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Note

Synthesis of All Four Possible Stereoisomers of 5,9-Dimethylpentadecane, the Major Sex Pheromone Component of the Coffee Leaf Miner Moth, *Perileucoptera coffeella*

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All of the four possible stereoisomers of 5,9-dimethylpentadecane, the major sex pheromone component of the coffee leaf miner moth (*Perileucoptera coffeella*), were synthesized by using the methyl esters of (*S*)- and (*R*)-3-hydroxy-2-methylpropanoic acid as chiral sources for the purpose of determining the stereochemistry of the pheromone.

Key words: sex pheromone; *Perileucoptera coffeella*; 5,9-dimethylpentadecane

The coffee leaf miner moth, *Perileucoptera coffeella*, is an important pest of coffee trees in Brazil. The female-produced sex pheromone of this leaf miner moth has been revealed by Francke *et al.* to consist of 5,9-dimethylpentadecane (**1**) and 5,9-dimethylhexadecane as the major and minor components, respectively (Scheme).[1)] A synthetic stereoisomeric mixture of the major component (**1**)[2)] has recently been shown to be practically useful as an attractant for male *P. coffeella* from a field trapping test conducted on a coffee plantation in Brazil.[3)] As the next step, we planned the synthesis of all of the four stereoisomers of **1** in order to determine the stereochemistry of the natural pheromone by monitoring the behavior of the moth to each stereoisomer. In this note, we describe the synthesis of the stereoisomers of **1** by using the methyl esters of (*S*)- and (*R*)-3-hydroxy-2-methylpropanoic acid, (*S*)-2 and (*R*)-**2**, as the chiral sources.

Following the procedure reported by Mori *et al.*,[4,5)] commercially available (*S*)-**2** was transformed into known alcohols (*S*)-**3** and (*S*)-**5**, which were then converted into the corresponding iodides [(*S*)-4 and (*S*)-**6**, respectively] by treating with a mixture of iodine, triphenylphosphine and imidazole in tetrahydrofuran.[6)] The corresponding enantiomers of the iodides, (*R*)-**4** and (*R*)-**6**, were also obtained analogously from (*R*)-**2** *via* the respective alcoholic precursors, (*R*)-**3** and (*R*)-**5**.[4,5,7)] The optical purity of each of these alcohols was determined to be virtually 100% e.e. from the ^{1}H-NMR analyses of their corresponding MTPA esters (see the Experimental section). Alkylation of the butyllithium-generated carbanion of methyl phenyl sulfone with (*S*)-**4** gave (*S*)-**7**[7)] in a 66% yield. Resulting sulfone (*S*)-**7** was then alkylated with (*S*)-**6** to give (5*S*,9*S*)-**8** in a 66% yield. Reductive removal of the sulfonyl moiety of (5*S*,9*S*)-**8** was first carried out by using sodium amalgam in ethanol in the presence or absence of disodium hydrogen phosphate.[8,9)] Under both conditons, however, a small amount of olefinic product(s) was produced together with the desired product, (5*S*,9*S*)-**1**, probably due to the elimination of benzenesulfinic acid caused by in situ-generated sodium ethoxide, although the amount of the by-product(s) produced was smaller under the former conditions. The same side reaction was recently observed by Shirai *et al.* in their synthesis of the pheromone components of the spring hemlock looper and pitch pine looper.[7)] By changing the reduction conditions from sodium amalgam in ethanol to lithium in liquid ethylamine,[9)] however, we could surpress this side reaction and obtain the desired product, (5*S*,9*S*)-**1**, in an 80% yield without contamination from the olefinic by-product(s). The (5*R*,9*S*)-isomer of **1** was similarly synthesized by alkylating (*S*)-**7** with (*R*)-**6**, this being followed by reduction of resulting sulfone (5*R*,9*S*)-**8** with lithium in liquid ethylamine in a 49% yield from the two steps. The other stereoisomers, (5*S*,9*R*)-**1**

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Abbreviation: MTPA, α-methoxy-α-(trifluoromethyl)phenylacetyl

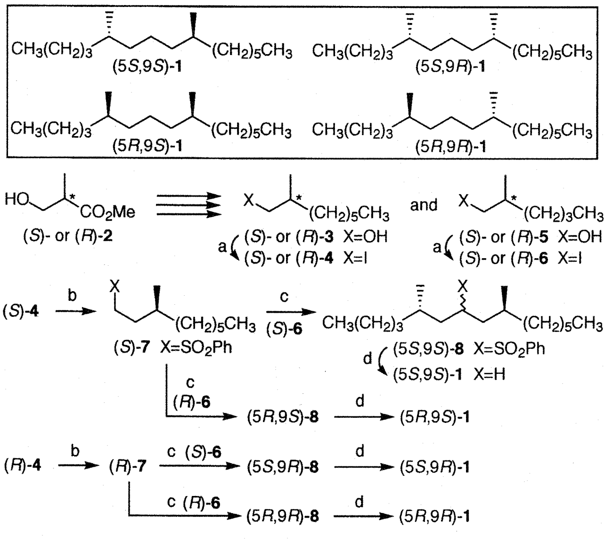
and (5*R*,9*R*)-**1**, were analogously derived from (*R*)-**4** *via* sulfone (*R*)-**7** in overall yields of 38% and 34%, respectively. The ^{1}H- and ^{13}C-NMR spectra of (5*S*,9*R*)-**1** and (5*R*,9*R*)-**1** were respectively identical with those of (5*R*,9*S*)-**1** and (5*S*,9*S*)-**1**. On the other hand, small but discernible differences between (5*R*,9*S*)-**1** and (5*S*,9*S*)-**1** were apparent in their ^{13}C-NMR spectra (see the Experimental section).

In conclusion, we accomplished the synthesis of all of the four stereoisomers of 5,9-dimethylpentadecane, the major sex pheromone component of *P. coffeella*, from commercially available (*S*)- and (*R*)-3-hydroxy-2-methylpropanoic acid methyl esters. The pheromonal activity of each stereoisomer is now being estimated by Prof. Vilela of Universidade Federal de Vicosa in Brazil, and the results will be reported elsewhere.

Experimental

IR spectra were measured with a Jasco FT/IR-5000 spectrometer, and ^{1}H-NMR spectra (500 MHz) were recorded with TMS as an internal standard in $CDCl_3$ by a Jeol JNM-A500 spectrometer. Optical rotation values were recorded with a Jasco DIP 370 spectrometer, and Merck silica gel 60 Art 7734 was used for silica gel column chromatography.

Determination of the optical purities of (S)- and (R)-3, and of (S)- and (R)-5. Each of the alcohols, (*S*)- and (*R*)-**3** (2 μl each), was treated overnight with (*S*)-MTPA chloride (6 μl) in pyridine (40 μl) at room temperature. Each reaction mixture was diluted with water, extracted with ether and finally concentrated *in vacuo* to give the corresponding (*R*)-MTPA ester, which was analyzed directly by ^{1}H-NMR. The signals due to the C-1 protons of the MTPA ester derived from (*S*)-**3** appeared at δ 4.07 (1H, dd, J = 11.0, 6.5 Hz) and δ 4.23 (1H, dd, J = 11.0, 5.5 Hz), while those derived from (*R*)-**3** were observed at δ 4.14 (1H, dd, J = 11.0, 6.0 Hz) and δ 4.16 (1H, dd, J = 11.0, 6.5 Hz). In each spectrum, no signals due to the corresponding diastereomers were apparent, which enabled us to conclude that both (*S*)- and (*R*)-**3** were optically pure. In a similar manner, (*S*)- and (*R*)-**5** were converted into the corresponding (*S*)-MTPA esters by treating with (*R*)-MTPA chloride. The C-1 protons of the MTPA ester derived from (*S*)-**5** resonated at δ 4.14 (1H, dd, J = 11.0, 6.0 Hz) and δ 4.16 (1H, dd, J = 11.0, 6.5 Hz), and those derived from (*R*)-**5** appeared at δ 4.07 (1H, dd, J = 11.0, and 6.5 Hz) and δ 4.23 (1H, dd, J = 11.0, 5.5 Hz), with no signals due to the corresponding diastereomer being apparent in either spectrum. Therefore, both (*S*)- and (*R*)-**5** were also determined to be optically pure.



Scheme. Synthesis of the Stereoisomers of the *P. coffeella* Pheromone. Reagents: a) I_2, Ph_3P, imidazole, THF; b) *n*-BuLi, methyl phenyl sulfone, THF-HMPA; c) *n*-BuLi, THF-HMPA; d) Li, $EtNH_2$

(S)- and (R)-1-iodo-2-methyloctane, [(*S*)-**4** and (*R*)-**4**], *and (S)- and (R)-1-iodo-2-methylhexane,* [(*S*)-**6** and (*R*)-**6**]. To a stirred mixture of (*S*)-**3** (3.00 g, 20.8 mmol), triphenylphosphine (6.54 g, 25.0 mmol) and imidazole (3.40 g, 44.9 mmol) in tetrahydrofuran (45 ml) was added portionwise iodine (6.33 g, 25.0 mmol) at room temperature. After 3 h, the reaction was quenched with 5% $Na_2S_2O_3$ aq., and the resulting mixture was extracted with ether. The ethereal solution was successively washed with 5% $Na_2S_2O_3$ aq., water and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was distilled to give 4.71 g (89%) of (*S*)-**4**. The other iodides, (*R*)-**4**, (*S*)-**6** and (*R*)-**6**, were similarly obtained in 83–90% yields. The optical rotation value of each iodide showed good agreement with that reported in the literature. (*S*)-**4**: bp 83–87°C (8 Torr); $[\alpha]_D^{21}$ +3.55° (c = 2.78, methanol), lit.5) $[\alpha]_D^{23.1}$ +3.42° (c = 3.10, methanol). (*R*)-**4**: bp 82–84 °C (8 Torr); $[\alpha]_D^{21}$ −3.64° (c = 2.05, methanol), lit.7) $[\alpha]_D^{25}$ −2.77° (c = 2.36, hexane). (*S*)-**6**: bp 81–83°C (24 Torr); $[\alpha]_D^{21}$ +2.78° (c = 3.37, methanol), lit.4) $[\alpha]_D^{23}$ +2.80° (c = 3.76, methanol). (*R*)-**6**: bp 80–83°C (24 Torr); $[\alpha]_D^{21}$ −3.27° (c = 3.34, methanol), lit.5) $[\alpha]_D^{22}$ −3.23° (c = 3.53, methanol).

(S)-3-Methyl-1-(phenylsulfonyl)nonane [(*S*)-**7**]. To a stirred solution of methyl phenyl sulfone (3.97 g, 25.4 mmol) in THF-HMPA (10:1, 110 ml) was added dropwise a solution of butyllithium in hexane (1.5 M, 16.9 ml, 25.4 mmol) at −78°C. After 30 min, a solution of (*S*)-**4** (4.61 g, 18.1 mmol) in THF (80 ml) was added, and the resulting mixture was allowed to warm gradually to room temperature over 10 h. The mixture was poured into sat. NH_4Cl aq. and extracted with ether. The ethereal solution was successively washed with water and brine, dried ($MgSO_4$) and

concentrated *in vacuo*. The residue was chromatographed over silica gel (80 g, hexane-ether, 15:1) to give 3.37 g (66%) of (*S*)-**7**, $[\alpha]_D^{21}$ +5.00° (c=4.00, chloroform), lit.[7] $[\alpha]_D^{23}$ +5.48° (c=1.58, chloroform). IR ν_{max} cm^{-1}: 3070 (s), 2960 (s), 2930 (s), 2860 (m), 1585 (w), 1460 (m), 1450 (m), 1405 (s), 1145 (s), 1090 (m), 790 (w), 745 (m). ^{1}H-NMR δ: 0.83 (3H, d, J=6.4 Hz, 3-CH_3), 0.87 (3H, t, J=7.0 Hz, 9-H_3), 1.10–1.30 (10H, m), 1.42–1.51 (1H, m, 3-H), 1.49–1.57 (1H, m, 2-H), 1.69–1.76 (1H, m, 2-H), 3.05 (1H, ddd, J=14.0, 11.0, 5.1 Hz, 1-H), 7.56–7.60 (2H, m, *m*-H_2), 7.64–7.68 (1H, m. *p*-H), 7.90–7.93 (2H, *o*-H_2). *Anal.* Found: C, 67.88; H, 9.29%. Calcd. for $C_{16}H_{26}O_2S$: C, 68.04; H, 9.28%.

(5S,7RS,9S)-5,9-Dimethyl -7-(phenylsulfonyl)pentadecane [(5*S*,9*S*)-**8**]. To a stirred solution of (*S*)-**7** (1.57 g, 5.56 mmol) in THF-HMPA (15:2, 34 ml) was added dropwise a solution of butyllithium in hexane (1.5 M, 4.08 ml, 6.12 mmol) at −78°C. After 30 min, a solution of (*S*)-**6** (1.38 g, 6.12 mmol) in THF (80 ml) was added, and the resulting mixture was allowed to warm gradually to room temperature over 10 h. The mixture was poured into sat. NH_4Cl aq. and extracted with ether. The ethereal solution was successively washed with water and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed over silica gel (40 g, hexane-ether, 15:1) to give 1.43 g (66%) of (5*S*,9*S*)-**8**, $[\alpha]_D^{21}$ +21.8° (c=2.26, chloroform). IR ν_{max} cm^{-1}: 3070 (w), 2960 (s), 2930 (s), 2860 (m), 1585 (w), 1460 (m), 1450 (m), 1380 (m), 1300 (s), 1150 (s), 1085 (m), 730 (s). ^{1}H-NMR δ: 0.768 (0.5×3H, d, J=6.5 Hz, 5-CH_3 or 9-CH_3), 0.771 (0.5×3H, d, J=6.5 Hz, 5-H_3 or 9-H_3), 0.84–0.90 (9H, m, 1-H_2, 15-H_3, 5-CH_3 or 9-CH_3), 0.95–1.07 (1H, m), 1.09–1.32 (H, m), 1.35–1.42 (1H, m), 1.42–1.48 (1H, m), 1.50–1.58 (1H, m), 1.61–1.67 (1H, m), 1.82–1.88 (1H, m), 3.03–3.08 (1H, m, 7-H), 7.54–7.58 (2H, m, *m*-H_2), 7.63–7.66 (1H, m, *p*-H), 7.87–7.89 (2H, m, *o*-H_2). *Anal.* Found: C, 72.59; H, 10.60%. Calcd. for $C_{23}H_{40}O_2S$: C, 72.58; H, 10.59%.

(5S,9S)-5,9-Dimethylpentadecane [(5*S*,9*S*)-**1**]. To stirred liquid ethylamine (30 ml) were added small pieces of lithium (0.54 g, 78 mmol) at −15 °C. After 30 min, a solution of (5*S*,9*S*)-**8** (0.570 g, 1.44 mmol) in THF (5 ml) was added, and the mixture was stirred at −15 °C for 2 h before being quenched with methanol. The mixture was stirred at room temperature for another 2 h to evaporate ethylamine, poured into sat. NH_4Cl aq. and extracted with ether. The ethereal solution was successively washed with water and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed over silica gel (Katayama silica gel 60 K230 W, 20 g, hexane) to give 0.28 g (80%) of (5*S*,9*S*)-**1**, $[\alpha]_D^{21}$ +6.23° (c=1.30, chloroform). IR ν_{max} cm^{-1}: 2960 (s), 2930 (s), 2860 (s), 1465 (m), 1380 (m), 1055 (w), 970 (w), 725 (w). ^{1}H-NMR δ: 0.840 (3H, d, J=6.6 Hz, 5-CH_3 or 9-CH_3), 0.842 (3H, d, J=6.6 Hz, 5-CH_3 or 9-CH_3), 0.88 (3H, t, J=7.0 Hz, 1-H_3 or 15-H_3), 0.89 (3H, t, J=7.0 Hz, 1-H_3 or 15-H_3), 1.03–1.12 (4H, m), 1.20–1.32 (22H, m), 1.32–1.40 (2H, m, 5-H, 9-H). ^{13}C-NMR δ: 14.03, 14.07, 19.64, 22.63, 22.98, 24.41, 27.00, 29.29, 29.63, 31.90, 32.68, 32.71, 36.79, 37.11, 37.34 (only 15 peaks were observed due to two overlapping peaks). *Anal.* Found: C, 84.89; H, 14.95%. Calcd. for $C_{17}H_{36}$: C, 84.91; H, 15.09%.

(5R,7RS,9S)-5,9-Dimethyl -7-(phenylsulfonyl)pentadecane [(5*R*,9*S*)-**8**]. In the same manner as that described for the preparation of (5*S*,9*S*)-**8**, coupling (*S*)-**7** (1.58 g, 5.56 mmol) with (*R*)-**6** (1.38 g, 6.12 mmol) afforded 1.33 g (60%) of (5*R*,9*S*)-**8**, $[\alpha]_D^{21}$ +0.47° (c=2.94, chloroform). IR ν_{max} cm^{-1}: 3070 (w), 2960 (s), 2930 (s), 2860 (m), 1585 (w), 1460 (m), 1450 (m), 1380 (m), 1300 (s), 1150 (s), 1085 (m), 730 (s). ^{1}H-NMR δ: 0.760 (0.5×3H, d, J=6.5 Hz, 5-CH_3 or 9-CH_3), 0.763 (0.5×3H, d, J=6.5 Hz, 5-H_3 or 9-H_3), 0.84–0.90 (9H, m, 1-H_2, 15-H_3, 5-CH_3 or 9-CH_3), 0.94–1.02 (1H, m), 1.03–1.15 (1H, m), 1.15–1.32 (H, m), 1.38–1.44 (1H, m), 1.44–1.51 (1H, m), 1.51–1.58 (1H, m), 1.64–1.70 (1H, m), 1.80–1.86 (1H, m), 3.01–3.09 (1H, m, 7-H), 7.54–7.58 (2H, br t, J=7.5 Hz, *m*-H_2), 7.62–7.66 (1H, m, *p*-H), 7.87–7.89 (2H, m, *o*-H_2). *Anal.* Found: C, 72.59; H, 10.55%. Calcd. for $C_{23}H_{40}O_2S$: C, 72.58; H, 10.59%.

(5R,9S)-5,9-Dimethylpentadecane [(5*R*,9*S*)-**1**]. In the same manner as that described for the preparation of (5*S*,9*S*)-**1**, reduction of (5*R*,9*S*)-**8** (1.33 g, 3.37 mmol) afforded 0.660 g (82%) of (5*R*,9*S*)-**1**, $[\alpha]_D^{21}$ −0.96° (c=4.18, chloroform). IR ν_{max} cm^{-1}: 2960 (s), 2930 (s), 2860 (s), 1465 (m), 1380 (m), 1055 (w), 970 (w), 725 (w). ^{1}H-NMR δ: 0.840 (3H, d, J=6.6 Hz, 5-CH_3 or 9-CH_3), 0.842 (3H, d, J=6.6 Hz, 5-CH_3 or 9-CH_3), 0.88 (3H, t, J=7.0 Hz, 1-H_3 or 15-H_3), 0.89 (3H, t, J=7.0 Hz, 1-H_3 or 15-H_3), 1.03–1.12 (4H, m), 1.20–1.32 (22H, m), 1.32–1.40 (2H, m, 5-H, 9-H). ^{13}C-NMR δ: 14.03, 14.07, 19.70, 22.63, 22.98, 24.41, 26.99, 29.28, 29.64, 31.90, 32.71, 32.73, 36.69, 37.02, 37.39 (only 15 peaks were observed due to two overlapping peaks). *Anal.* Found: C, 85.17; H, 15.12%. Calcd. for $C_{17}H_{36}$: C, 84.91; H, 15.09%.

(R)-3-Methyl -1-(phenylsulfonyl)nonane [(*R*)-**7**]. In the same manner as that described for the preparation of (*S*)-**7**, alkylation of methyl phenyl sulfone (5.55 g, 34.8 mmol) with (*R*)-**4** (5.90 g, 23.2 mmol) afforded 4.33 g (66%) of (*R*)-**7**, $[\alpha]_D^{21}$ −5.24 (c=4.21, chloroform). The IR and ^{1}H-NMR spectra were identical with those of (*S*)-**7**. *Anal.* Found: C, 67.78; H, 9.04%. Calcd. for $C_{16}H_{26}O_2S$: C, 68.04; H, 9.28%.

(5S,7RS,9R)-5,9-Dimethyl-7-(phenylsulfonyl)pentadecane [(5*S*,9*R*)-**8**]. In the same manner as that described for the preparation of (5*S*,9*S*)-**8**, coupling (*R*)-**7** (1.52 g, 5.50 mmol) with (*S*)-**6** (1.38 g, 6.02 mmol) afforded 1.39 g (64%) of (5*S*,9*R*)-**8**, $[\alpha]_D^{21}$ −19.4° ($c=2.45$, chloroform). The IR and ^{1}H-NMR spectra were identical with those of (5*R*,9*S*)-**8**. *Anal.* Found: C, 72.57; H, 10.50%. Calcd. for $C_{23}H_{40}O_2S$: C, 72.58; H, 10.59%.

(5S,9R)-5,9-Dimethylpentadecane [(5*S*,9*R*)-**1**]. In the same manner as that described for the preparation of (5*S*,9*S*)-**1**, reduction of (5*S*,9*R*)-**8** (0.81 g, 2.05 mmol) afforded 0.44 g (89%) of (5*S*,9*R*)-**1**, $[\alpha]_D^{21}$ +1.14° ($c=3.81$, chloroform). The IR, ^{1}H- and ^{13}C-NMR spectra were identical with those of (5*R*,9*S*)-**1**. *Anal.* Found: C, 84.82; H, 15.08%. Calcd. for $C_{17}H_{36}$: C, 84.91; H, 15.09%.

(5R,7RS,9R)-5,9-Dimethyl-7-(phenylsulfonyl)pentadecane [(5*R*,9*R*)-**8**]. In the same manner as that described for the preparation of (5*S*,9*S*)-**8**, coupling (*R*)-**7** (1.46 g, 5.28 mmol) with (*R*)-**6** (1.31 g, 5.81 mmol) afforded 1.17 g (56%) of (5*R*,9*R*)-**8**, $[\alpha]_D^{21}$ −19.4° ($c=2.45$, chloroform). The IR and ^{1}H-NMR spectra were identical with those of (5*S*,9*S*)-**8**. *Anal.* Found: C, 72.58; H, 10.61%. Calcd. for $C_{23}H_{40}O_2S$: C, 72.58; H, 10.59%.

(5R,9R)-5,9-Dimethylpentadecane [(5*R*,9*R*)-**1**]. In the same manner as that described for the preparation of (5*S*,9*S*)-**1**, reduction of (5*R*,9*R*)-**8** (1.17 g, 2.96 mmol) afforded 0.66 g (92%) of (5*R*,9*R*)-**1**, $[\alpha]_D^{21}$ −6.43° ($c=1.48$, chloroform). The IR, ^{1}H-and ^{13}C-NMR spectra were identical with those of (5*S*,9*S*)-**1**. *Anal.* Found: C, 84.91; H, 15.02%. Calcd. for $C_{17}H_{36}$: C, 84.91; H, 15.09%.

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