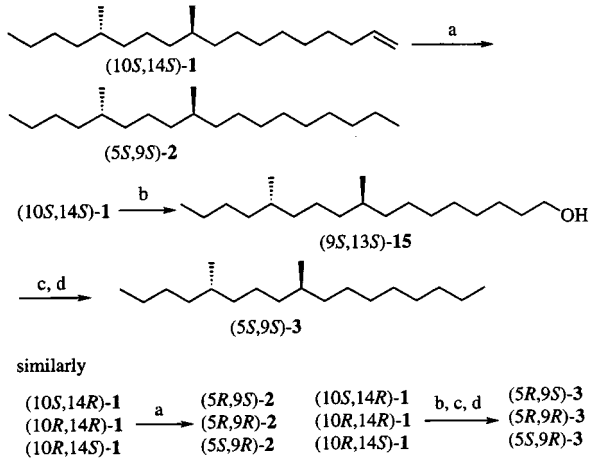
Synthesis of the four stereoisomers of **1** is summarized in Scheme 3. Treatment of the aldehyde (*S*)-**10** with the Grignard reagent derived from (*S*)-**13b** furnished the alcohol (5*S*,7*RS*,9*S*)-**14a**, whose mesylate **14b** was reduced with lithium triethylhydroborate (Super-Hydride®) to give (10*S*,14*S*)-**1** in 36% overall yield based on (*S*)-**10** (3 steps). In the same manner (*S*)-**10** and (*R*)-**13b** afforded (10*S*,14*R*)-**1**. The synthesis of (10*R*,14*R*)- and (10*R*,14*S*)-**1** was concluded by chromatographic purification of the final products (see above).

Scheme 4 shows the conversion of **1** into **2** and **3**. Hydrogenation of (10*S*,14*S*)-**1** on platinum oxide furnished (5*S*,9*S*)-**2**. Similarly, other stereoisomers of **1** were also hydrogenated to give (5*R*,9*S*)-, (5*R*,9*R*)- and (5*S*,9*R*)-**2**.



Scheme 3. Synthesis of **1**: reagents: (a) (*S*)-2-methylhexylmagnesium bromide [from (*S*)-**13b**] THF (60%); (b) MsCl, C_5H_5N; (c) $LiBEt_3H$, THF [60% based on (5*S*,7*RS*,9*S*)-**14a**]

(5*S*,9*S*)-5,9-Dimethylheptadecane (**3**) was prepared from (10*S*,14*S*)-**1** by ozonolysis with reductive workup to give (9*S*,13*S*)-**15** followed by tosylation of **15** and reduction of the resulting tosylate with lithium tetrahydroaluminate. The remaining three stereoisomers of **3** were also synthesized in the same manner by employing the corresponding three stereoisomers of **1**. All of the synthetic stereoisomers of **1**, **2** and **3** were sent to Prof. G. Gries (Simon Fraser University, Canada), and the biological result will be published separately in due course.[10]



Scheme 4. Synthesis of **2** and **3**: reagents: (a) H_2, PtO_2, hexane (60%); (b) O_3, hexane, CH_2Cl_2, MeOH then $NaBH_4$ (c) TsCl, C_5H_5N; (d) $LiAlH_4$, THF [84% based on (9*S*,13*S*)-**15**]

Experimental Section

General: All boiling points are uncorrected. – IR: Jasco A-102. – ^{1}H NMR: Jeol 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 rotations: Jasco DIP-1000. − Refractive indices: ATAGO Abbe 1T. − Mass spectra: Jeol JMS-SX102A or Hitachi M-80B.

(*S*)-3-Methyl-6-(tosyloxy)hexyl Acetate [(*S*)-5b]: To a stirred and ice-cooled solution of (*S*)-**5a** (7.79 g, 44.7 mmol) and TsCl (11.2 g, 58.6 mmol) in dry pyridine (40 mL) and CH_2Cl_2 (40 mL) was added DMAP (68 mg, 0.56 mmol). The mixture was stirred for 6 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, water, a saturated aqueous $NaHCO_3$ solution and brine, dried with $MgSO_4$, and concentrated in vacuo to give 15.1 g (quant.) of crude (*S*)-**5b**. − IR (film): $\tilde{\nu}_{max}$ = 1740 cm^{-1} (s, C=O), 1600 (m, aromatic C=C), 1465 (m), 1360 (s, S=O), 1250 (s), 1180 (s, S=O). − ^1H NMR (90 MHz, $CDCl_3$): δ = 0.87 (d, *J* = 5.7 Hz, 3 H, 3-Me), 1.04−1.90 (m, 7 H, 2-, 3-, 4-, 5-H), 2.03 (s, 3 H, $COCH_3$), 2.45 (s, 3 H, Ar−CH_3), 4.02 (t, *J* = 6.4 Hz, 2 H, 6-H), 4.06 (t, *J* = 6.2 Hz, 2 H, 1-H), 7.34 (d, *J* = 8.3 Hz, 2H, aromatic), 7.79 (d, *J* = 8.3 Hz, 2 H, aromatic). − This was employed in the next step without further purification.

(*R*)-3-Methyl-6-(tosyloxy)hexyl Acetate [(*R*)-5b]: In the same manner as described above, (*R*)-**5a** (7.08 g, 40.6 mmol) was converted into 12.2 g (91%) of (*R*)-**5b**. The IR and ^1H-NMR spectra are identical with those of (*S*)-**5b**. This was employed in the next step without further purification.

Crude (*S*)-3-Methyl-11-dodecenyl Acetate [(*S*)-6]: 5-Hexenylmagnesium bromide was prepared from 5-hexenyl bromide (6.1 g, 37 mmol) and magnesium (1.09 g, 44.8 mmol) in dry THF (50 mL). This reagent was added dropwise to a solution of (*S*)-**5b** (7.22 g, 22.0 mmol), HMPA (5.4 mL) and $Li_2CuBr_2SMe_2SPh$ (0.10 M THF solution, 13 mL, 1.3 mmol) in dry THF (70 mL) at room temp. with stirring. After stirring for 14 h, a saturated aqueous NH_4Cl solution was slowly added, and the mixture was extracted with diethyl ether. The ethereal extract was washed with water and brine, dried with $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on silica gel (150 g). Elution with *n*-hexane/ethyl acetate (100:1) gave 3.76 g [73% based on (*S*)-**5a**] of a 7:3 mixture of (*S*)-**6** and (*S*)-**7** (checked by GLC), b.p. 123−124°C/3.5 Torr, n_D^{24} = 1.4464, $[\alpha]_D^{23}$ = −3.09 (*c* = 3.70, $CHCl_3$). − GLC [column: GL Science Inc., TC-WAX (15 m × 0.53 mm ID), 100°C + 1.0°C/min; carrier gas: He, pressure 1.8 kg/cm^2]: t_R = 6.46 min [70%, (*S*)-**6**], 8.60 min [30%, (*S*)-**7**]. − IR (film): $\tilde{\nu}_{max}$ = 3080 cm^{-1} (vw, = C−H), 1740 (s, C=O), 1640 (w, C=C), 1240 (s, C−O). − ^1H NMR (90 MHz, $CDCl_3$): δ = 0.90 (d, *J* = 5.6 Hz, 3 H, 3-Me), 1.10−2.20 (m, 17 H, 2-, 3-, 4-, 5-, 6-, 7-, 8-, 9-, 10-H), 2.04 (s, 3 H, $COCH_3$), 4.10 (t, *J* = 6.7 Hz, 2 H, 1-H), 4.93 (d-like, *J* = 10 Hz, 1 H, 12-H_{cis}), 4.97 (d-like, *J* = 17 Hz, 1 H, 12-H_{trans}), 5.82 (ddt, *J* = 16, 9.8, 6.4 Hz, 1 H, 11-H). − $C_{15}H_{28}O_2$ (240.4): calcd. C 74.95, H 11.74; found C 74.92, H 11.50.

Crude (*R*)-3-Methyl-11-dodecenyl Acetate [(*R*)-6]: In the same manner as described above, (*R*)-**5b** (3.10 g, 9.44 mmol) was converted into 1.64 g [66% based on (*R*)-**5a**] of (*R*)-**6**. This material contained 12% (by GLC) of (*R*)-**7**; b.p. 133−135°C/Torr, n_D^{25} = 1.4430, $[\alpha]_D^{24}$ = + 3.16 (*c* = 3.56, $CHCl_3$). − GLC [column: GL Science Inc., TC-WAX (15 m × 0.53 mm ID), 100°C + 1.0°C/min; carrier gas: He, pressure 1.8 kg/cm^2]: t_R = 6.50 min [88%, (*R*)-**6**], 8.58 min [12%, (*R*)-**7**]. − The IR and ^1H NMR spectra are identical with those of (*S*)-**6**. − $C_{15}H_{28}O_2$ (240.4): calcd. C 74.95, H 11.74; found C 74.69, H12.13.

(*S*)-3-Methyl-11-dodecen-1-ol [(*S*)-8] and (*S*)-7-Cyclopentyl-3-methyl-1-heptanol [(*S*)-9]: A solution of KOH (2.0 g, 36 mmol) in MeOH (50 mL) was added to (*S*)-**6** (6.16 g, 25.6 mmol). The mixture was stirred at room temp. for 3 h. It was then poured into ice/water and extracted with ethyl acetate. The extract was washed with a saturated aqueous NH_4Cl solution, water and brine, dried with $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on silica gel (100 g). Elution with *n*-hexane/ethyl acetate (20:1) gave 4.60 g (90%) of the mixture of (*S*)-**8** and (*S*)-**9**. This mixture (3.70 g) was chromatographed on SiO_2·$AgNO_3$ (SiO_2 40 g, $AgNO_3$ 8.3 g). Elution with *n*-hexane/ethyl acetate (20:1) gave 1.00 g (27%) of (*S*)-**9**. − ^1H NMR (90 MHz, $CDCl_3$): δ = 0.89 (d, *J* = 6.4 Hz, 3 H, 3-Me), 1.00−1.90 (m, 21 H, 2-, 3-, 4-, 5-, 6-, 7-H, cyclopentyl, O-H), 3.68 (t, *J* = 6.6 Hz, 2 H, 1-H). − EI MS: *m*/*z* = 180 [M − H_2O^+]. − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 19.5, 25.1, 27.2, 29.0, 29.5, 32.66, 32.67, 36.2, 37.1, 39.9, 40.1, 61.0. − Further elution with *n*-hexane/ethyl acetate (10:1) gave 2.57 g (63%) of (*S*)-**8**, n_D^{22} = 1.4531, $[\alpha]_D^{20}$ = − 2.97 (*c* = 1.33, $CHCl_3$). − IR (film): $\tilde{\nu}_{max}$ = 3330 cm^{-1} (bs, O−H), 3090 (m, =C−H), 1645 (m, C=C), 1055 (m, C−O). − ^1H NMR (90 MHz, $CDCl_3$): δ = 0.89 (d, *J* = 5.9 Hz, 3 H, 3-Me), 1.00−1.75 (m, 16 H, 2-, 3-, 4-, 5-, 6-, 7-, 8-, 9-H, O-H), 2.04 (q like, *J* = 6.4 Hz, 2 H, 10-H), 3.68 (t, *J* = 6.6 Hz, 2 H, 1-H), 4.92 (d-like, *J* = 9.0 Hz, 1 H, 12-H_{cis}) 4.97 (d-like, *J* = 17 Hz, 1 H, 12-H_{trans}) 5.82 (ddt, *J* = 17, 9.8, 6.4 Hz, 1 H, 11-H). − $C_{13}H_{26}O$ (198.4): calcd. C 78.72, H 13.21; found C 78.53, H13.04.

Crude (*R*)-3-Methyl-11-dodecen-1-ol [(*R*)-8]: In the same manner as described above, (*R*)-**6** (5.74 g, 23.9 mmol) was converted into 4.55 g (96%) of the mixture of (*R*)-**8** and (*R*)-**9**. The obtained impure (*R*)-**8** was employed in the next step without further purification, n_D^{22} = 14559, $[\alpha]_D^{23}$ = + 3.40 (*c* = 5.79, $CHCl_3$). The IR and ^1H-NMR spectra are almost identical with those of (*S*)-**8**.

(*S*)-3-Methyl-11-dodecenal [(*S*)-10]: A solution of (*S*)-**8** (2.35 g, 11.8 mmol) in CH_2Cl_2 (30 mL) was added to a stirred suspension of PCC (5.17 g, 24.0 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred at room temp. for 1.5 h, then diluted with diethyl ether and filtered through Florisil. The filtrate was concentrated in vacuo. The residue was chromatographed on silica gel (40 g). Elution with *n*-hexane gave 2.06 g (89%) of (*S*)-**10**, n_D^{23} = 1.4488, $[\alpha]_D^{22}$ = −10.0 (*c* = 1.22, $CHCl_3$). − IR (film): $\tilde{\nu}_{max}$ = 3100 cm^{-1} (m, = C−H) 2730 (m, CHO), 1730 (s, C=O), 1640 (m, C=C), 910 (s). − ^1H NMR (90 MHz, $CDCl_3$): δ = 0.95 (d, *J* = 6.4 Hz, 3 H, 3-Me), 1.04−1.60 (m, 13 H, 3-, 4-, 5-, 6-, 7-, 8-, 9-H), 1.80−2.20 (m, 2 H, 10-H), 2.20−2.50 (m, 2 H, 2-H), 4.93 (d, *J* = 9.5 Hz, 1 H, 12-H_{cis}), 4.97 (d, *J* = 17 Hz, 1 H, 12-H_{trans}), 5.82 (ddt, *J* = 17, 9.8, 6.6 Hz, 1 H, 11-H), 9.76 (t, *J* = 2.1 Hz, 1 H, CHO). − HR MS; *m*/*z*: found 196.1824 [M^+], calcd. for $C_{13}H_{24}O$ 196.1828.

Crude (*R*)-3-Methyl-11-dodecenal [(*R*)-10]: In the same manner as described above, (*R*)-**8** (1.36 g, 6.86 mmol) was converted into 1.17 g (87%) of (*R*)-**10**, n_D^{23} = 1.4467, $[\alpha]_D^{22}$ = + 12.1 (*c* = 1.26, $CHCl_3$). The IR and ^1H NMR spectra are virtually identical with those of (*S*)-**10**. − HR MS; *m*/*z*: found 196.1825 [M^+], calcd. for $C_{13}H_{24}O$ 196.1828.

(*R*)-2-Methylhexyl Tosylate [(*R*)-13a]: TsCl (20.3 g, 106 mmol) was added to an ice-cooled and stirred solution of (*R*)-**12** (9.87 g, 84.9 mmol) and dry pyridine (20 mL) in CH_2Cl_2 (130 mL). To this mixture was added DMAP (56 mg, 0.46 mmol) and the mixture was stirred at 4°C for ca. 48 h. To this was added water with ice-cooling. Then it was poured into 3 M hydrochloric acid and extracted with diethyl ether. The ethereal extract was washed with 1 M hydrochloric acid, water, a saturated aqueous $NaHCO_3$ solution and brine, dried with $MgSO_4$ and concentrated in vacuo to give 22.8 g (99%) of crude (*R*)-**13a**. − IR (film): $\tilde{\nu}_{max}$ = 1600 cm^{-1} (m, benzene ring), 1365 (s, S=O), 1180 (s, S=O). − ^1H NMR (90 MHz, $CDCl_3$): δ = 0.84 (t, *J* = 6.4 Hz, 6-H), 0.88 (d, *J* = 6.6 Hz, 2-Me),

1.00−1.95 (m, 7 H, 2-, 3-, 4-, 5-H), 2.45 (s, 3 H, Ar-CH_3), 3,84 (dd, J = 9.5, 5,9 Hz, 2 H, 1-H), 7.34 (d, J = 8.1 Hz, 2 H, aromatic), 7.79 (d, J = 8.3 Hz, 2 H, aromatic). − This was employed in the next step without further purification.

(*S*)-2-Methylhexyl Tosylate [(*S*)-13a]: In the same manner as described above, (*S*)-**12** (3.31 g, 28.5 mmol) was converted into 7.28 g (94%) of crude (*S*)-**13a**. The IR and ^{1}H NMR spectra are identical with those of (*R*)-**13a**. This was employed in the next step without further purification.

(*R*)-2-Methylhexyl Bromide [(*R*)-13b]: Lithium bromide (10.9 g, 126 mmol) was added to a solution of (*R*)-**13a** (22.8 g, 84.3 mmol) in dry acetone (150 mL). The mixture was stirred and heated under reflux for ca. 6 h. To this was added water and the solvent was removed by distillation. The residue was poured into water, and extracted with *n*-pentane. The pentane extract was washed with water and brine, dried with $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on silica gel and distilled to give 10.8 g [71%, based on (*R*)-**12**] of (*R*)-**13b**, b.p. 72−74°C/30 Torr, n_D^{24} = 1.4492, $[\alpha]_D^{22}$ = +0.60 (c = 1.90, $CHCl_3$). − IR (film): $\tilde{\nu}_{max}$ = 1230 cm^{-1} (s). − ^{1}H NMR (90 MHz, $CDCl_3$): δ = 0.97 (t, J = 6.4 Hz, 3 H, 6-H), 1.01 (d, J = 6.4 Hz, 3 H, 2-Me), 1.10−1.60 (m, 6 H, 3-, 4-, 5-H), 1.60−1.90 (m, 1 H, 2-H), 3.36 (dd, J = 9.8, 5.5 Hz, 2 H, 1-H).

(*S*)-2-Methylhexyl Bromide [(*S*)-13b]: In the same manner as described above, (*S*)-**13a** (7.28 g, 26.9 mmol) was converted into 3.27 g [64%, based on (*S*)-**12**] of (*S*)-**13b**, b.p. 72°C/28 Torr, $[\alpha]_D^{23}$ = −0.47 (c = 2.23, $CHCl_3$). The IR and NMR spectra are identical with those of (*R*)-**13b**.

(5*S*,7*RS*,9*S*)-5,9-Dimethyl-17-octadecen-7-ol [(5*S*,7*RS*,9*S*)-14a]: (*S*)-2-Methylhexylmagnesium bromide was prepared from (*S*)-**13b** (1.40 g, 7.82 mmol) and magnesium (0.31 g, 13 mmol) in dry THF (8 mL). This reagent was added dropwise to an ice-cooled and stirred solution of (*S*)-**10** (0.96 g, 4.9 mmol) in dry THF (5 mL). The mixture was stirred at 0°C for 0.5 h. To this was slowly added a saturated aqueous NH_4Cl solution and the mixture was extracted with diethyl ether. The ethereal extract was washed with water and brine, dried with $MgSO_4$ and concentrated in vacuo. The residue was chromatographed on silica gel (80 g). Elution with *n*-hexane/ethyl acetate (75:1 to 50:1) gave 865 mg (60%) of (5*S*,7*RS*,9*S*)-**14a**, n_D^{23} = 1.4565, $[\alpha]_D^{22}$ = + 6.69 (c = 1.31, $CHCl_3$). − IR (film): $\tilde{\nu}_{max}$ = 3350 cm^{-1} (br., m, O−H), 3090 (w, = C−H), 1640 (m, C=C). − ^{1}H NMR (90 MHz, $CDCl_3$): δ = 0.86−0.93 (m, 9 H, 1-H, 5-, 9-Me), 1.00−1.70 (m, 25 H, 2-, 3-, 4-, 5-, 6-, 8-, 9-, 10-, 11-, 12-, 13-, 14-, 15-H, O−H), 1.90−2.20 (m, 2 H, 16-H), 3.75 (br. s, 1 H, 7-H), 4.93 (d-like, J = 10 Hz, 1 H, 18-H$_{cis}$), 4.97 (d-like, J = 17 Hz, 1 H, 18-H$_{trans}$), 5.83 (ddt, J = 17, 9.9, 6.7 Hz, 1 H, 17-H). − $C_{20}H_{40}O$ (296.5): calcd. C 81.01, H 13.60; found C 80.86, H 13.83.

(5*R*,7*RS*,9*S*)-5,9-Dimethyl-17-octadecen-7-ol [(5*R*,7*RS*,9*S*)-14a]: In the same manner as described above, (*R*)-**13b** (1.74 g, 9.72 mmol) and (*S*)-**10** (1.01 g, 5.14 mmol) were converted into 897 mg (59%) of (5*R*,7*RS*,9*S*)-**14a**, n_D^{24} = 1.4564, $[\alpha]_D^{22}$ = − 1.04 (c = 1.13, $CHCl_3$). − IR (film): $\tilde{\nu}_{max}$ = 3350 cm^{-1} (br., m, O−H), 3090 (w, = C−H), 1640 (m, C=C). − ^{1}H NMR (90 MHz, $CDCl_3$): δ = 0.60−1.00 (m, 9 H, 1-H, 5-, 9-Me), 1.00−1.70 (m, 25 H, 2-, 3-, 4-, 5-, 6-, 8-, 9-, 10-, 11-, 12-, 13-, 14-, 15-H, O−H), 1.80−2.20 (m, 2 H, 16-H), 3.78 (bs, 1 H, 7-H), 4.93 (d-like, J = 10 Hz, 1 H, 18-H$_{cis}$), 4.97 (d-like, J = 17 Hz, 1 H, 18-H$_{trans}$), 5.83 (ddt, J = 17, 9.9, 6.6 Hz, 1 H, 17-H). − $C_{20}H_{40}O$ (296.5): calcd. C 81.01, H 13.60; found C 80.95, H 13.56.

Crude (5*R*,7*RS*,9R)-5,9-Dimethyl-17-octadecen-7-ol [(5*R*,7*RS*,9R)-14a]: In the same manner as described above, (*R*)-**13b** (1.51 g, 8.43 mmol) and (*R*)-**10** (1.09 g, 5.55 mmol) were converted into 0.96 g (58%) of (5*R*,7*RS*,9*R*)-**14a**, n_D^{23} = 1.4592, $[\alpha]_D^{21}$ = − 6.46 (c = 1.47, $CHCl_3$). − The IR and ^{1}H-NMR spectra are virtually identical with those of (5*S*,7*RS*,9*S*)-**14a**. − $C_{20}H_{40}O$ (296.5): calcd. C 81.01, H 13.60; found C 81.46, H 13.05.

Crude (5*S*,7*RS*,9*R*)-5,9-Dimethyl-17-octadecen-7-ol [(5*S*,7*RS*,9*R*)-14a]: In the same manner as described above, (*S*)-**13b** (1.53 g, 8.54 mmol) and (*R*)-**10** (1.17 g, 5.96 mmol) was converted into 1.13 g (64%) of (5*S*,7*RS*,9*R*)-**14a**, n_D^{23} = 1.4582, $[\alpha]_D^{20}$ = + 1.62 (c = 1.08, $CHCl_3$). The IR and ^{1}H-NMR spectra are almost identical with those of (5*R*,7*RS*,9*S*)-**14a**. − $C_{20}H_{40}O$ (296.5): calcd. C 81.01, H 13.60; found C 81.33, H 13.14.

(10*S*,12*RS*,14*S*)-10,14-Dimethyl-12-mesyloxy-1-octadecene [(10*S*,12*RS*,14*S*)-14b]: MsCl (0.53 g, 4.7 mmol) was added to an ice-cooled and stirred solution of (5*S*,7*RS*,9*S*)-**14a** (668 mg, 2.25 mmol) in dry pyridine (5 mL). The mixture was stirred at 4°C for about 13 h. Then water was added to this solution, and the mixture was extracted with *n*-hexane. The hexane extract was washed with 1 M hydrochloric acid, water, a saturated aqueous $NaHCO_3$ solution and brine, dried with $MgSO_4$ and concentrated in vacuo to give 813 mg (96%) of crude (10*S*,12*RS*,14*S*)-**14b**. − IR (film): $\tilde{\nu}_{max}$ = 3090 cm^{-1} (w, =C−H), 1640 (m, C=C) 1350 (s, S=O), 1180 (s, S=O). − ^{1}H NMR (90 MHz, $CDCl_3$): δ = 0.70−1.00 (m, 9 H, 18-H, 10-, 14-Me), 1.00−1.80 (m, 24 H, 4-, 5-, 6-, 7-, 8-, 9-, 10-, 11-, 13-, 14-, 15-, 16-, 17-H), 1.85−2.20 (m, 2 H, 3-H), 2.99 (s, 3 H, SO_2−CH_3), 4.80 (br. s, 1 H, 12-H), 4.93 (d-like, J = 10 Hz, 1 H, 1-H$_{cis}$), 4.97 (d-like, J = 17 Hz, 1 H, 1-H$_{trans}$), 5.83 (ddt, J = 17, 10, 6.7 Hz, 1 H, 2-H). − This was employed in the next step without further purification.

(10*S*,12*RS*,14*R*)-10,14-Dimethyl-12-mesyloxy-1-octadecene [(10*S*,12*RS*,14*R*)-14b]: In the same manner as described above (5*R*,7*RS*,9*S*)-**14a** (743 mg, 2.51 mmol) was converted into 912 mg (97%) of (10*S*,12*RS*,14*R*)-**14b**. − IR (film): $\tilde{\nu}_{max}$ = 3100 cm^{-1} (w, = C−H), 1645 (m, C=C) 1340 (s, S=O), 1180 (s, S=O). − ^{1}H NMR (90 MHz, $CDCl_3$): δ = 0.70−1.10 (m, 9 H, 18-H, 10-, 14-Me), 1.10−1.80 (m, 24 H, 4-, 5-, 6-, 7-, 8-, 9-, 10-, 11-, 13-, 14-, 15-, 16-, 17-H), 1.85−2.20 (m, 2 H, 3-H), 2.98 (s, 3 H, SO_2 −CH_3), 4.80 (br. s, 1 H, 12-H), 4.93 (d-like, J = 11 Hz, 1 H, 1-H$_{cis}$), 4.97 (d-like, J = 17 Hz, 1 H, 1-H$_{trans}$), 5.83 (ddt, J = 17, 10, 6.7 Hz, 1 H, 2-H). − This was employed in the next step without further purification.

Crude (10*R*,12*RS*,14*R*)-10,14-Dimethyl-12-mesyloxy-1-octadecene [(10*R*,12*RS*,14*R*)-14b]: In the same manner as described above (5*R*,7*RS*,9*R*)-**14a** (369 mg, 1.24 mmol) was converted into 487 mg (quant.) of (10*R*,12*RS*,14*R*)-**14b**. The IR and ^{1}H-NMR spectra are almost identical with those of (10*S*,12*RS*,14*S*)-**14b**. This was employed in the next step without further purification.

Crude (10*R*,12*RS*,14*S*)-10,14-Dimethyl-12-mesyloxy-1-octadecene [(10*R*,12*RS*,14*S*)-14b]: In the same manner as described above (5*S*,7*RS*,9*R*)-**14a** (955 mg, 3.22 mmol) was converted into 1.20 g (99%) of (10*R*,12*RS*,14*S*)-**14b**. The IR and ^{1}H-NMR spectra are almost identical with those of (10*S*,12*RS*,14*R*)-**14b**. This was employed in the next step without further purification.

(10*S*,14*S*)-10,14-Dimethyl-1-octadecene [(10*S*,14*S*)-1]: Lithium triethylhydroborate in THF (1.0 M, 35 mL, 35 mmol) was added to an ice-cooled and stirred solution of (10*S*,12*RS*,14*S*)-**14b** (813 mg, 2.17 mmol) in THF (40 mL) under argon. It was stirred at room temp. for about 42 h. Then water was slowly added to this solution. The mixture was poured into water and extracted with *n*-hexane. The hexane extract was washed with water and brine, dried with $MgSO_4$ and concentrated in vacuo. The residue was chromato-

graphed on silica gel (7 g). Elution with *n*-hexane gave crude (10*S*,14*S*)-**1**. This crude material contained about 20% (by ^{1}H NMR) of olefinic compounds formed by elimination of methanesulfonic acid from (10*S*,12*RS*,14*S*)-**14b**. It was dissolved in CH_2Cl_2 (10 mL), and *m*-CPBA (70%, 0.11 g, 0.45 mmol) was added at 0°C. The mixture was stirred at room temp. for 1.5 h, and then a saturated aqueous $Na_2S_2O_3$ solution and a saturated aqueous $NaHCO_3$ solution were added. It was extracted with *n*-hexane. The hexane extract was washed with water and brine, dried with $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on silica gel (8 g). Elution with *n*-hexane gave 375 mg [60% based on (10*S*,12*RS*,14*S*)-**14a**] of (10*S*,14*S*)-**1**, n_D^{24} = 1.4470, $[\alpha]_D^{21}$ = +1.92 (*c* = 1.06, $CHCl_3$). − GLC [column: GL Science Inc., Neutrabond-5 (30 m × 0.25 mm ID), 100°C + 3.0°C/min; carrier gas: He, pressure 1.7 kg/cm^2]: t_R = 32.6 min (98%). − EI MS; *m*/*z* (%): 41 (50), 57 (97), 85 (37), 125 (13), 127 (5), 153 (30), 155 (3), 223 (3), 239 (1), 280 (22). − IR (film): $\tilde{\nu}_{max}$ = 3090 cm^{-1} (w, =C−H), 2970 (s, C−H), 2940 (s, C−H), 2870 (s, C−H), 1640 (m, C=C), 1460 (m), 1375 (m), 995 (w), 910 (m), 725 (w). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85 (d, *J* = 6.4 Hz, 6 H, 10-, 14-Me) 0.90 (t, *J* = 6.4 Hz, 3 H, 18-H), 1.00−1.45 (m, 29 H, 4-, 5-, 6-, 7-, 8-, 9-, 10-, 11-, 12-, 13-, 14-, 15-, 16-, 17-H), 2.05 (q, *J* = 6.8 Hz, 2 H, 3-H), 4.93 (ddt, *J* = 10.2, 2.0, 1.2 Hz, 1 H, 1-H$_{cis}$), 5.00 (ddt, *J* = 17.1, 1.9, 1.7 Hz, 1 H, 1-H$_{trans}$), 5.82 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1 H, 2-H). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.2, 19.7, 23.1, 24.5, 27.1, 29.0, 29.2, 29.4, 29.6, 30.0, 32.8, 33.9, 36.9, 37.2, 37.4, 114.1, 139.2. − $C_{20}H_{40}$: calcd. 280.3128; found 280.3120 (HRMS).

(10*S*,14*R*)-10,14-Dimethyl-1-octadecene [(10*S*,14*R*)-1]: In the same manner as described above, (10*S*,12*RS*,14*R*)-**14b** (912 mg, 2.43 mmol) was converted into 340 mg [48%, based on (10*S*,12*RS*,14*R*)-**14a**] of (10*S*,14*R*)-**1**, n_D^{23} = 1.4472, $[\alpha]_D^{22}$ = − 0.91 (*c* = 1.17, $CHCl_3$). − GLC [column: GL Science Inc., Neutrabond-5 (30 m × 0.25 mm ID), 100°C + 3.0°C/min; carrier gas: He, pressure 1.7 kg/cm^2]: t_R = 32.2 min (100%). − EI MS; *m*/*z* (%): 41 (50), 57 (100), 85 (40), 125 (13), 127 (5), 153 (33), 155 (3), 223 (3), 239 (1), 280 (23). − IR (film): $\tilde{\nu}_{max}$ = 3090 cm^{-1} (w, =C−H), 2970 (s, C−H), 2940 (s, C−H), 2870 (s, C−H), 1640 (m, C=C), 1460 (m), 1375 (m), 995 (w), 910 (m), 725 (w). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.82−0.87 (m, 6 H, 10-, 14-Me) 0.89 (t, *J* = 6.6 Hz, 3 H, 18-H), 1.01−1.38 (m, 29 H, 4-, 5-, 6-, 7-, 8-, 9-, 10-, 11-, 12-, 13-, 14-, 15-, 16-, 17-H), 2.05 (q, *J* = 6.75 Hz, 2 H, 3-H), 4.93 (ddt, *J* = 10.2, 2.1, 1.2 Hz, 1 H, 1-H$_{cis}$), 5.00 (ddt, *J* = 17.2, 2.1, 1.6 Hz, 1 H, 1-H$_{trans}$), 5.82 (ddt, *J* = 17.0, 10.3, 6.6 Hz, 1 H, 2-H). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.2, 19.8, 23.1, 24.5, 27.1, 29.0, 29.2, 29.4, 29.6, 30.0, 32.8, 33.8, 36.8, 37.1, 37.4, 114.1, 139.3. − $C_{20}H_{40}$: calcd. 280.3128; found 280.3110 (HRMS).

(10*R*,14*R*)-10,14-Dimethyl-1-octadecene [(10*R*,14*R*)-1]: In the same manner as described for the preparation of (10*S*,14*S*)-**1**, (10*R*,12*RS*,14*R*)-**14b** (487 mg, 1.30 mmol) was converted into (10*R*,14*R*)-**1**. This material contained the cyclic compound derived from (*R*)-**9**. This (10*R*,14*R*)-**1** was chromatographed on SiO_2·$AgNO_3$. Elution with *n*-hexane gave 106 mg [30%, based on (10*R*,12*RS*,14*R*)-**14a**] of (10*R*,14*R*)-**1**, n_D^{23} = 1.4471, $[\alpha]_D^{21}$ = − 1.70 (*c* = 1.27, $CHCl_3$). − GLC [column: GL Science Inc., Neutrabond-5 (30 m × 0.25 mm ID), 100°C + 3.0°C/min; carrier gas: He, pressure 1.7 kg/cm^2]: t_R = 32.4 min (99%). The EI-MS, IR and NMR spectra are identical with those of (10*S*,14*S*)-**1**. − $C_{20}H_{40}$: calcd. 280.3128; found 280.3131 (HRMS).

(10*R*,14*S*)-10,14-Dimethyl-1-octadecene [(10*R*,14*S*)-1]: In the same manner as described for the preparation of (10*R*,14*R*)-**1**, (10*R*,12*RS*,14*S*)-**14b** (1.20 g, 3.20 mmol) was converted into 295 mg [33% after chromatographic purification on SiO_2·$AgNO_3$, based on (10*R*,12*RS*,14*S*)-**14a**] of (10*R*,14*S*)-**1**, n_D^{24} = 1.4473, $[\alpha]_D^{22}$ = + 1.35 (*c* = 1.14, $CHCl_3$). − GLC [column: GL Science Inc., Neutrabond-5 (30 m × 0.25 mm ID), 100°C + 3.0°C/min; carrier gas: He, pressure 1.7 kg/cm^2]: t_R = 32.4 min (98%). The EI-MS, IR and NMR spectra are identical with those of (10*S*,14*R*)-**1**. − $C_{20}H_{40}$: calcd. 280.3128; found 280.3139 (HRMS).

(5*S*,9*S*)-5,9-Dimethyloctadecane [(5*S*,9*S*)-2]: A mixture of (10*S*,14*S*)-**1** (9.2 mg, 33 μmol) and PtO_2 (ca. 1 mg) in *n*-hexane (1 mL) was stirred under hydrogen for 1 d. This mixture was filtered through Celite and the filtrate was concentrated in vacuo to give 9.5 mg (quant.) of (5*S*,9*S*)-**2**. − GLC [column: GL Science Inc., Neutrabond-5 (30 m × 0.25 mm ID), 120°C +3.0°C/min; carrier gas: He, pressure 1.8 kg/cm^2]: t_R = 25.4 min (98.3%). − EI MS; *m*/*z* (%): 28 (16), 43 (78), 57 (100), 71 (67), 85 (76), 99 (24), 113 (12), 127 (7), 154 (25), 155 (30), 225 (16), 282 (4). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.840 and 0.842 (each d, *J* = 6.4 Hz, 6 H, 5-, 9-Me), 0.88 and 0.89 (each t, *J* = 6.9 Hz, 6 H, 1-, 18-H), 1.03−1.42 (m, 30 H, 2-, 3-, 4-, 5-, 6-, 7-, 8-, 9-, 10-, 11-, 12-, 13-, 14-, 15-, 16-, 17-H). − $C_{20}H_{42}$: calcd. 282.3284; found 282.3291 (HRMS).

(5*R*,9*S*)-5,9-Dimethyloctadecane [(5*R*,9*S*)-2]: In the same manner as described above, (10*S*,14*R*)-**1** (10.2 mg, 36.4 μmol) was converted into 10.6 mg (quant.) of (5*R*,9*S*)-**2**. − GLC [column: GL Science Inc., Neutrabond-5 (30 m × 0.25 mm ID), 120°C + 3.0°C/min; carrier gas: He, pressure 1.8 kg/cm^2]: t_R = 25.6 min (98.2%). − EI MS: *m*/*z* (%) = 28 (33), 43 (78), 57 (100), 71 (67), 85 (77), 99 (24), 113 (13), 127 (8), 154 (24), 155 (30), 225 (18), 282 (4). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.842 and 0.844 (each d, *J* = 6.4 Hz, 6 H, 5-, 9-Me), 0.88 and 0.89 (each t, *J* = 6.9 Hz, 6 H, 1-, 18-H), 1.01−1.42 (m, 30 H, 2-, 3-, 4-, 5-, 6-, 7-, 8-, 9-, 10-, 11-, 12-, 13-, 14-, 15-, 16-, 17-H). − $C_{20}H_{42}$: calcd. 282.3284; found 282.3267 (HRMS).

(5*R*,9*R*)-5,9-Dimethyloctadecane [(5*R*,9*R*)-2]: In the same manner as described for the preparation of (5*S*,9*S*)-**2**, (10*R*,14*R*)-**1** (9.3 mg, 33 μmol) was converted into 9.7 mg (quant.) of (5*R*,9*R*)-**2**. − GLC [column: GL Science Inc., Neutrabond-5 (30 m × 0.25 mm ID), 120°C + 3.0°C/min; carrier gas: He, pressure 1.8 kg/cm^2]: t_R = 25.5 min (98.2%). The EI-MS and NMR spectra are identical with those of (5*S*,9*S*)-**2**. − $C_{20}H_{42}$: calcd. 282.3284; found 282.3292 (HRMS).

(5*S*,9*R*)-5,9-Dimethyloctadecane [(5*S*,9*R*)-2]: In the same manner as described for the preparation of (5*S*,9*S*)-**2**, (10*R*,14*S*)-**1** (10.9 mg, 38.9 μmol) was converted into 11.3 mg (quant.) of (5*S*,9*R*)-**2**. − GLC [column: GL Science Inc., Neutrabond-5 (30 m × 0.25 mm ID), 120°C + 3.0°C/min; carrier gas: He, pressure 1.8 kg/cm^2]: t_R = 25.5 min (97.2%). The EI-MS and NMR spectra are identical with those of (5*R*,9*S*)-**2**. − $C_{20}H_{42}$: calcd. 282.3284; found 282.3287 (HRMS).

(9*S*,13*S*)-9,13-Dimethyl-1-heptadecanol [(9*S*,13*S*)-15]: Ozone was bubbled into a solution of (10*S*,14*S*)-**1** (16.6 mg, 59.3 μmol) in *n*-hexane/CH_2Cl_2/MeOH (1:1:1, 3 mL) at −78°C until saturation. To this solution, $NaBH_4$ (20 mg, 36 μmol) was added. After removal of the cooling bath, the stirring was continued for 5 h. This mixture was poured into dild. hydrochloric acid and extracted with diethyl ether. The extract was washed with water, a saturated aqueous $NaHCO_3$ solution and brine, dried with $MgSO_4$, and concentrated in vacuo. The residue was purified by PTLC [elution with *n*-hexane/ethyl acetate (3:1)] to give 13.8 mg (82%) of (9*S*,13*S*)-**15**. − ^{1}H NMR (90 MHz, $CDCl_3$): δ = 0.75−1.00 (m, 9 H, 9-, 13-Me, 17-H) 1.00−1.75 (m, 29 H, 2-, 3-, 4-, 5-, 6-, 7-, 8-, 9-, 10-, 11-, 12-, 13-, 14-, 15-, 16-H, O−H), 3.64 (t, *J* = 6.3 Hz, 2 H, 1-H). − This was employed in the next step without further purification.

(9*S*,13*R*)-9,13-Dimethyl-1-heptadecanol [(9*S*,13*R*)-15]: In the same manner as described above, (10*S*,14*R*)-**1** (11.1 mg, 39.6 μmol) was converted into 9.8 mg (87%) of (9*S*,13*R*)-**15**. − ^{1}H NMR (90 MHz, $CDCl_3$): δ = 0.75−1.00 (m, 9 H, 9-, 13-Me, 17-H) 1.00−1.75 (m, 29 H, 2-, 3-, 4-, 5-, 6-, 7-, 8-, 9-, 10-, 11-, 12-, 13-, 14-, 15-, 16-H, O−H), 3.64 (t, *J* = 6.3 Hz, 2 H, 1-H). − This was employed in the next step without further purification.

(9*R*,13*R*)-9,13-Dimethyl-1-heptadecanol [(9*R*,13*R*)-15]: In the same manner as described for the preparation of (9*S*,13*S*)-**15**, (9*R*,13*R*)-**1** (13.3 mg, 47.5 μmol) was converted into 12.4 mg (92%) of (9*R*,13*R*)-**15**. The ^{1}H-NMR spectrum is identical with that of (9*S*,13*S*)-**15**. This was employed in the next step without further purification.

(9*R*,13*S*)-9,13-Dimethyl-1-heptadecanol [(9*R*,13*S*)-15]: In the same manner as described for the preparation of (9*S*,13*S*)-**15**, (9*R*,13*S*)-**1** (10.0 mg, 35.7 μmol) was converted into 7.2 mg (71%) of (9*R*,13*S*)-**15**. The ^{1}H-NMR spectrum is identical with that of (9*S*,13*R*)-**15**. This was employed in the next step without further purification.

(5*S*,9*S*)-5,9-Dimethylheptadecane [(5*S*,9*S*)-3]: To a solution of (9*S*,13*S*)-**15** (13.8 mg, 48.6 μmol) in pyridine (1 mL), TsCl (15 mg, 79 μmol) was added at 0°C. This mixture was stirred at 4°C for 12 h. It was then poured into water and extracted with diethyl ether. The extract was washed with water, a saturated aqueous $NaHCO_3$ solution and brine, dried with $MgSO_4$, and concentrated in vacuo to give 21.0 mg (quant.) of the corresponding tosylate. The resulting tosylate was dissolved into THF (2 mL), and $LiAlH_4$ (50 mg, 1.3 mmol) was added to this solution. After stirring at room temp. for 12 h, it was then poured into a dild. hydrochloric acid and extracted with *n*-hexane. The extract was washed with water, a saturated aqueous $NaHCO_3$ solution and brine, dried with $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on silica gel (2 g). Elution with *n*-hexane gave 11.0 mg (84%) of (5*S*,9*S*)-**3**. − GLC [column: GL Science Inc., Neutrabond-5 (30 m × 0.25 mm ID), 120°C + 3.0°C/min; carrier gas: He, pressure 1.7 kg/cm^2]: t_R = 22.2 min (97.3%). − EI MS; *m*/*z* (%): 43 (88), 57 (100), 71 (67), 85 (88), 99 (20), 113 (10), 140 (15), 155 (18), 211 (13), 268 (2). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.840 and 0.842 (each d, *J* = 6.5 Hz, 6 H, 5-, 9-Me), 0.88 and 0.89 (each t, *J* = 6.9 Hz, 6 H, 1-, 17-H), 1.03−1.42 (m, 28 H, 2-, 3-, 4-, 5-, 6-, 7-, 8-, 9-, 10-, 11-, 12-, 13-, 14-, 15-, 16-H). − $C_{19}H_{40}$: calcd. 268.3128; found 268.3127 (HRMS).

(5*R*,9*S*)-5,9-Dimethyheptadecane [(5*R*,9*S*)-3]: In the same manner as described above, (9*S*,13*R*)-**15** (9.8 mg, 34 μmol) was converted into 8.9 mg (99%) of (5*R*,9*S*)-**3**. − GLC [column: GL Science Inc., Neutrabond-5 (30 m × 0.25 mm ID), 120°C + 3.0°C/min; carrier gas: He, pressure 1.7 kg/cm^2]: t_R = 22.1 min (98.3%). − EI MS; *m*/*z* (%): 43 (84), 57 (100), 71 (67), 85 (78), 99 (20), 113 (10), 140 (14), 155 (18), 268 (2). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.841 and 0.843 (each d, *J* = 6.4 Hz, 6 H, 10-, 14-Me), 0.88 and 0.89 (each t, *J* = 6.9 Hz, 6 H, 1-, 18-H), 1.01−1.42 (m, 30 H, 2-, 3-, 4-, 5-, 6-, 7-, 8-, 9-, 10-, 11-, 12-, 13-, 14-, 15-, 16-, 17-H). − $C_{19}H_{40}$: calcd. 268.3128; found 268.3132 (HRMS).

(5*R*,9*R*)-5,9-Dimethylheptadecane [(5*R*,9*R*)-3]: In the same manner as described for the preparation of (5*S*,9*S*)-**3**, (9*R*,13*R*)-**15** (12.4 mg, 43.6 μmol) was converted into 10.0 mg (85%) of (5*R*,9*R*)-**3**. − GLC [column: GL Science Inc., Neutrabond-5 (30 m × 0.25 mm ID), 120°C + 3.0°C/min; carrier gas: He, pressure 1.7 kg/cm^2]: t_R = 22.4 min (97.2%). The EI-MS and ^{1}H-NMR spectra are identical with those of (5*S*,9*S*)-**3**. − $C_{19}H_{40}$: calcd. 268.3128; found 268.3122 (HRMS).

(5*S*,9*R*)-5,9-Dimethylheptadecane [(5*S*,9*R*)-3]: In the same manner as described for the preparation of (5*S*,9*S*)-**3**, (9*R*,13*S*)-**15** (7.2 mg, 25 μmol) was converted into 4.2 mg (62%) of (5*S*,9*R*)-**3**. − GLC [column: GL Science Inc., Neutrabond-5 (30 m × 0.25 mm ID), 120°C + 3.0°C/min; carrier gas: He, pressure 1.7 kg/cm^2]: t_R = 22.2 min (97.1%). − The EI-MS and ^{1}H-NMR spectra are identical with those of (5*R*,9*S*)-**3**. − $C_{19}H_{40}$: calcd. 268.3128; found 268.3133 (HRMS).

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[10] ***Note added in proof*** (February 15, 1999): Out of the four stereoisomers of **1**, only (10*R*,14*R*)-**1** elicited responses from male *L. prunifoliella* antennae in electrophysiological recordings (personal communiction of Prof. G. Gries to K. M. dated January 17, 1999).

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