Pergamon

Tetrahedron 58 (2002) 315–319

TETRAHEDRON

Identification and synthesis of homoterpenoids emitted from elm leaves after elicitation by beetle eggs

Robert Wegener and Stefan Schulz*

Institut für Organische Chemie, Technische Universität Braunschweig, Hagenring 30, D-38106 Braunschweig, Germany

Received 4 July 2001; revised 9 October 2001; accepted 9 November 2001

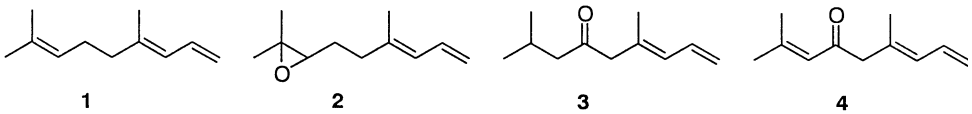
Abstract—Egg deposition of the elm leaf beetle *Xanthogaleruca luteola* on the leaves of the field elm causes the emission of volatiles attracting the parasitoid *Oomyzus gallerucae*. The present study describes the identification and synthesis of the homoterpenoids: (*E*)-2,6-dimethyl-6,8-nonadien-4-one, (*E*)-2,6-dimethyl-2,6,8-nonatrien-4-one, and (*R*,*E*)-2,3-epoxy-2,6-dimethyl-6,8-nonadiene. These compounds may be involved in attracting the egg parasitoid.

1. Introduction

The field elm, *Ulmus minor*, is the food plant of the elm leaf beetle, *Xanthogaleruca luteola* (Coleoptera, Chrysomelidae), which is a known pest species. The beetle deposits its eggs on the elm leaves which causes the emission of volatiles guiding a parasitoid wasp, *Oomyzus gallerucae* (Hymenoptera, Eulophidae), to these leaves.[1] The parasitoid lays its eggs inside the beetle eggs, which is beneficial for the elm. Host plants emitting volatiles in response to an external cue is a known defense mechanism.[2] The homoterpene (*E*)-4,8-dimethyl-1,3,7-nonatriene **1** (DMNT, Scheme 1) is a typical example of such an induced volatile; it is produced in response to herbivory by a variety of plants (e.g. Dicke[2]). We recently reported that terpenes are the major volatiles induced in the elm tree by the egg deposition of *X. luteola*, and that sesquiterpenes released after treatment of leaves with the plant hormone jasmonic acid attract the parasitoid.[3] Nevertheless, the volatile profiles induced by jasmonic acid or the eggs are not identical, and, besides sesquiterpenes, monoterpenes and homoterpenes are induced as well. In the present paper, we report on the identification and synthesis of new derivatives of homoterpenoids.

2. Results and discussion

The gas chromatography–mass spectrometry analysis of extracts obtained by headspace sampling with a modified closed-loop-stripping apparatus[4] of elm leaves with beetle eggs revealed **1** as the major homoterpene,[3] accompanied by three minor oxygenated analogues. Isolation of these components was not possible because of their low concentration in the headspace samples. The mass spectrum of compound **2** (Fig. 1), is similar to the spectrum of the related monoterpene epoxyocimene.[5] Epoxidation of **1** with 3-chloro-perbenzoic acid (MCPBA)[6] proved that this compound was the epoxyhomoterpene **2**, which has previously been reported as a constituent of several orchid and cactus scents (e.g. *Selenicereus hamatus*).[7] However, the stereochemistry of **2** has not been established previously and no mass spectrum has been published. To elucidate the enantiomeric composition of natural **2**, we synthesized this epoxide via an asymmetric dihydroxylation route (Scheme 2). Reaction of **1**[8] with AD-mix-β resulted mainly in the diol **5**. The dihydroxylation mainly takes place at the isolated trisubstituted double bond, as has been reported for the related monoterpene ocimene.[9] The mesylate **6** was formed by treatment with 1 equiv. CH_3SO_2Cl and triethylamine, but was not isolated. However, nuclear magnetic



Scheme 1.

Keywords: homoterpenes; induced volatiles; Sharpless dihydroxylation; terpenes; (*E*)-4,8-dimethyl-1,3,7-nonatriene; elm; leaf beetle; parasitoid; *Ulmus minor*; elm leaf beetle; *Oomyzus gallerucae*.

* Corresponding author. Tel.: +49-531-391-7353; fax: +49-531-391-5272; e-mail: stefan.schulz@tu-bs.de

0040–4020/02/$ - see front matter
PII: S0040-4020(01)01149-8

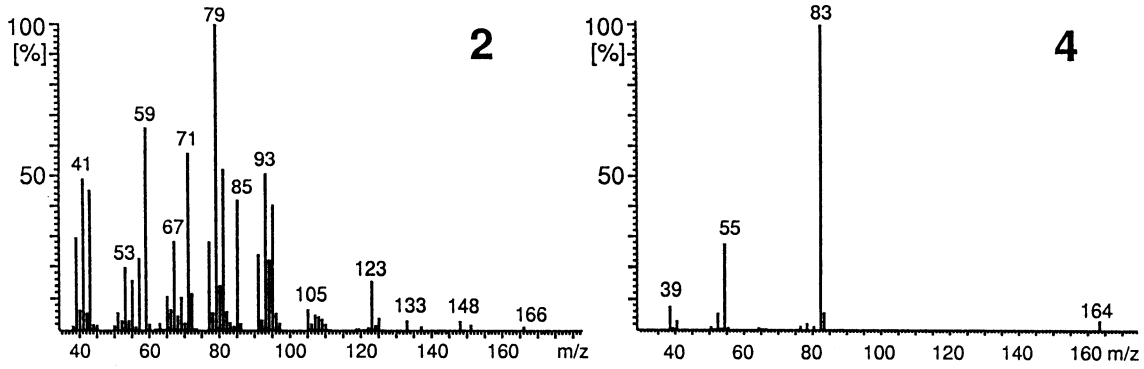
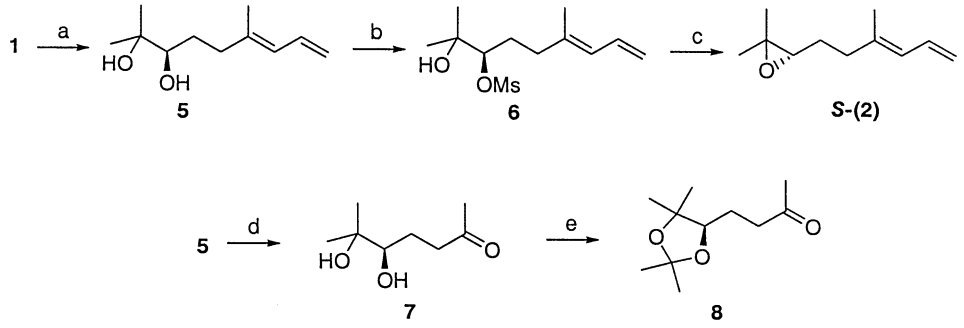


Figure 1. Mass spectra of (*E*)-2,3-epoxy-2,6-dimethyl-6,8-nonadiene (**2**) and (*E*)-2,6-dimethyl-2,6,8-nonatrien-4-one (**4**).

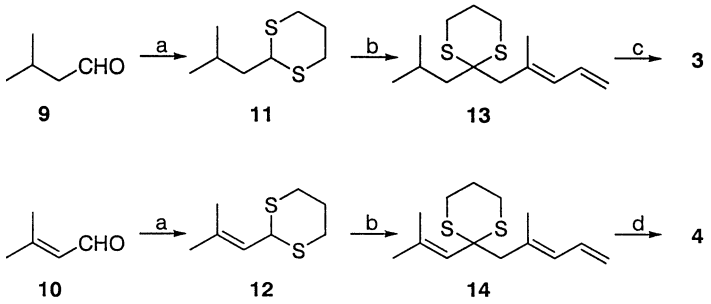


Scheme 2. *Reagents and conditions*: (a) AD-Mix-β, $CH_3SO_2NH_2$, *tert*-BuOH, H_2O (1:1), 0°C, 65%; (b) CH_3SO_2Cl, Et_3N, CH_2Cl_2, room temperature; (c) K_2CO_3, MeOH, room temperature, 33% (2 steps); (d) 1: O_3, 2: $(CH_3)_2S$, 53%; (e) acetone, camphorsulfonic acid, room temperature, 70%.

resonance spectra confirmed that mesylation took place at the secondary alcohol. Treatment of **6** with a mild base resulted in enantiomerically pure (*S*)-epoxide **2**. Comparison of natural, *rac*-, and (*S*)-**2** by GC using a chiral cyclodextrine phase showed that **2** from elm leaves was solely (*R*)-configured. The assignment of enantiomers obtained in the asymmetric dihydroxylation was based on the Sharpless model.[10] To test this model, the double bonds of **5** were cleaved by ozonolysis, resulting in the known ketone **7**, whose stereochemisty was confirmed by NMR.[11] We synthesized **7** by the reported procedure[11] and compared it with the ozonolysis product after transforming both samples to the acetonide **8** by enantioselective GC. These comparisons showed that the configuration at C-3 was congruent with the Sharpless model and matched the stereoselectivity in the dihydroxylation of ocimene.[9]

The second minor component of the elm samples could readily be identified as the ketone **3** (cyclanthone) by its MS[6] and comparison with an authentic synthetic standard. This compound was recently identified in the flower scent of *Cyclanthus bipartitus* (Cyclanthaceae).[6]

The last unknown compound showed a very simple mass spectrum (Fig. 1) with a molecular ion at *m/z* 164, 2 amu less than **3** and predominant ion fragments at *m/z* 55 and 83. Based on these data we proposed **4** (Scheme 1) as the structure for this previously uncharacterized homoterpenoid. Both ketones **3** and **4** were synthesized by a Corey–Seebach approach at low temperatures (Scheme 3). Addition of (*E*)-5-bromo-4-methylpenta-1,3-diene[12] at −78°C to the deprotonated dithianes **11**[13] and **12**[14] obtained from 3-methylbutanal **9** and 3-methyl-2-butenal **10**, respectively, resulted in formation of **13** and **14**. Since **13** and **14** could not be separated from **11** and **12** by flash chromatography, the deprotection of the dithianes was performed with these



Scheme 3. *Reagents and conditions*: (a) $HS(CH_2)_3SH$, $BF_3{\cdot}(CH_2CH_3)_2O$, 0°C, 92% (**11**), 97% (**12**); (b) 1: BuLi, THF, −40°C, 2: (*E*)-5-bromo-4-methylpenta-1,3-diene, −80°C; (c) $AgNO_3$, EtOH, H_2O (1:1), 17% (2 steps); (d) H_5IO_6, THF, room temperature, 30% (2 steps).

mixtures of mono- and dialkylated dithianes. While **14** was deprotected with H_5IO_6, this reaction failed with **13**, for which $AgNO_3$ in ethanol proved effective. Both compounds were identical with the respective elm tree volatiles. Our synthesis of **3** and **4** via the dithianes is quick and simple. Previously, **3** was synthesized by a longer route using a Reformatski coupling of 3-methyl-2-butenal and ethyl 4-bromocrotonate as a key step.[6]

In the present study we have confirmed the presence of compounds **1**, (*R*)-**2**, **3**, and **4** in the induced volatiles of the elm tree. Their concentration is highest in leaves on which the parasitoid laid its eggs, while all other leaf types (undamaged leaves, artificially damaged leaves, leaves on which the adult beetle was feeding) emit lower amounts. Cyclanthone **3** is also emitted in similar amounts during feeding (Wegener, Schulz, Hilker, Meiners, Hermenau, unpublished results). The synthetic products of **1**, (*R*)-**2**, **3**, and **4** enable electrophysiological studies considering their function in the tritrophic interactions between the elm tree, its herbivore, and the parasitoid.

3. Experimental

3.1. General methods

Headspace samples. Headspace samples were taken 72 h after starting the induction by closed loop analysis. Using a modified closed-loop-stripping apparatus,[4] samples were taken 6 h from elm twigs with 10–20 leaves, which carried 15–20 egg masses (i.e. about 1 egg mass per leaf). The charcoal filters (1 mg) used as traps were extracted with approximately 20 μl dichloromethane.

Analysis. Samples were analyzed by gas chromatography–mass spectrometry using a Hewlett Packard GC 6890 MSD 5973 with a split/splitless inlet, equipped with a 30 m HP5MS capillary column (id=0.25 mm, film thickness =0.25 μm). The oven temperature was 50°C (for 5 min), then 5°C/min to 300°C. Helium flow rate was set at 1 ml/min in constant flow mode. The mass spectrometer operated at 70 eV EI ionization mode. Enantiomeric separations were performed on a ThermoQuest 8000 Top GC with a flame ionization detector, a 15 m capillary column (id=0.25 mm) coated with heptakis(6-*O*-TBDMS-2,3-di-*O*-acetyl)-β-cyclodextrine (60% OV1701, w/w),[15] and hydrogen as carrier gas.

Synthesis. Optical rotations were measured on a Dr. Kernchen Propol digital automatic polarimeter. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker AM-400 (400 MHz). Chemical shifts are reported in ppm from tetramethylsilane (δ=0.00 ppm) as internal standard. Data are reported as follows: chemical shift, integration, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, br=broadened, m=multiplet), coupling constant(s), and assignment. Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on an AM-400 (100 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane using the solvent resonance as an internal standard ($CDCl_3$: δ=77.0 ppm). Reactions were monitored by thin layer chromatography on silica-coated plates (Macherey-Nagel, Polygram SIL G/UV_{254}). Column chromatography was performed on Merck silica gel (particle size 0.063–0.2 mm ASTM) unless otherwise stated. Non-aqueous reactions were conducted in flame-dried glassware and dry nitrogen atmosphere. Dry tetrahydrofurane was distilled from potassium with benzophenone, dry dichloromethane from CaH_2, and dry diethyl ether from $LiAlH_4$ under nitrogen atmosphere. Solvents were distilled before use. All other commercially available reagents were used as received.

3.1.1. (+)-(*R*,*E*)-2,6-Dimethyl-6,8-nonadien-2,3-diol (5). Methanesulfonamide (0.62 g, 6.5 mmol) was added to a cooled solution of AD-mix-β (9.31 g) in 75 ml water and *tert*-BuOH (v/v 1:1). The mixture was stirred at 0°C for 84 h after adding 1.0 g (6.7 mmol) of (*E*)-4,8-dimethyl-1,3,7-nonatriene (**1**).[8] Then Na_2SO_3 (10 g) was added and the mixture warmed to room temperature. The aqueous phase was extracted four times with dichloromethane. The combined extracts were dried ($MgSO_4$) and the solvent removed under reduced pressure. Finally, column chromatography (petroleum ether/diethyl ether, 1:1) yielded 0.8 g of **5** (65%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ=6.57 (dt, H, *J*=16.8, 10.6 Hz, H8), 5.91 (d, H, *J*=10.9 Hz, H7), 5.11 (dd, H, *J*=16.8, 1.8 Hz, H9a), 5.00 (dd, H, *J*=10.2, 1.5 Hz, H9b), 3.35 (dd, H, *J*=10.4, 2.0 Hz, H3), 2.0–2.4 (m, 2H, H5), 1.4–1.7 (m, 2H, H4), 1.78 (s, 3H, C6-CH_3), 1.21 (s, 3H, C2-CH_3), 1.16 (s, 3H, C2-CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz) δ=139.0 (C6), 133.2 (C8), 125.9 (C7), 115.0 (C9), 78.1 (C3), 73.1 (C2), 36.8 (C5), 29.6 (C4), 26.4 (C2-CH_3), 23.2 (C2-CH_3), 16.5 (C6-CH_3). EIMS *m*/*z* (%) 184 (1, M^+), 167 (2), 166 (15), 123 (8), 108 (3), 95 (32), 94 (35), 93 (21), 82 (32), 81 (30), 72 (16), 71 (27), 67 (31), 59 (100), 53 (13), 43 (28). $[\alpha]^{22}_D$=+17.8 (*c*=0.041, CH_2Cl_2). HRMS, calcd for $C_{11}H_{20}O_2$ 184.1463, found 184.1467.

3.1.2. (+)-(*S*,*E*)-2,3-Epoxy-2,6-dimethyl-6,8-nonadiene (*S*-(2)). Triethylamine (0.09 ml) followed by methanesulfonyl chloride (0.037 ml) were added to a cool solution (0°C) of **5** (100 mg, 0.54 mmol) in 1.4 ml dichloromethane. This solution was stirred during 3 h at room temperature. After adding 0.2 ml diethyl ether, the solution was filtered through celite and silica and the solvent was removed by rotary evaporation resulting in **6**. NMR showed that the secondary mesylate had been formed almost exclusively and **6** was used without further purification. ^{1}H NMR (CD_2Cl_2, 400 MHz) δ=6.58 (dt, H, *J*=16.6, 10.9 Hz, H8), 5.91 (d, H, *J*=10.9 Hz, H7), 5.11 (dd, H, *J*=16.6, 1.6 Hz, H9a), 5.00 (dd, H, *J*=10.9, 1.6 Hz, H9b), 4.52 (dd, H, *J*=9.5, 2.8 Hz, H3), 3.11 (s, 3H, SO_2CH_3), 2.05–2.35 (m, 2H, H5), 1.65–1.8 (m, 2H, H4), 1.77 (s, 3H, CH_3), 1.24 (s, 3H, CH_3), 1.23 (s, 3H, CH_3). ^{13}C NMR (CD_2Cl_2, 100 MHz) δ=138.3 (C6), 133.5 (C8), 126.4 (C7), 115.3 (C9), 90.3 (C3), 72.5 (C2), 39.0 (SO_2CH_3), 36.4 (C5), 29.4 (C4), 27.0 (CH_3), 23.7 (CH_3), 16.7 (CH_3). The crude mesylate was stirred with 0.146 g K_2CO_3 in 1.6 ml methanol for 30 min. Most of the methanol was removed by rotary evaporation, 10 ml water was added before the epoxide was extracted four times with dichloromethane. The combined organic extracts were dried ($MgSO_4$), and the solvent was removed. After column chromatography on silica (petroleum ether/diethyl ether, 9:1) 30 mg of (*S*)-**2** was obtained (33% for 2 steps). ^{1}H NMR ($CDCl_3$,

400 MHz) δ=6.57 (dt, H, J=16.7, 10.6 Hz, H8), 5.89 (d, H, J=10.6 Hz, H7), 5.11 (dd, H, J=16.7, 1.6 Hz, H9a), 5.01 (dd, H, J=10.5, 1.6 Hz, H9b), 2.72 (t, H, J=6.2 Hz, H3), 2.12–2.35 (m, 2H, H5), 1.78 (s, 3H, C6-CH_3), 1.61–1.71 (m, 2H, H4), 1.30 (s, 3H, C2-CH_3), 1.26 (s, 3H, C2-CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz) δ=138.3 (C6), 133.2 (C8), 125.9 (C7), 115.1 (C9), 64.0 (C3), 58.4 (C2), 36.4 (C5), 27.3 (C4), 24.8 (C2-CH_3), 18.7 (C2-CH_3), 16.6 (C6-CH_3). EIMS m/z (%) 166 (2, M^+), 151 (2), 148 (3), 123 (14), 95 (39), 94 (22), 93 (49), 85 (40), 81 (53), 79 (100), 71 (59), 59 (65), 43 (52), 41 (53). $[\alpha]^{22}_D$=+17.8 (c=0.045, diethyl ether). The enantiomeric excess was determined by GC on a 15 m fused silica column coated with heptakis(6-*O*-TBDMS-2,3-di-*O*-acetyl)-β-cyclodextrine (60% OV1701, w/w). The GC oven was 50°C for 5 min, then 3°C/min to 180°C. The retention times were (*S*)-**2**: 22.4 min and (*R*)-**2**: 22.9 min. No (*R*)-enantiomer was detected, ee>99%. HRMS, calcd for $C_{11}H_{18}O$ 166.1358, found 166.1354.

3.1.3. Ozonolysis of 5. A solution of **5** (0.093 g, 0.50 mmol) in 5 ml dry dichloromethane was cooled to −78°C. At this temperature, ozone was bubbled through the solution for 2 h. After adding 0.5 ml dimethyl sulfide, the solution was warmed to room temperature. A mixture of the ketone (0.043 g of **7** (53%)) and two hemiacetals was obtained by chromatography on silica (petroleum ether/diethyl ether, 1:1). For authentication, acetonide **8** was synthesized from **7** according to Brimble et al.[11] Its spectral data were found to be as reported by Brimble et al.[11] The ee was determined by GC on a 15 m fused silica column coated with heptakis(6-*O*-TBDMS-2,3-di-*O*-acetyl)-β-cyclodextrine (60% OV1701, w/w). The GC oven temperature was set at 75°C. The retention times were (*R*)-**8**: 20.4 min and (*S*)-**8**: 21.3 min. No (*R*)-enantiomer was detected in the synthesis of (*S*)-**8**, ee>99%.

3.1.4. 2-(2-Methylpropyl)-1,3-dithiane (11) and 2-(2-methyl-1-propenyl)-1,3-dithiane (12). The respective aldehyde (26.7 mmol, 3-methylbutanal and 3-methyl-2-butenal) was dissolved in 1.5 ml dry diethyl ether. 1,3-Propanedithiol (3.04 g, 28.1 mmol) was added at 0°C. After stirring for 10 min, 1.7 ml of $BF_3{\cdot}O(CH_2CH_3)_2$ was added very carefully. The solution was stirred for an additional 10 min at 0°C. The solvent was evaporated under reduced pressure to get the dithianes.

11: yield 92%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ=4.08 (t, H, J=7.5 Hz, H2), 2.75–3 (m, 4H, H4, H6), 1.8–2.2 (m, 3H, H5, H2′), 1.59 (t, 2H, J=7.3 Hz, H1′), 0.93 (d, 6H, J=6.6 Hz, C2′(CH_3)$_2$). ^{13}C NMR δ=45.5 (C2), 44.1 (C1′), 30.3 (C4,C6), 26.0 (C5), 24.8 (C2′), 22.2 (C2′-Me). EIMS m/z (%) 176 (56, M^+), 161 (2), 133 (15), 121 (10), 119 (100), 101 (8), 91 (6), 87 (9), 73 (11), 69 (12), 59 (7), 45 (12), 41 (14), 39 (6).

12: yield 97%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ=5.14 (m, H, H1′), 4.87 (d, H, J=10.0 Hz, H1), 2.75–3 (m, 4H, H4, H6), 1.8–2.2 (m, 2H, H5), 1.74–1.76 (m, 6H, 2CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz) δ=137.7 (C2′), 121.1 (C1′), 44.4 (C2), 30.5 (C4,C6), 25.6 (CH_3), 24.9 (C5), 18.3 (CH_3). EIMS m/z (%) 174 (100, M^+), 159 (8), 141 (7), 127 (4), 117 (11), 109 (19), 100 (29), 99 (83), 85 (86), 67 (15), 65 (12), 59 (8), 45 (18), 41 (20).

3.1.5. (*E*)-2-(2-Methyl-2,4-pentadienyl)-2-(2-methylpropyl)-1,3-dithiane (13) and (*E*)-2-(2-methyl-2,4-pentadienyl)-2-(2-methyl-1-propenyl)-1,3-dithiane (14). A solution of **11** (3.25 mmol) in 20 ml dry THF was cooled to −40°C and 3.2 mmol butyllithium (2.0 ml of 1.6 M solution in hexane) was added. The mixture was stirred for 3 h. After cooling to −80°C, 0.52 g (3.25 mmol) (*E*)-5-bromo-4-methylpenta-1,3-diene[12] was slowly added. At this temperature, the mixture was stirred for an additional 4 h before it was poured into 50 ml water. After extraction with diethyl ether, the combined organic extracts were dried ($MgSO_4$) and the solvent evaporated. Chromatography on silica (petroleum ether/diethyl ether, 40:1) yielded 545 mg of the dialkylated and monoalkylated dithianes.

13: ^{1}H NMR ($CDCl_3$, 400 MHz) δ=6.55 (dt, H, J=16.8, 10.6 Hz, H4′), 5.94 (d, H, J=10.6 Hz, H3′), 5.16 (d, H, J=16.6 Hz, H5′a), 5.05 (d, H, J=10.2 Hz, H5′b), 2.8–3.0 (m, 4H, H4, H6), 2.74 (s, 2H, H1′), 1.8–2.0 (m, 5H, H5, H1″, H2″), 1.95 (s, 3H, C2′-CH_3), 1.02 (d, 6H, J=6.8 Hz, H3″). ^{13}C NMR ($CDCl_3$, 100 MHz) δ=134.3 (C2′), 132.6 (C4′), 131.0 (C3′), 115.7 (C5′), 53.7 (C2), 49.3 (C1′), 47.5 (C1″), 30.1 (C4,C6), 26.2 (C5), 24.8 (C2″), 21.9 (C2″-$(CH_3)_2$), 19.1 (C2′-CH_3). EIMS m/z (%) 256 (1, M^+), 199 (1), 177 (11), 176 (12), 175 (100), 133 (21), 125 (4), 119 (19), 91 (6), 79 (5), 59 (5), 43 (5). Using the procedure described above, 3.53 mmol dithiane **12** gave 880 mg crude **14**.

14: ^{1}H NMR ($CDCl_3$, 400 MHz) δ=6.56 (dt, H, J=16.7, 10.6 Hz, H4′), 5.97 (d, H, J=10.7 Hz, H3′), 5.52 (m, H, H1″), 5.14 (dd, H, J=16.9, 1.8 Hz, H5′a), 5.04 (dd, H, J=10.2, 1.7 Hz, H5′b), 2.75–2.99 (m, 4H, H4, H6), 2.82 (s, 2H, H1′), 1.9–2.1 (m, 2H, H5), 1.95 (d, 3H, J=1.4 Hz, C2″-CH_3), 1.86 (s, 3H, C2′-CH_3), 1.77 (d, 3H, J=1.3 Hz, C2″-CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz) δ=138.4 (C2″), 134.2 (C2′), 132.8 (C4′), 130.9 (C3′), 127.9 (C1″), 115.2 (C5′), 53.1 (C2), 50.6 (C1′), 27.8 (C4, C6), 27.6 (C2″-Me), 25.3 (C5), 19.2 (C2″-Me), 18.4 (C2′-Me). EIMS m/z (%) 254 (1, M^+), 179 (3), 175 (9), 174 (10), 173 (100), 133 (1), 117 (1), 111 (1), 105 (4), 99 (19), 91 (5), 65 (4), 55 (3), 45 (2), 41 (7), 39 (3).

3.1.6. (*E*)-2,6-Dimethyl-6,8-nonadien-4-one (3). A solution of 0.5 g $AgNO_3$ in 2.5 ml water was added to a stirred solution of 0.148 g of crude **13** in 25 ml ethanol. The mixture was stirred for 3 h at 40°C before it was poured into 50 ml water. The solution was extracted three times with diethyl ether, the extracts were combined, washed with brine, dried with $MgSO_4$, and finally the solvent was removed under reduced pressure. Chromatography on ALOX N deactivated with 10% water, using petroleum ether as eluent, gave 25 mg pure **3** (17% over two steps). ^{1}H NMR (C_6D_6, 400 MHz) δ=6.48 (dt, H, J=16.6, 10.6 Hz, H8), 5.81 (d, H, J=10.7 Hz, H7), 5.10 (d, H, J=16.6 Hz, H9a), 4.99 (d, H, J=10.5 Hz, H9b), 2.72 (s, 2H, H5), 2.2–2.0 (m, H, H2), 1.92 (d, 2H, J=7.8 Hz, H3), 1.60 (s, 3H, C6-CH_3), 0.76 (d, 6H, J=7.6 Hz, H1). ^{13}C NMR (C_6D_6, 100 MHz) δ=206.1 (C4), 133.2 (C8), 132.8 (C6), 129.9 (C7), 116.2 (C9), 54.3 (C5), 50.3 (C3), 24.0 (C2), 22.5 (C1), 16.9 (C6-CH_3). EIMS m/z (%) 166 (13), 86 (4), 85 (69), 81 (11), 79 (8), 67 (3), 58 (5), 57 (100), 55 (3), 43 (9),

41 (27), 39 (9). HRMS, calcd for $C_{11}H_{18}O$ 166.1358, found 166.1357.

3.1.7. (*E*)-2,6-Dimethyl-2,6,8-nonatrien-4-one (4). A solution of 0.43 g of crude dithiane **14** in 25 ml dry diethyl ether and 10 ml dry THF was cooled to 0°C. At this temperature, 0.78 g (3.4 mmol) H_5IO_6 in 10 ml dry THF was added dropwise during 3 min. After 15 min of stirring at room temperature, the reaction mixture was washed with a saturated solution of sodium sulfite in water. The aqueous phase was extracted four times with diethyl ether, the organic extracts were combined and dried ($MgSO_4$), and the solvent was removed under reduced pressure. Chromatography on ALOX N deactivated with 10% water (petroleum ether/diethyl ether, 9:1) yielded 87 mg (30% over 2 steps) of **4**. ^{1}H NMR (C_6D_6, 400 MHz), δ=6.49 (dt, H, J=16.8, 10.6 Hz, H8), 5.8–5.9 (m, 2H, H3, H7), 5.08 (d, H, J=16.8 Hz, H9a), 4.96 (d, H, J=10.3 Hz, H9b), 2.90 (s, 2H, H5), 2.07 (s, 3H, C2-CH_3), 1.65 (s, 3H, C6-CH_3), 1.39 (s, 3H, C2-CH_3). ^{13}C NMR (C_6D_6, 100 MHz) δ=196.8 (C4), 155.1 (C2), 133.5 (C6), 133.4 (C8), 129.8 (C3), 123.1 (C7), 116.1 (C9), 55.6 (C5), 27.2 (C2-CH_3), 20.5 (C2-CH_3), 16.8 (C6-CH_3). EIMS *m/z* (%) 164 (3), 84 (6), 83 (100), 81 (1), 79 (2), 77 (2), 65 (1), 56 (1), 55 (28), 54 (1), 53 (6), 51 (1), 41 (3), 40 (1), 39 (8). HRMS, calcd for $C_{11}H_{16}O$ 164.1201, found 164.1205.

Acknowledgements

Financial support from the Deutsche Forschungsgemeinschaft and the Fonds der chemischen Industrie is gratefully acknowledged.

References

1. Meiners, T.; Hilker, M. *Oecologia* **1997**, *112*, 87–93.
2. Dicke, M. *J. Plant Physiol.* **1994**, *143*, 465–472.
3. Wegener, R.; Schulz, S.; Meiners, T.; Hadwich, K.; Hilker, M. *J. Chem. Ecol.* **2001**, *27*, 499–515.
4. Boland, W.; Ney, P.; Jänicke, L.; Gassmann, G. A Closed-Loop-Stripping Technique as a Versatile Tool for Metabolic Studies of Volatiles. In *Analysis of Volatiles: Method, Application*; Schreiber, P., Ed.; de Gruyter: Berlin, 1984; pp 371–380.
5. Anisimov, A. V.; Chau, F. L.; Tarakanova, A. V.; Lebedev, M. Yu.; Berentsveig, V. V. *J. Org. Chem., USSR (Engl. Transl.)* **1992**, *28*, 1105–1108.
6. Schultz, K.; Kaiser, R.; Knudsen, J. T. *Flavour Fragrance J.* **1999**, *14*, 185–190.
7. Kaiser, R. Trapping, Investigation and Reconstruction of Flower Scents. In *Perfumes: Art, Science and Technology*; Müller, P. M., Lamparsky, D., Eds.; Elsevier: London, 1991; pp 213–250.
8. Leopold, E. *Org. Synth.* **1985**, *64*, 164–174.
9. Moore, C. J.; Possner, S.; Hayes, P.; Paddon-Jones, G. C.; Kitching, W. *J. Org. Chem.* **1999**, *64*, 9742–9744.
10. Sharpless, K. B.; Amberg, W.; Bennani, Y. L.; Crispino, 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*, 2768–2771.
11. Brimble, M. A.; Rowan, D. D.; Spicer, J. A. *Synthesis* **1995**, 1263–1266.
12. Piers, E.; Jung, G. L.; Ruediger, E. H. *Can. J. Chem.* **1987**, *65*, 670–682.
13. Kruse, C. G.; Wijsman, A.; van der Gen, A. *J. Org. Chem.* **1979**, *44*, 1847–1851.
14. Poulter, C. D.; Hughes, J. M. *J. Am. Chem. Soc.* **1976**, *99*, 3830–3837.
15. König, W. A. *Chirality* **1998**, *65*, 499–504.