An Asymmetric Dihydroxylation Route to (3*R*,5*E*)-2,6-Dimethyl-2,3-epoxyocta-5,7-diene: The Major Volatile Component from Male Fruit-Spotting Bugs

Christopher J. Moore

Queensland Department of Primary Industries, Yeerongpilly, Queensland 4105, Australia

Sven Possner, Patricia Hayes, Gregory C. Paddon-Jones, and William Kitching*

Department of Chemistry, The University of Queensland, Brisbane, Queensland 4072, Australia

Received September 7, 1999

Introduction

The fruit-spotting bug, *Amblypelta nitida* (Heteroptera: Coreidae), and the banana spotting bug, *A. lutescens*, are very serious pests of most fruit and nut crops in tropical and subtropical Australia. There appear to be few natural enemies of this pest, and costly control is based largely on prophylactic use of endosulfan, but use of this agent has its troublesome aspects.[1] Some information on the chemistry of fruit-spotting bugs is available,[2] but in the case of *A. nitida* males, the major component of the aeration extract, which co-occurs with hexanal, *n*-hexyl acetate, and nonanal, is of unknown constitution. With the likelihood that this component would mediate communication in *A. nitida*, we now report the structure, synthesis, and absolute stereochemistry of this compound, which will expedite behavioral trials and possible biocontrol of this pest.

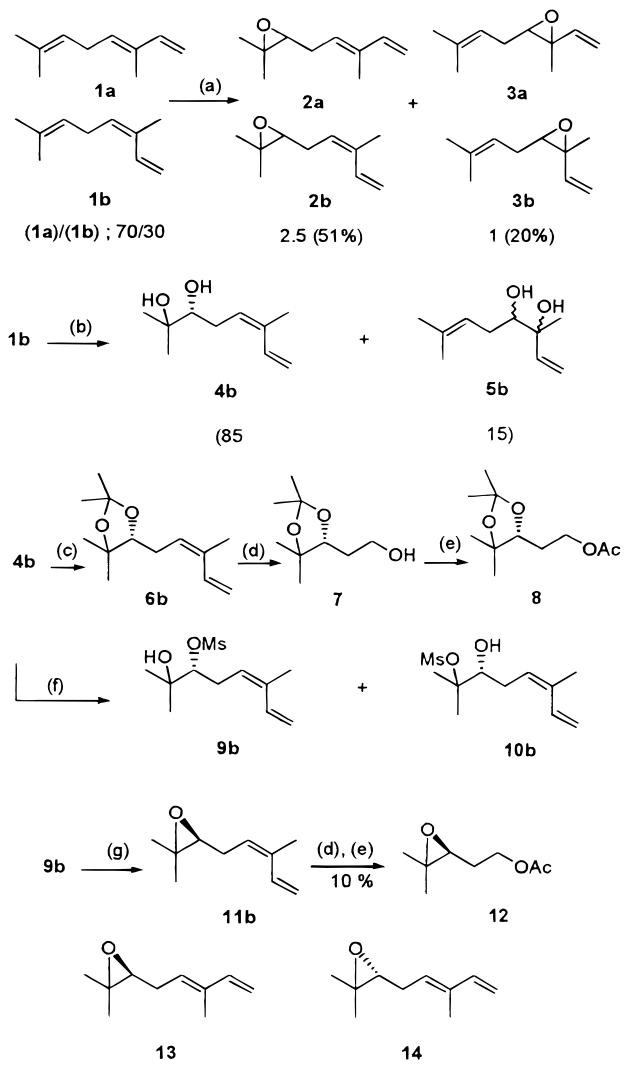
Results and Discussion

CI-MS analysis indicated a molecular weight of 152 for this dominant component, which lacked exchangeable protons and was unaffected by $NaBH_4$. No library match for the EI-MS was found, but a number of monoterpene epoxides with M = 152 could be eliminated.[2] On some occasions, significant levels of ocimene were present in the aeration volatiles, and hence, an "ocimene epoxide" (MW = 152) was considered a possibility.

Peracid epoxidation (*m*-CPBA) of an *E*/*Z* mixture of *β*-ocimene (**1a**, **1b**) yielded two regioisomeric epoxides, each as an isomeric pair. No epoxidation of the terminal double bond was observed (Scheme 1). GC−MS comparisons (including co-injections) of the natural epoxide with the separated isomers (**2a**, **2b**, **3a**, **3b**) established that the natural epoxide had the constitution **2a**, the first "ocimene epoxide" identified from a natural source.

The question of the absolute stereochemistry of (**2a**) was next addressed. In view of the 2,3-regioselectivity of peracid epoxidation, an approach to enantiomers of the epoxide system **2a**, **2b** based on asymmetric dihydroxylation of *β*-ocimene was considered. We were not aware of any report describing the dihydroxylation of a substrate incorporating both a trisubstituted double bond and a conjugated diene,[3] although other terpenoid systems had been examined.[4] Treatment of commercial *β*-ocimene (**1b**, >97% *Z*) with AD-Mix-*β* (in the presence of methanesulfonamide) in the normal way[3] led to predominant dihydroxylation of the isolated 2,3-double bond (~85%), along with a significant level (~15%) at the internal (5,6) double bond of the conjugated diene, in an overall yield

Scheme 1[a]



[a] Key: (a) *m*-CPBA, 71%; (b) AD-Mix-*β*, $CH_3SO_2NH_2$, *t*-BuOH/H_2O 1:1, 58%; (c) 2,2-dimethoxypropane, *p*-TsOH, CH_2Cl_2, 58%; (d) (i) O_3, DMS, CH_2Cl_2, (ii) $NaBH_4$, MeOH, 52%; (e) Ac_2O, Pyr, 100%; (f) CH_3SO_2Cl, Et_3N, CH_2Cl_2, rt, 100%; (g) K_2CO_3, MeOH, 45%.

* To whom correspondence should be addressed. E-mail: kitching@chemistry.uq.edu.au.

(1) See, for example, the Workshop Report: *Fruit Spotting Bug in North-Eastern Australia*; Waite, G., Fay, H., Rogers, J., Eds.; Cooperative Research Centre for Tropical Pest Management, 8 July, 1993, Mareeba, Qld.

(2) Aldrich, J. R.; Waite, G. K.; Moore, C. J.; Payne, J. A.; Lusby, W. R.; Kochansky, J. P. *J. Chem. Ecol.* **1993**, *19*, 2767. Baker, J. T.; Blake, J. D.; Macleod, J. K.; Ironside, D. A.; Johnson, I. C. *Aust. J. Chem.* **1972**, *25*, 393.

(3) (a) Sharpless, K. B.; Augbery, W.; Bennano, Y. L. Crispiro, G. A.; Hartung, J.; Jeong, K.-S.; Kwong, H.-L.; Morikawa, K.; Wang, Z.-M.; Xu, D.; Zhang, X.-L. *J. Org. Chem.* **1992**, *57*, 2768. (b) Kolb, H. C.; VanNieuwenlize, M. S.; Sharpless, K. B. *Chem. Rev.* **1994**, *94*, 2483.

(4) Vidari, G.; Dapiaggi, A.; Zanoni, G.; Garlaschelli, L. *Tetrahedron Lett.* **1993**, *34*, 6485.

10.1021/jo991407t CCC: $18.00
Published on Web 11/25/1999

of 58% (Scheme 1). It is possible to conclude from the mnemonic of Sharpless,[3] depending on how R_L, R_M, and R_S are assigned, that the major diol **4b** is the 3*R* isomer,[5] but **5b** is left unassigned.

Flash chromatography led to separation of the required **4b** from **5b**, and the former was converted to its acetonide **6b**, but this was not sufficiently separated into enantiomers on the *β*-cyclodextrin column to assay the induction level in the AD-reaction. Ozonolysis−reduction ($NaBH_4$) of **6b** provided protected triol **7** with $[\alpha]^{23}_D$ +19.6 (*c* 0.82, EtOH), which may be compared with $[\alpha]^{22}_D$ −21.2 (EtOH)[6] and −21.0 (EtOH)[7] reported for the enantiomer. This indicates an ee of at least 96% in the AD reaction, which is supported by enantioselective gas chromatography of the derived acetate **8** and its racemate (Scheme 1).

Mono-mesylation of the diol (**4b**) at the secondary center (C-3) followed by mild base treatment was envisaged to form the epoxide with inversion of configuration, thus providing the (3*S*)-epoxide. Treatment of the diol with 1 equiv of freshly distilled mesyl chloride, in the presence of Et_3N, led to monomesylate formation, with the secondary/tertiary ratio (i.e., **9b**:**10b**) dependent on the temperature of mesylation. At −15 °C, secondary mesylation was hardly detectable; at 0 °C the mixture was ca. 2:1 in favor of the secondary mesylate, but at 23 °C, was ca. 7:1 (Scheme 1). This is based on the observation that mesylation of the secondary alcohol to form **9b** causes a substantial downfield shift of the methine proton resonance from *δ* 3.40 to *δ* 4.45, whereas mesylation of the adjacent *tert*-alcohol to form **10b** hardly affects this chemical shift. This temperature variation in mesylation selectivity is presumably associated with conformer populations and hydroxyl group accessibility within these. There was no NMR evidence that chloride ion displacement of secondary mesylate intervened prior to base treatment and epoxide formation. This was further confirmed by the very high ee's of the final epoxides, as chloride intervention prior to cyclization would provide an overall racemizing effect.

Stirring a predominantly secondary mesylate mixture (**9b**, **10b**) with K_2CO_3 in MeOH caused rapid conversion (∼30 min, rt) to the epoxide **11b** (Scheme 1), whereas the minor *tert*-mesylate **10b** reacted much more slowly and did not form an epoxide. The pure epoxide **11b** (flash chromatography), exhibited $[\alpha]^{25}_D$ −3.5 (*c* 2.38, $CHCl_3$) and was nicely separated into its enantiomers on a *β*-cyclodextrin phase and showed >95% ee. Confirmation that **11b** is *S*-configured was provided in the following way. The epoxide on ozonolysis, reduction, and acetylation provided **12** of >97% ee based on enantioselective gas chromatographic comparisons with the separately synthesized racemic acetate and with $[\alpha]^{23}_D$ −19.5 (*c* 0.4, $CHCl_3$). This latter value may be compared with the literature value of $[\alpha]^{25}_D$ +3.70, for the predominantly 3*R* isomer (27% ee,)[8] which was stereochemically correlated with authentic (*S*)-(−)-4-methyl-1,3-pentanediol in turn previously related to L-(−)-glyceraldehyde.[9] A calculated value of $[\alpha]^{25}_D$ +13.7 for the optically pure 3*R* isomer may be deduced from the published data,[8] which were based on Mosher ester analyses.

The sequence of reactions (outlined in Scheme 1) that commences with (*Z*)-*β*-ocimene (**1b**) has also been conducted with predominantly (*E*)-*β*-ocimene (*E*:*Z* 70:30), so that the corresponding compounds including the *E* isomer **13** have been acquired. With the availability of **11b** and its *E* isomer **13** ($[\alpha]^{25}_D$ −5.0 (*c* 1.1, CH_2Cl_2)), of known absolute configuration, GC comparisons, including coinjection studies, established that the major volatile component from *A. nitida* males is **14**, i.e., the title compound with 3*R*,5*E* stereochemistry. Behavioral studies are planned.

Experimental Section

General Methods. ^1H NMR spectra were recorded at 400 and 200 MHz and ^{13}C NMR spectra at 50 and 100 MHz, with either TMS (*δ* = 0) or the signal for residual $CHCl_3$ in the $CDCl_3$ solvent (*δ*7.24) as internal standards for ^1H NMR and the central peak of the $CDCl_3$ triplet (*δ* = 77.00 ppm) for ^{13}C NMR spectra. *J* values are reported in Hz. Flash chromatography was performed with Kiesel S (0.032−0.063 mm). Enantioselective gas chromatography was conducted using a permethylated *β*-cyclodextrin column (SGE, 50 m; 0.25 *μ*m).

(±)-(5*E*,*Z*)-2,6-Dimethyl-2−3-epoxyocta-5,7-diene (2a, 2b). A mixture of (*E*)- and (*Z*)-*β*-ocimene (**1a**/**1b** = 70:30) (205 mg, 1.5 mmol) was dissolved in CH_2Cl_2 (10 mL), and *m*-chloroperbenzoic acid (325 mg, 1.5 mmol, technical grade, 80%) was added to this stirred and cooled (0 °C) solution. After being stirred at room temperature (1 h), the solution was washed with aqueous sodium hydrogen carbonate. The separated organic phase was dried (Na_2SO_4) and carefully reduced in volume. The regioisomeric epoxides **2** and **3** were separated by flash chromatography on silica gel with 5% ethyl acetate in hexane as eluant, with **3** eluting earlier. The *E*,*Z* isomers **2a**,**b** and **3a**,**b** were separated by normal-phase HPLC using 1% diethyl ether in hexane. In this way, 115 mg (0.76 mmol) (51%) of **2a**,**b** and 45 mg (0.3 mmol) (20%) of **3a**,**b** were obtained prior to HPLC separation of these *E*,*Z* pairs. **2a**: ^1H NMR ($CDCl_3$, 200 MHz) *δ* 6.38 (dd, *J* 17.3, 10.0, H7), 5.51 (t, *J* 7.7, H5), 5.12 (d, *J* 17.3, H8a), 4.97 (d, *J* 10.8, H8b), 2.76 (t, *J* 6.4, H3), 2.46 (ddd, *J* 15.4, 6.7, 6.7, H4a), 2.29 (ddd, *J* 15.4, 6.7, 6.7, H4b), 1.75 (s, CH_3), 1.30 (s, CH_3), 1.29 (s, CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz) *δ* 141.1 (C7), 136.1 (C6), 127.0 (C5), 111.6 (C8), 63.4 (C3), 58.4 (C2), 28.3 (C4), 24.8 (CH_3), 18.7 (CH_3), 11.9 (CH_3). **2b**: ^1H NMR ($CDCl_3$, 200 MHz) *δ* 6.72 (ddd, *J* 17.3, 10.8, 8.0, H7), 5.41 (t, *J* 7.6, H5), 5.23 (d, *J* 17.2, H8a), 5.12 (d, *J* 10.8, H8b), 2.74 (t, *J* 6.4, H3), 2.47 (ddd, *J* 15.4, 7.0, 7.0, H4a), 2.32 (ddd, *J* 15.4, 7.0, 7.0, H4b), 1.83 (dd, *J* 2.4, 1.2, CH_3), 1.30 (s, CH_3), 1.29 (s, CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz) *δ* 134.6 (C7), 133.3 (C6), 124.9 (C5), 114.4 (C8), 63.6 (C3), 58.4 (C2), 27.4 (C4), 24.8 (CH_3), 18.7 (CH_3), 19.8 (CH_3); HREIMS calcd for $C_{10}H_{16}O$ 152.1201, found 152.1199. **3a**: ^1H NMR ($CDCl_3$, 400 MHz) *δ* 5.65 (dd, *J* 17.4, 10.7, H7), 5.26 (dd, *J* 17.4, 1.1, H8a), 5.15 (dd, *J* 10.7, 1.1, H8b), 2.78 (t, *J* 6.4, H5), 2.37 (m, H4), 2.19 (m, H4b), 1.71 (d, *J* 1.1, CH_3), 1.52 (s, CH_3), 1.40 (s, CH_3); ^{13}C NMR ($CDCl_3$, 50 HMz) *δ* 140.9, 136.1, 118.6, 115.7, 64.8, 59.5, 28.0, 25.7, 17.9, 15.0. **3b**: ^1H NMR ($CDCl_3$, 400 MHz) *δ* 5.82 (dd, *J* 17.4, 10.9, H7), 2.87 (t, *J* 6.4, H5), 2.26 (m, H4a), 2.08 (m, H4b), 1.69 (d, *J* 1.1, CH_3), 1.40 (s, CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz) *δ* 134.5, 118.8, 117.7, 65.4, 60.4, 29.7, 25.7, 21.6, 17.9 (one signal not located). The data for the minor isomers **3a** and **3b** are incomplete because of some signal overlapping and low quantities. The ^1H NMR and mass spectral data match those reported for **2a** and **2b** acquired by H_2O_2 epoxidation in the presence of sodium tungstate.[10]

(5) This is consistent with the observation that treatment of 5-bromo-2-methyl-2-pentene with AD-Mix-α etc. forms (3*S*)-5-bromo-2-methylpentane-2,3-diol. Vidari, G.; Landranchi, G.; Sartore, P.; Serra, S. *Tetrahedron: Asymmetry* **1995**, *6*, 2977.

(6) Meier, V. H.; Uëbelhart, P.; Eugster, C. H. *Helv. Chim. Acta* **1986**, *69*, 106.

(7) Nakagawa, N.; Mori, K. *Agric. Biol. Chem.* **1984**, *48*, 2799.

(8) Rossiter, B. E.; Sharpless, K. B. *J. Org. Chem.* **1984**, *49*, 3707.

(9) Büchi, G.; Crombie, L.; Godin, P. J.; Kaltenbronn, J. S.; Siddalingaiah, K. S.; Whiting, D. A. *J. Chem. Soc.* **1961**, 2843. (*R*)-(+)-4-methyl-1,3-pentanediol derived from (*R*)-(+)-4-methyl-3,4-epoxypentanol of 27% ee had $[\alpha]^{22}_D$ +6.67 ($CHCl_3$),[8] whereas (*S*)-(−)4-methyl-1,3-pentanediol exhibited $[\alpha]^{27}_D$ −6.9 ($CHCl_3$), indicating incomplete optical resolution of (±)-3-hydroxy-4-methylpentanoic acid.

(10) Anisimov, A. V.; Chau, F. L.; Tarakanova, A. V.; Lebedev, M. Yu.; Berentoreig, V. V. *Zh. Org. Kh.* **1992**, *28*, 1403.

(3*R*,5*Z*)-2,6-Dimethyl-5,7-diene-2,3-diol (4b). Water (36 mL) and *tert*-butyl alcohol (36 mL) were mixed in a 100 mL round-bottom flask, and AD-Mix β (Aldrich) (10.28 g) was added. This two-phase mixture was cooled to 0 °C, and $CH_3SO_2NH_2$ (680 mg) was added. (*Z*)-β-Ocimene (97%, Fluka) (1.00 g, 7.35 mmol) was then added, and the mixture was stirred at 0 °C for 84 h. The reaction was treated with sodium sulfite (11 g) at 0 °C and then allowed to warm to room temperature. The diols **4b** and **5b** were extracted into CH_2Cl_2 (3 × 50 mL), which was separated, dried ($MgSO_4$), and concentrated on a rotary evaporator. The resulting yellow oil was immediately purified by flash chromatography (silica gel, 10% EtOAc in hexane), which furnished, in order of elution, the minor isomer **5b** (123 mg, ∼10%) and the major desired isomer **4b** (600 mg, ∼48%). **4b**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.73 (ddd, *J* 17.3, 10.8. 0.8, H7), 5.46 (t, *J* 7.8, H5), 5.24 (d, *J* 17.3, H8a), 5.12 (d, *J* 10.8, H8b), 3.41 (t, *J* 6.6, H3), 2.32 (t, *J* 6.6, H4), 2.09 (brs, OH), 1.85 (s, CH_3), 1.68 (brs, OH), 1.22 (s, CH_3), 1.17 (s, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 135.1 (C6), 133.2 (C7), 126.8 (C5), 114.7 (C8), 77.9 (C3), 72.7 (C2), 29.8 (C4), 26.5 (CH_3), 23.6 (CH_3), 19.9 (CH_3). Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.70. Found: C, 70.63; H, 10.71.

Dioxolane (6b). Diol **4b** (100 mg, 0.59 mmol) was dissolved in CH_2Cl_2−dimethoxypropane (10 mL, 1:1) to which was added *p*-toluenesulfonic acid (∼5 mg). The mixture was stirred for 5 h, quenched by the addition of aqueous $NaHCO_3$, and stirred for 10 min. The reaction mixture was extracted with ether and washed with saturated NaCl solution. The ether extracts were dried ($MgSO_4$), carefully reduced in volume, and then chromatographed (silica gel, petroleum ether) to furnish **6b** (72 mg, 58%). **6b**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.73 (ddd, *J* 17.2, 10.8, 0.8, H7), 5.39 (t, *J* 7.4, H5), 5.22 (d, *J* 17.2, H8a), 5.12 (dt, *J* 10.8, 1.5, H8b), 3.72 (dd, *J* 7.9, 5.7, H3), 2.44−2.31 (m, H4), 1.82 (q, *J* 1.2 CH_3), 1.40 (s, CH_3), 1.32 (s, CH_3), 1.22 (s, CH_3) 1.10 (s, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 134.1, (C6), 133.3 (C7), 125.9 (C5), 114.4 (C8), 106.6, 83.0 (C2), 80.2 (C3), 28.5, 27.6, 26.9, 26.2, 22.9, 19.8; HREIMS calcd for $C_{12}H_{18}O_2$ (M − 15) 195.1385, found 195.1379.

(*R*)-(+)-2-(2,2,4,4-Tetramethyl-1,3-dioxolan-5-yl)ethanol (7). Dioxolane (**6b**) (70 mg, 0.33 mmol) was dissolved in CH_2Cl_2 (5 mL), cooled to −78 °C, and treated with O_3 until a blue color persisted, which was then discharged with the O_2 flow. Dimethyl sulfide (excess) was added to the cooled solution, which was allowed to warm to room temperature. After 2 h, $NaBH_4$ (63 mg, 5 equiv) in MeOH (1 mL) was added, and the mixture was stirred at room temperature for 12 h. Saturated NH_4Cl solution was added followed by extraction with ether, which was separated and dried ($MgSO_4$). The desired alcohol (**7**) was purified by flash chromatography (silica gel, ether/petroleum ether 1:1) to provide 30 mg (52%). The ^{1}H NMR spectrum matched those previously reported:[6,11] ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.1, 25.8, 27.0, 28.5, 31.7, 61.5, 80.4, 82.4, 107.2; $[\alpha]^{23}_D$ +19.6 (*c* 0.82, EtOH).

(*R*)-(+)-2-(2,2,4,4-Tetramethyl-1,3-dioxolan-5-yl)ethyl Acetate (8). Alcohol **7** (10 mg, 0.06 mmol) in CH_2Cl_2 (1 mL) was treated with acetic anhydride (50 μL) and pyridine (100 μL) and stirred overnight. Saturated $CuSO_4$ solution was added, and the organic phase was separated, dried ($MgSO_4$), and concentrated to provide the essentially pure acetate **8**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.26 (ddd, *J* 10.9, 7.5, 5.2, H5a), 4.12 (ddd, *J* 10.9, 7.2, 7.0, H5b), 3.75 (dd, *J* 9.8, 3.1, H3), 2.03 (s, CH_3), 1.81 (dtd, *J* 14.0, 4.5, 1.6, H4a), 1.71 (dtd, *J* 14.0, 7.6, 3.2, H4b), 1.38 (d, *J* 0.5, CH_3), 1.30 (d, *J* 0.5, CH_3), 1.23 (s, CH_3), 1.08 (s, CH_3);. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 171.0, 107.0, 80.1, 79.9, 62.1, 28.8, 28.5, 26.9, 25.8, 22.5, 20.9; HREIMS calcd for $C_{10}H_{17}O_4$ (M − 15) 201.1126, found 201.1133.

(3*S*,5*Z*)-2,6-Dimethyl-2,3-epoxyocta-5,7-diene (11b). Diol **4b** (468 mg, 2.75 mmol) was dissolved in CH_2Cl_2 (7 mL) together with Et_3N (440 μL), and the solution was cooled to 0 °C before the addition of freshly distilled (P_2O_5) methanesulfonyl chloride (187 μL). This mixture was then allowed to warm to room temperature and stirred for 3 h, after which ether (1 mL) was added, followed by filtration through a pad of Celite and concentration. The secondary mesylate (**9b**) had formed almost quantitatively as judged by the ^{1}H NMR spectrum: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.69 (ddd, J17.3, 10.8, 0.9, H7), 5.44 (t, 7.7, H6), 5.28 (brd, *J* 17.2, H8a), 5.14 (dt, *J* 10.8, 1.5, H8b), 4.54 (dd, *J* 9.6, 3.2, H3), 2.95 (s, CH_3), 2.4−2.7 (m, 2H), 1.70 (s, CH_3), 1.27 (s, CH_3), 1.25 (s, CH_3); EIMS (*m*/*z*) 230 (0.4, M^+ -18), 152 (6.3), 134 (5.7), 123 (13.7), 111 (4.8), 109 (16.5), 107 (20.6), 93 (18.5), 82 (26.9), 71 (25.7), 67 (29.6), 55 (18.2), 43 (100), 41 (25.5). The above mesylate **9b** was not purified but processed to the epoxide **11b** by dissolution in MeOH (8 mL) to which was added dry K_2CO_3 (742 mg, 2 equiv). The reaction mixture was stirred for ca. 0.5 h, after which time GC examination confirmed complete consumption of the mesylate **9b**. Concentration was followed by dilution with H_2O and extraction with CH_2Cl_2. The separated organic phase was dried ($MgSO_4$) and carefully concentrated to provide epoxide **11b**. Flash chromatography on silica gel (1% ethyl acetate/hexane) provided 190 mg of (**11**b) (45% from diol (**4b**)) with $[\alpha]^{25}_D$ −3.5 (*c* 2.38, $CHCl_3$). The ^{1}H and ^{13}C NMR spectra are listed above for the corresponding racemic epoxide **2b**. (*E*)-Epoxide **13** was acquired utilizing the procedure outlined above, but applied to a 70:30 *E*/*Z* mixture of β-ocimene and had $[\alpha]^{25}$ −5.09 (*c* 1.09, CH_2Cl_2). The ^{1}H and ^{13}C NMR spectra are listed above for the corresponding racemic epoxide **2a**.

(−)-(*S*)-4-Methyl-3,4-epoxypentan-1-ol Acetate (12). Epoxide **11b** was ozonized and reduced to the primary alcohol and acetylated as described above for the conversion of **6b** to **8**. The ^{1}H NMR spectrum and EI mass spectrum matched those previously reported:[8] ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.7, 20.9, 24.7, 28.5, 58.2, 61.3, 61.8, 171.0; $[\alpha]^{23}_D$ −19.5 (*c* 0.4, $CHCl_3$). Authentic (±)-**12** was prepared by peracid epoxidation of commercially available 4-methylpent-3-enol, followed by acetylation.

Acknowledgment. The authors are grateful to Geoff Waite and Russell Parker of the Queensland Horticulture Institute for the supply of fruit-spotting bugs.

Supporting Information Available: Copies of the ^{1}H and ^{13}C NMR spectra of compounds **2a**, **6b** and **8**. This material is available via the Internet at http://pub.acs.org.

JO991407T

(11) Terashima, S.; Tseng, C. C.; Hayashi, M.; Koga, K. *Chem. Pharm. Bull.* **1979**, *27*, 758.