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Synthesis of the (5*S*,9*R*)-isomer of 5,9-dimethylpentadecane, the major component of the female sex pheromone of the coffee leaf miner moth, *Leucoptera coffeella*☆

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Abstract—(5*S*,9*R*)-5,9-Dimethylpentadecane, one of the stereoisomers of the major component of the female sex pheromone of the coffee leaf miner moth (*Leucoptera coffeella*), was synthesized by starting from (*R*)-3-methyl-4-butanolide and (*S*)-citronellal.

1. Introduction

In 1988, Francke et al. identified 5,9-dimethylpentadecane **1** (Fig. 1) as the major component of the female sex pheromone of the coffee leaf miner moth, *Leucoptera coffeella*.[2] Since then, three syntheses of **1** as a racemic and diastereomeric mixture[3,4] or the (5*RS*,9*S*)-isomer[5] were reported. In 2000, Kuwahara et al. described the synthesis of all four stereoisomers of **1**,[6] while in 2003 Moreira and Corrêa reported the synthesis of (5*S*,9*S*)-, (5*R*,9*S*)-, and (5*S*,9*R*)-**1**.[7]

Despite these efforts, the absolute configuration of the natural pheromone still remains unknown. It was mentioned in Zarbin's paper that a mixture of (5*S*,9*S*)-**1** and (5*R*,9*S*)-**1**, as well as a racemic and diastereomeric mixture of **1** attracted the insects, while other stereoisomers [(5*R*,9*S*)- and (5*S*,9*R*)-**1**] did not.[4] Very recently, however, we were informed that (5*S*,9*R*)-**1** showed the highest activity in a field test, while (5*S*,9*S*)-**1** was about one thirds as active as (5*S*,9*R*)-**1**.[8] The other two isomers were almost inactive. Therefore, we decided to develop a new synthesis for (5*S*,9*R*)-**1**.

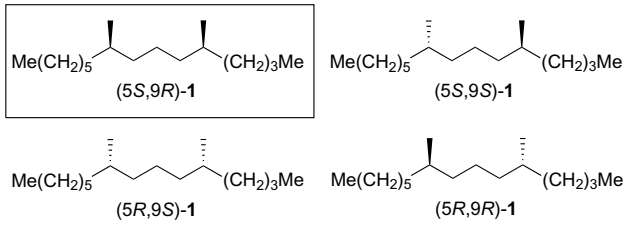

Figure 1. Structures of the stereoisomers of 5,9-dimethylpentadecane, the major component of the female sex pheromone of the coffee leaf miner moth.

As shown in Scheme 1, Kuwahara et al. converted the enantiomers of methyl 3-hydroxy-2-methylpropanoate to (*R*)-**2** and (*S*)-**4**, and employed methyl phenyl sulfone **3** as the linchpin to connect **2** and **4** as reported by us.[9] This was a reliable route, but rather complicated. Corrêa's route was straightforward by starting from neoisopulegol **5**, but quite lengthy via **6**. Accordingly, their syntheses provided only small amounts of (5*S*,9*R*)-**1**.[6,7]

2. Results and discussion

In our synthetic plan, as shown in Scheme 1, (*R*)-3-methyl-4-butanolide **7** and (*S*)-citronellal **8** were chosen as the starting materials. The former **7** (>99% ee[10]) was given to us by Dr. Sakashita of Mitsubishi Rayon Co., while the latter **8** (97% ee) was a commercial product of Takasago International Corporation. Both enantiomers of **8** are employed frequently in enantioselective synthesis.[11] Lactone **7** would give (*R*)-**2**, whose combination with (*S*)-**8** would eventually furnish (5*S*,9*R*)-**1**.

Scheme 2 summarizes our synthesis of (5*S*,9*R*)-**1**. The reduction of the lactone (*R*)-**7** with diisobutylaluminum

☆ Pheromone synthesis, Part 236. For Part 235, see Ref. 1.

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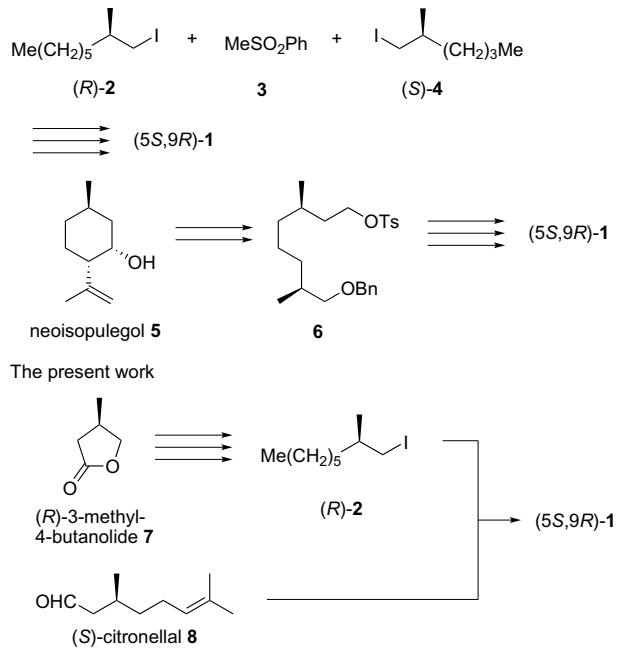
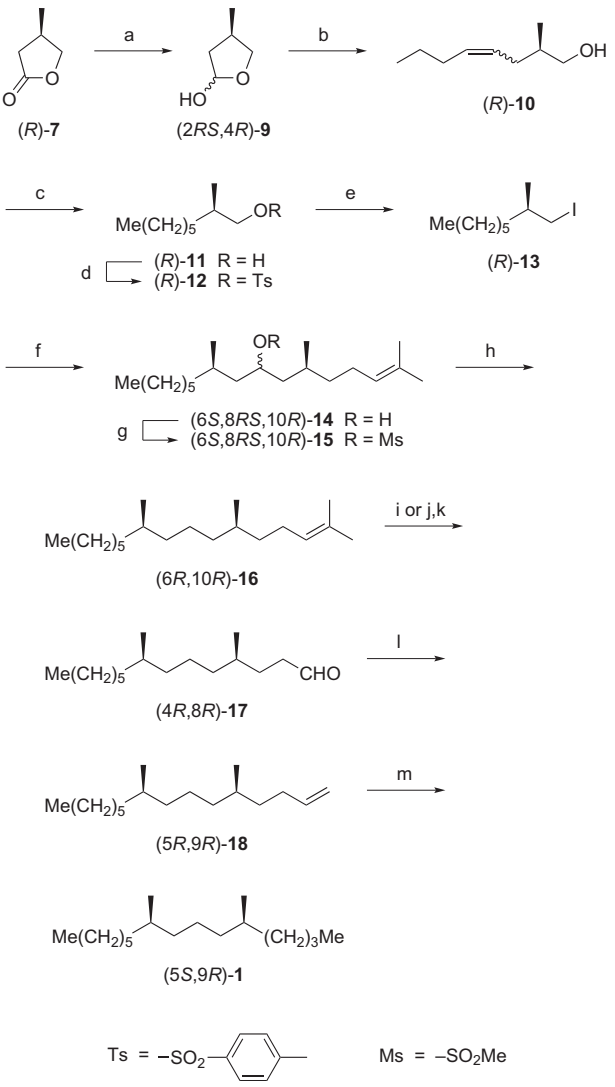


Scheme 1. Various syntheses of (5*S*,9*R*)-5,9-dimethylpentadecane.

hydride (DIBAL-H) gave lactol (2*RS*,4*R*)-**9**. This was treated with the Wittig reagent prepared from *n*-butyltriphenylphosphonium iodide and *n*-butyllithium in THF to give alkene (*R*)-**10** as an *E*/*Z*-mixture (*E*/*Z* = ca. 1:4 as judged by ^{13}C NMR analysis). The hydrogenation of (*R*)-**10** over palladium-charcoal afforded the known (*R*)-2-methyl-1-octanol **11**, $[\alpha]_D^{24} = +12.1$ (*c* 2.43, EtOH){Ref. 12 $[\alpha]_D^{25} = +13.2$ (*c* 1.63, EtOH)}. The corresponding tosylate **12** was subjected to the Finkelstein reaction with lithium bromide in *N*,*N*-dimethylformamide (DMF) to give the corresponding bromide. Unfortunately, conversion of this bromide to the Grignard reagent afforded a poor yield under conventional conditions with magnesium in THF.

Accordingly, we decided to employ (*R*)-2-methyloctyllithium instead of the Grignard reagent. Tosylate **12** was treated with sodium iodide in DMF to give iodide (*R*)-**13**. Transmetallation of **13** with *t*-butyllithium in pentane/ether[13,14] gave the lithio derivative, which was treated with (*S*)-citronellal **8** to give alcohol (6*S*,8*RS*,10*R*)-**14**. The corresponding mesylate **15** was reduced with lithium aluminum hydride to give alkene (6*R*,10*R*)-**16** in 64% yield based on (*R*)-**13**.

Lemieux–Johnson oxidation of **16** with osmium tetroxide and sodium periodate in aqueous THF furnished aldehyde (4*R*,8*R*)-**17**. An excessive reaction time (2–3 days) at this stage resulted in the further oxidation of **17** to the corresponding carboxylic acid. Purer **17** could be obtained in a better yield by the epoxidation of **16** with *m*-chloroperbenzoic acid (MCPBA) followed by the treatment of the resulting epoxide with periodic acid dihydrate in THF/Et_2O. The treatment of **17** with methylene triphenylphosphorane gave terminal alkene (5*R*,9*R*)-**18**. Finally, the hydrogenation of **18** over Adams platinum oxide in ethyl acetate afforded the desired (5*S*,9*R*)-5,9-dimethylpentadecane **1** as an oil, $[\alpha]_D^{25} = +1.0$ (*c* 2.23, $CHCl_3$) {Ref. 6 $[\alpha]_D^{21} = +1.1$ (*c* 3.81, $CHCl_3$)}. Its IR, ^1H, and ^{13}C NMR spectroscopic properties were in good agreement with those reported previously.[6,7] Although modern GC analysis on a chiral stationary phase does not allow the determination of the enantiomeric purity of synthetic **1**, it was thought to be 97% ee, reflecting the enantiomeric purity of the starting (*S*)-citronellal **8**.



Scheme 2. Synthesis of (5*S*,9*R*)-5,9-dimethylpentadecane **1**. Reagents and conditions: (a) DIBAL-H, THF, −60 to −55°C, 45 min, 92%; (b) Ph_3P(*n*-Bu)I, *n*-BuLi, THF, 10–20 °C, 1.25 h, 47%; (c) H_2, Pd–C, EtOH, room temp, 2 h, 92%; (d) TsCl, C_5H_5N, DMAP, 0–5 °C, 2 h, quant.; (e) NaI, DMF, 55–60 °C, 2 h, 97%; (f) *t*-BuLi (2 equiv), Et_2O, −70 to −50 °C, 20 min, then room temp, −70 to −40 °C, (*S*)-**8**, room temp, 1.5 h, 83%; (g) MsCl, CH_2Cl_2, C_5H_5N, 0–5 °C, 3 d, quant.; (h) $LiAlH_4$, THF, reflux, 1 h, 77%; (i) OsO_4, $NaIO_4$, THF, H_2O, room temp, 2 d, quant. (70% purity); (j) MCPBA, CH_2Cl_2, 0–5 °C, 45 min, quant.; (k) $HIO_4{\cdot}2H_2O$, THF, Et_2O, 0–5 °C, 20 min, 85%; (l) Ph_3P(Me)Br, *n*-BuLi, THF, 0–5 °C, 1 h, 81%; (m) H_2, PtO_2, EtOAc, room temp, 30 min, 96%.

3. Conclusion

In conclusion, (5*S*,9*R*)-5,9-dimethylpentadecane **1** was synthesized in 16% overall yield (12 steps) based on (*R*)-3-

methyl-4-butanolide **7** or 42% (7 steps) in turn based on (*S*)-citronellal **8**. The present synthesis was more efficient than the previous ones.[6,7] Since both the enantiomers of citronellal **8** are commercially available, the present route can also provide (5*R*,9*R*)-**1**.

At the time when the synthesis of (5*S*,9*R*)-**1** was completed, we were informed that a racemic and diastereomeric mixture of **1** showed sufficient pheromone activity for practical use in Brazil.[8] Zarbin et al. published the same biological observation.[4] The bioassay results of the four stereoisomers of **1** are unfortunately not reproducible but fluctuate. The absolute configuration of natural **1** therefore remains unknown.

4. Experimental

4.1. General

Boiling points are uncorrected values. Refractive indices (n_D) were measured on an Atago DMT-1 refractometer. The optical rotations were measured on a Jasco P-1020 polarimeter. IR spectra were measured on a Jasco FT/IR-410 spectrometer. ^{1}H NMR spectra (400 MHz, TMS at $\delta = 0.00$ as an internal standard) and ^{13}C NMR spectra (100 MHz, $CDCl_3$ at $\delta = 77.0$ as an internal standard) were recorded on a Jeol JNM-AL 400 spectrometer. GC–MS were measured on Agilent Technologies 5975 inert XL. HRMS were recorded on a Jeol JMS-SX102A. Column chromatography was carried out on Merck Kieselgel 60 Art 1.07734.

4.2. (2*RS*,4*R*)-4-Methyloxacyclopentan-2-ol 9

A solution of DIBAL-H (0.97 M in hexane, 45 mL 43.7 mmol) was added dropwise to a cooled and stirred solution of (*R*)-3-methyl-4-butanolide (**8**, Mitsubishi Rayon Co., >99% ee; bp 118–119 °C/42 Torr; $[\alpha]_D^{18} = +25.8$ (*c* 3.72, MeOH), $[\alpha]_D^{24} = +3.6$ (*c* 4.82, hexane), 4.0 g, 40 mmol) in dry THF (60 mL) at −60 to −55 °C over 15 min under Ar. After stirring for 30 min at −60 °C, the reaction was quenched by the addition of saturated NH_4Cl solution (15 mL) with stirring at −60 °C. The mixture was diluted with Et_2O (200 mL). Stirring was continued for 40 min at room temperature, when gelatinous precipitates of $Al(OH)_3$ appeared. The suspension was mixed with $MgSO_4$, and filtered through Celite. The filtrate was concentrated in vacuo to give 3.7 g (92%) of crude **9**; ν_{max} (film): 3402 (s, O–H), 1055 (s, C–O), 1001 (s, C–O). This was employed for the next step without further purification.

4.3. (2*R*,4*EZ*)-2-Methyl-4-octen-1-ol 10

To an ice-cooled and stirred suspension of $Ph_3P(n\text{-Bu})I$ (90.0 g, 202 mmol) in dry THF (240 mL) was added a solution of *n*-BuLi in hexane (1.6 M, 126 mL, 202 mmol) dropwise over 15 min at 10–15 °C under Ar. Then a solution of crude **9** (8.9 g, 87 mmol) in dry THF was added dropwise over 15 min to the ice-cooled and red solution of the resulting Wittig reagent at 10–15 °C with vigourous stirring. After stirring for 1 h at 15–20 °C, the mixture was diluted with $MeOH/H_2O$ (3:2, 100 mL), and extracted with hexane. The hexane extract was washed with $MeOH/H_2O$ (3:2, 100 mL), water and brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was distilled to give 5.9 g (47%) of **10** as an oil, bp 122–125 °C/55 Torr; $n_D^{23} = 1.4490$; $[\alpha]_D^{22} = +7.8$ (*c* 3.26, EtOH); ν_{max} (film): 3338 (s, O–H), 1039 (s, C–O); δ_H ($CDCl_3$): 0.87–0.94 (6H, m, 2 × CH_3), 1.33–1.42 (2H, m, 7-CH_2), 1.56 (1H, br s, O–H), 1.65–1.75 (1H, m, 2-CH), 1.85–2.18 (4H, m), 3.40–3.54 (2H, m, 1-CH_2), 5.35–5.50 (2H, CH=CH); δ_C ($CDCl_3$): 13.8, 16.5, 22.6, 29.3, 30.9, 34.7, 36.3, 68.0, 127.5 (*Z*), 128.0 (*E*), 131.0 (*Z*), 132.0 (*E*) (*Z*/*E* = ca. 4:1). HRMS calcd for $C_9H_{18}O$ (M^+) 142.1358; found, 142.1357.

4.4. (*R*)-2-Methyl-1-octanol 11

Palladium-charcoal (0.4 g, 10%) was added to a solution of **10** (5.85 g, 41 mmol) in EtOH (20 mL). The suspension was stirred under H_2 (balloon) for 2 h at room temperature. The catalyst was filtered off through Celite, and the solid was washed with EtOH. The combined solution was concentrated in vacuo. The residue was distilled to give 5.41 g (92%) of **11** as an oil, bp 128–133 °C/73 Torr or 119–121 °C/45 Torr; $n_D^{22} = 1.4338$; $[\alpha]_D^{24} = +12.1$ (*c* 2.43, EtOH); {Ref. 12: $[\alpha]_D^{25} = +13.2$ (*c* 1.63, EtOH)}; ν_{max} (film): 3354 (s, O–H), 1034 (s, C–O); δ_H ($CDCl_3$): 0.88 (3H, t, *J* 6.8; CH_2CH_3), 0.91 (3H, d, *J* 6.8, $CHCH_3$), 1.05–1.92 [12H, m (1.27, br s)], 1.48 (1H, br s), 1.60 (1H, m), 3.41 (1H, dd, *J* 6.8, 10.8 C*H*HOH), 3.50 (1H, dd, *J* 6.8, 10.8, CH*H*OH). HRMS calcd for $C_9H_{18}(M^+ - H_2O)$ 126.1409; found 126.1417.

4.5. (*R*)-2-Methyloctyl tosylate 12

Tosyl chloride (9.5 g, 50 mmol) was added portionwise to a stirred and ice-cooled solution of **11** (6.1 g, 42 mmol) in dry C_5H_5N (30 mL). A small amount (ca. 10 mg) of DMAP was added and the mixture was stirred at 0–5 °C for 2 h. Then Et_2O and ice-water were added to the mixture. The Et_2O layer was separated and the aqueous layer was extracted with Et_2O. The combined Et_2O solution was washed with H_2O, dil HCl, aq $NaHCO_3$ solution and brine, dried over $MgSO_4$, and concentrated in vacuo to give 12.9 g (quant.) of **12** as an oil, ν_{max} (film): 1599 (w, arom C=C), 1362 (s), 1178 (s), 1188 (s), 966 (s); δ_H ($CDCl_3$): 0.87 (3H, t, *J* 7.2, CH_2CH_3), 0.88 (3H, d, *J* 6.8, $CHCH_3$), 1.05–1.35 (10H, m), 1.76 (1H, m), 2.45 (3H, s, $C_6H_4CH_3$), 3.80 (1H, dd, *J* 6.8, 10.0, C*H*HOTs), 3.88 (1H, dd, *J* 6.8, 10.0, CH*H*OTs), 7.34 (2H, d, *J* 8.8, arom H), 7.79 (2H, d, *J* 8.8, arom H). This was employed for the next step without further purification.

4.6. (*R*)-2-Methyloctyl iodide 13

Sodium iodide (15.0 g, 100 mmol) was added to a solution of **12** (12.8 g, 43 mmol) in DMF (75 mL). The mixture was stirred and heated at 55–60 °C for 2 h. After cooling, the mixture was diluted with water, and extracted with hexane. The hexane extract was washed with water containing a trace amount of $Na_2S_2O_3$ and brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was distilled to give

10.6 g (97%) of **13** as an oil, bp 107–109 °C/10 Torr; $n_D^{23} = 1.4822$; $[\alpha]_D^{21} = -2.3$ (*c* 4.75, hexane); ν_{max} (film): 2956 (s), 2925 (s), 2854 (m), 1458 (m), 1377 (w), 1194 (m); δ_H ($CDCl_3$): 0.88 (3H, t, *J* 6.8, CH_2CH_3), 0.97 (3H, d, *J* 6.4, $CHCH_3$), 1.15–1.40 (10H, m), 1.44 (1H, m), 3.15 (1H, dd, *J* 5.6, 5.6, C*H*HI), 3.24 (1H, dd, *J* 5.6, 5.6, CH*H*I). HRMS calcd for $C_9H_{19}I$ 254.0531; found 254.0522.

4.7. (6*S*,8*RS*,10*R*)-2,6,10-Trimethyl-2-hexadecen-8-ol 14

A solution of *t*-BuLi in pentane (1.7 M, 12.5 mL, 21 mmol) was added dropwise to a stirred and cooled solution of **13** (2.54 g, 10 mmol) in dry Et_2O (20 mL) over 10 min at −70 to −50 °C under Ar. The mixture was stirred for 10 min at −70 °C, then warmed to room temperature, and left to stand for 30 min. The mixture was cooled again at −70 °C. A solution of (*S*)-**8** (Takasago, 97% ee, 1.39 g, 9 mmol) in dry Et_2O (5 mL) was added to the stirred and cooled mixture at −70 to −40°C over 5 min. Then the cooling bath was removed, and the stirred mixture was left to stand for 1.5 h at room temperature. The reaction was quenched with dil HCl–NH_4Cl and the mixture was extracted with Et_2O. The extract was washed with sat. $NaHCO_3$ solution and brine, dried over $MgSO_4$, and concentrated in vacuo. The crude product (2.87 g) was chromatographed over SiO_2 (20 g). Hydrocarbon impurities (0.3 g) were removed by elution with hexane. Subsequent elution with hexane/EtOAc (20:1) afforded 2.35 g (83%) of **14** as an oil, $n_D^{23} = 1.4585$; $[\alpha]_D^{21} = +1.7$ (*c* 2.64, hexane); ν_{max} (film): 3346 (s, O–H), 1061 (m), 1020 (m); δ_H ($CDCl_3$): 0.85–0.94 (9H, m, CH_3), 1.00–1.50 [18H, m(1.18 br s)], 1.55–1.65 (1H), 1.60 (3H, s, C=CCH_3), 1.68 (3H, s, C=CCH_3), 1.90–2.10 (2H, m, 3-CH_2), 3.74–3.82 (1H, m, C*H*OH), 5.10 (1H, t-like, C=CH). HRMS calcd for $C_{19}H_{38}O$ 282.2923; found 282.2924.

4.8. (6*S*,8*RS*,10*R*)-8-Methanesulfonyloxy-2,6,10-trimethyl-2-hexadecene 15

Methanesulfonyl chloride (2 mL = ca. 3.0 g, 26 mmol) was added dropwise to a stirred and ice-cooled solution of **14** (2.11 g, 7.5 mmol) in dry CH_2Cl_2 (10 mL) and dry pyridine (10 mL). The mixture was left to stand for three days in a refrigerator. The mixture was then diluted with ice-water, and extracted with Et_2O. The extract was washed with dil HCl, water, satd $NaHCO_3$ solution and brine, dried over $MgSO_4$, and concentrated in vacuo to give 2.8 g (quant.) of crude **15** as an oil, ν_{max} (film): 1338 (s), 1174 (s), 902 (s), δ_H ($CDCl_3$): 0.85–1.00 (9H, m, CH_3), 1.10–1.50 [16H, m (1.19 br s)], 1.58 (1H, m), 1.61 (3H, s, C=CCH_3), 1.68 (3H, s, C=CCH_3), 1.70–1.80 (1H, m), 1.90–2.10 (2H, m), 2.98 (3H, s, SO_2CH_3), 4.85–4.95 (1H, m, CHOMs), 5.10 (1H, m, C=CH). This was employed for the next step without further purification.

4.9. (6*S*,10*R*)-2,6,10-Trimethyl-2-hexadecene 16

A solution of **15** (2.8 g, 7.5 mmol) in dry THF (10 mL) was added to a stirred suspension of $LiAlH_4$ (0.8 g, 21 mmol) in dry THF (10 mL). The mixture was stirred and heated at reflux for 1 h. The reaction was quenched by the addition of water to a stirred and ice-cooled mixture. Next Et_2O and ice-dil HCl were added, and the mixture was extracted with Et_2O. The extract was washed with water, satd $NaHCO_3$ solution and brine, dried over $MgSO_4$, and concentrated in vacuo. The residue (2.4 g) was chromatographed over SiO_2 (20 g). Elution with hexane gave 1.79 g (77%) of **16**, $n_D^{22} = 1.4514$; $[\alpha]_D^{16} = +1.85$ (*c* 3.23, hexane); ν_{max} (film): 2956 (s), 2925 (s), 2856 (s), 1460 (m), 1377 (m), 970 (w), 829 (w), 725 (w); δ_H ($CDCl_3$): 0.83 (3H, d, *J* 6.4, $CHCH_3$), 0.86 (3H, d, *J* 6.8, $CHCH_3$), 0.88 (3H, t, *J* 6.4, CH_2CH_3), 1.00–1.42 (20H, m), 1.60 (3H, s), 1.68 (3H, s), 1.96 (2H, m, 4-CH_2), 5.10 (1H, t-like, C=CH). HRMS calcd for $C_{19}H_{38}$ 266.2974; found 266.2976.

4.10. (4*R*,8*R*)-4,8-Dimethyltetradecanal 17

4.10.1. Lemieux–Johnson oxidation of 16. A solution of OsO_4 (50 mg) in *t*-BuOH (5 mL) and powdered $NaIO_4$ (4.8 g, 22 mmol) were added to a stirred solution of **16** (1.70 g, 6.4 mmol) in a mixture of THF (30 mL) and water (10 mL) at room temperature under Ar. The stirring was continued for 2 d at room temperature, while the tan-colored mixture turned colorless. It was then diluted with water, and extracted with hexane. The extract was washed with water and brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was chromatographed over SiO_2 (20 g). Elution with hexane/EtOAc (10:1) gave **17** (1.66 g, quant), whose IR spectrum revealed contamination with the corresponding carboxylic acid. Further NMR analysis indicated that **17** was only of ca. 70% purity.

4.10.2. Epoxidation of 16 followed by cleavage of the epoxide. MCPBA (77% purity, 1.2 g, 5.4 mmol) was added portionwise to a stirred and ice-cooled solution of **16** (1.20 g, 4.5 mmol) in dry CH_2Cl_2 (20 mL) at 0–5 °C. After stirring for 45 min at 0–5 °C, the mixture was diluted with Et_2O. The solution was washed with K_2CO_3 solution containing a small amount of $Na_2S_2O_3$ and brine, dried over $MgSO_4$, and concentrated in vacuo to give 1.3 g (quant.) of the epoxide, ν_{max} (film): 1122 (m), 739 (w); δ_H ($CDCl_3$): 0.80–0.90 (9H, m, CH_3), 1.00–1.60 (22H, m), 1.27 [3H, s, $CH_3C(O)$], 1.31[3H, s, $CH_3C(O)$], 2.70 (1H, t, *J* 6, OCH). A solution of this epoxide (1.3 g, 4.5 mmol) in Et_2O (5 mL) was added dropwise to a stirred and ice-cooled solution of $HIO_4{\cdot}2H_2O$ (1.3 g, 5.7 mmol) in THF (25 mL) at 0–5 °C. After stirring for 20 min at 0–5 °C, the mixture was diluted with water, and extracted with Et_2O. The extract was washed with water, satd $NaHCO_3$ solution and brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was chromatographed over SiO_2 (15 g). Elution with hexane/EtOAc (10:1) gave 0.87 g (85%) of **17** as an oil, $n_D^{18} = 1.4490$; $[\alpha]_D^{22} = +1.33$ (*c* 3.41, hexane); ν_{max} (film): 2956 (s), 2925 (s), 2856 (s), 2713 (m, O=C–H), 1728 (s, C=O), 1462 (m), 1412 (w), 1379 (m), 1020 (w), 970 (w), 902 (w), 725 (w); δ_H ($CDCl_3$): 0.84 (3H, d, *J* 7.2, $CHCH_3$), 0.87 (3H, d, *J* 6.8 $CHCH_3$), 0.88 (3H, t, *J* 6.8, CH_2CH_3),0.90–1.70 (20H, m), 2.35–2.50 (2H, m, CH_2CHO), 9.77 (1H, t, *J* 2, C*H*O). HRMS calcd for $C_{16}H_{32}O$ 240.2453; found 240.2455.

4.11. (5*R*,9*R*)-5,9-Dimethyl-1-pentadecene 18

A solution of methylene triphenylphosphorane was prepared by adding a solution of *n*-BuLi in hexane (1.6 M, 4.5 mL, 7.2 mmol) to a stirred and ice-cooled suspension of Ph_3PMeBr (2.70 g, 7.2 mmol) in dry THF (30 mL) at 5–10 °C under Ar. A solution of **17** (0.87 g, 3.6 mmol) in dry THF (10 mL) was added dropwise to the stirred and ice-cooled Wittig reagent. The mixture was stirred at 0–5 °C for 1 h, quenched with a mixture of MeOH/water (3:2), and extracted with hexane. The hexane extract was washed with a mixture of MeOH/water (3:2), water and brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was chromatographed over SiO_2 (15 g). Elution with hexane gave 0.70 g (81%) of **18** as a colorless oil, $n_D^{20} = 1.4426$; $[\alpha]_D^{21} = +2.3$ (*c* 2.89, hexane); ν_{max} (film): 3078 (w), 2956 (s), 2925 (s), 2856 (s), 1641 (w, C=C), 1462 (m), 1377 (m), 993 (w), 908 (m, C=CH_2); δ_H ($CDCl_3$): 0.84 (3H, d, *J* 6.8, CHCH_3), 0.86 (3H, d, *J* 6.4 CHCH_3), 0.88 (3H, t, *J* 6.8, CH_2CH_3), 1.00–1.50 (20H, m), 2.05 (2H, m, C=CCH_2), 4.92 (1H, d-like, *J* 10, C=CH*H*), 4.98 (1H, d-like, *J* 17.2, C=CH*H*). HRMS calcd for $C_{17}H_{34}$ 238.2661; found 238.2656.

4.12. (5*S*,9*R*)-5,9-Dimethylpentadecane 1

Adams PtO_2 (100 mg) was added to a solution of **18** (0.60 g, 2.5 mmol) in EtOAc (10 mL). The suspension was vigorously stirred under H_2 (balloon) for 30 min at room temperature. The catalyst was removed by filtration through SiO_2 (3 g). The SiO_2 column was washed with hexane. The combined filtrate and washings were concentrated in vacuo to give 0.58 g (96%) of **1** as an oil, $n_D^{20} = 1.4371$; $[\alpha]_D^{23} = +1.0$ (*c* 2.23, $CHCl_3$); {Ref. 6 $[\alpha]_D^{21} = +1.1$ (*c* 3.81, $CHCl_3$)}; ν_{max} (film): 2956 (s), 2925 (s), 2856 (s), 1464 (m), 1377 (m), 727 (w); δ_H ($CDCl_3$): 0.84 (6H, d, *J* 6.4, 2 × CHCH_3), 0.882 (3H, t, *J* 6.8, CH_2CH_3), 0.887 (3H, t, *J* 6.8, CH_2CH_3), 1.00–1.45 (24H, m); δ_C ($CDCl_3$): 14.21, 14.26, 19.84, 22.78, 23.13, 24.54, 27.12, 29.42, 29.77, 32.03, 32.80, 32.82, 36.82, 37.14, 37.50. HRMS calcd for $C_{17}H_{36}$ 240.2817; found 240.2812.

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