Highly Stereoselective Total Syntheses of β-Farnesene, β-Sinensal, and Dendrolasin Employing 2-(Hydroxymethyl)-4-(phenylthio)-1-butene as a Building Block

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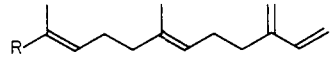
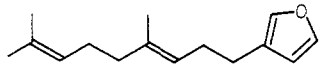
The use of 2-(hydroxymethyl)-4-(phenylthio)-1-butene (**2**) for the synthesis of the title compounds is described. The aldehyde **4** obtained by Claisen rearrangement of **2** via a vinyl ether was converted to **5a** by 2-propenyllithium. The carboxylic acid **6a** was provided by the Claisen rearrangement of **5b** via a siloxy vinyl ether. The aldehyde **6d** was obtained by reduction of **6a** with $LiAlH_4$ followed by oxidation of **6c** with NCS–Me_2S–Et_3N. Treatment of **6d** with $Ph_3P{=}CH_2$ gave **7a**, which was transformed to β-farnesene (**1a**) by oxidation followed by pyrolysis. Then, treatment of **6d** with $CH_3CH(Li)CH{=}NC_6H_{11}$ gave **7c**, which was converted to β-sinensal (**1b**). The sulfoxide **7b** was treated with Ac_2O–catalytic $(CF_3CO)_2O$ at room temperature for 72 h to give **8a**, which was transformed to **8b** by reduction with $NaBH_4$. Epoxidation of **8b** followed by oxidation gave dendrolasin (**1c**).

β-Farnesene (**1a**) and β-sinensal (**1b**) are sesquiterpenes that have the same carbon skeleton. The former is a



1a, R = CH_3
b, R = CHO



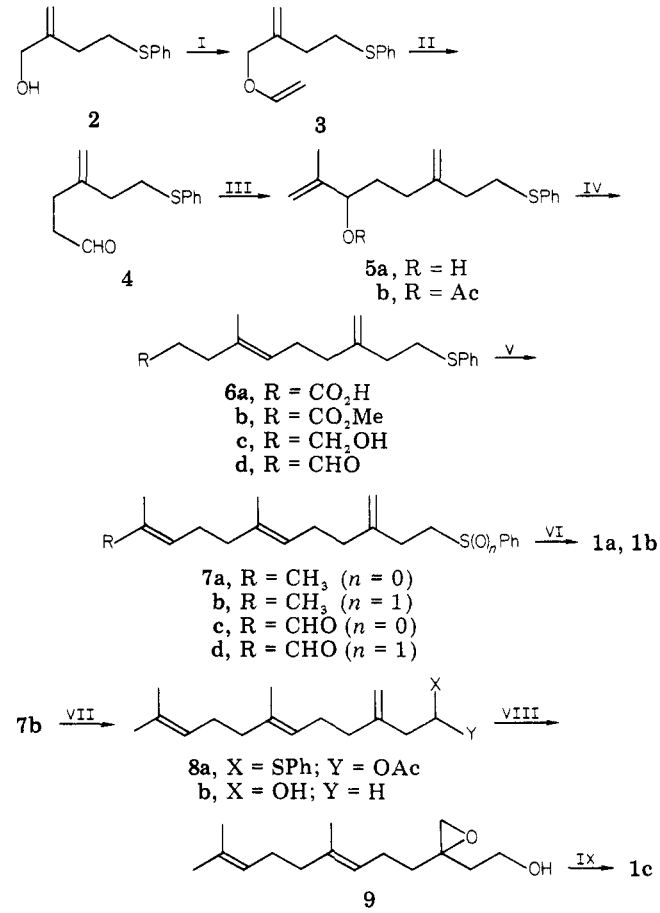
1c

natural aphid alarm pheromone,[1] the latter a component of the essential oil of Chinese orange.[2] Several synthetic approaches to **1a**[3] and **1b**[4] have been reported so far. In designing an efficient synthesis of these compounds, two synthetic problems have to be considered. The first is the method of forming an acid-sensitive terminal isoprene unit. In many of the reports dealing with **1a** and **1b**, myrcene derivatives have been used as building blocks for this moiety. The second is how to frame the 15-carbon chain involving a trisubstituted *E* olefin with high stereoselectivity. As for the synthesis of dendrolasin (**1c**),[5a] isolated from the mandibular gland of ants, elaboration of the furan skeleton is the important objective.

Currently we are interested in the application of 2-(hydroxymethyl)-4-(phenylthio)-1-butene (**2**)[6] to the total synthesis of terpenoids by making use of functionalities involved in **2**. So far we have synthesized myrcene,[7] citral,[7] squalane,[7] isophytol,[7] β-ionone,[8] and γ-irones[8] by employing **2**. The strategy used in the present study is depicted in Scheme I.

Notable features are as follows. First, the homoallylic sulfide system is an excellent synthon for a terminal isoprene unit because it can be generated in the final step of the synthesis by pyrolysis of a corresponding sulfoxide (step VI). This offers a solution to the first problem mentioned above. Next, the allylic alcohol moiety is suitable for 2-carbon elongation by a Claisen rearrangement via a vinyl ether (step II). The aldehyde thus obtained permits introduction of a 5-carbon chain and a

Scheme I[a]



[a] (I) $CH_2{=}CHOEt$, $Hg(OAc)_2$, reflux; (II) xylene, 140 °C; (III) $CH_2{=}CH(Li)CH_3$, Et_2O, 0 °C, Ac_2O-py; (IV) LICA, THF, −78 °C, HMPA, *t*-$BuMe_2SiCl$, reflux, CH_2N_2, $LiAlH_4$, NCS-Me_2S-Et_3N, −23 °C; (V) $Ph_3P{=}C(Me)_2$, THF, reflux, MeOH-H_2O_2, room temperature, $CH_3CH(Li)CH{=}NC_6H_{11}$, Et_2O, −78 °C to room temperature, $(CO_2H)_2$, MeOH-H_2O_2, room temperature; (VI) toluene, $NaHCO_3$, (VII) Ac_2O-catalytic $(CF_3CO)_2O$, room temperature, $NaBH_4$, EtOH, room temperature; (VIII) $VO(acac)_2$, *t*-BuOOH, PhH, reflux; (IX) CrO_3-py, CH_2Cl_2, room temperature, SiO_2.

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concomitant introduction of an *E* olefin (step III and IV). Thus, reaction of **4** with isopropenyllithium at 0 °C afforded the allylic alcohol **5a**, whose acetate **5b** on reaction with lithium isopropylcyclohexylamide at −78° °C in THF and then with HMPA and *t*-BuMe$_2$SiCl[9] followed by acid hydrolysis of the reaction mixture gave the carboxylic acid **6a**. GLC analysis of the corresponding methyl ester **6b** showed the exclusive formation of the *E* isomer with a stereoselectivity greater than 99%. Wittig condensation of aldehyde **6d** with Ph$_3$P=C(CH$_3$)$_2$ afforded **7a**, while treatment of **6d** with the anion of propylidenecyclohexylamine followed by acidolysis yielded **7c**.[10] The stereochemistry of the newly formed double bond in the latter compound was fully confirmed by analogy to the method of Büchi et al.[10] Finally, the thiophenyl function allows smooth oxidation of the α-carbon by a Pummerer reaction to the α-acetoxy phenyl sulfide **8a** (step VII). However, preparation of the homoallyl alcohol **8b** by alkaline hydrolysis of **8a** was difficult because migration of the double bond in the initially formed β,γ-unsaturated aldehyde under basic conditions was unavoidable. This difficulty was bypassed by employing our discovery[11] that α-acetoxy homoallylic phenyl sulfides can be converted to homoallyl alcohol by NaBH$_4$ reduction without double bond migration. As the transformation of a homoallyl alcohol to a furan is already known,[5] our sequence of reactions involving the Pummerer reaction followed by NaBH$_4$ reduction constitutes a new synthetic method for furan derivatives from a homoallylic sulfide.

Experimental Section

Reactions requiring anhydrous conditions were carried out under a nitrogen atmosphere. Commercially available reagents were distilled before use. Solvents were purified by standard methods. ^{1}H NMR spectra were recorded in CCl_4 on a Hitachi R-24B spectrometer (60 MHz) with Me_4Si as an internal standard. IR spectra were obtained as neat films on a JASCO IRA-I spectrometer.

Vinyl Ether 3. A solution of **2** (6.0 g, 31 mmol) and Hg(OAc)$_2$ (500 mg, 1.6 mmol) in ethyl vinyl ether (100 mL) was heated under reflux for 12 h. The mixture was poured into ice–water and extracted with hexane. The organic layer was successively washed with water and saturated sodium bicarbonate solution and dried ($MgSO_4$). Removal of the solvent and purification of the residue by column chromatography (silica gel, 100:1 hexane–ether) provided **3** (5.67 g, 83%): ^{1}H NMR δ 2.35 (t, 2 H, C=CCH$_2$, *J* = 7 Hz), 2.97 (t, 2 H, CH$_2$S, *J* = 7 Hz), 3.92 (dd, 1 H, CH=CO, *J* = 7 and 2 Hz), 4.10 (s, 2 H, CH$_2$O), 4.12 (dd, 1 H, CH=CO, *J* = 14 and 2 Hz), 4.91 (s, 1 H, C=CH), 5.02 (s, 1 H, C=C), 6.30 (dd, 1 H, C=CHO, *J* = 14 and 7 Hz), 6.95–7.35 (m, 5 H, SPh).

Aldehyde 4. A solution of **3** (5.67 g, 25.8 mmol) in xylene (70 mL) was heated under reflux for 3 h. After evaporation of the solvent, the residue was chromatographed (silica gel, 10:1 hexane–ether) to give the aldehyde **4** (4.6 g, 81 %); ^{1}H NMR δ 2.07–2.52 (m, 6 H, C=CH$_2$, CH$_2$CO), 2.94 (t, 2 H, CH$_2$S, *J* = 7 Hz), 4.72 (br s, 2 H, C=CH$_2$), 6.92–7.32 (m, 5 H, SPh), 9.57 (br s, 1 H, CHO); IR (film) 1719 (C=O), 1640 and 1580 (C=C). Anal. Calcd. for C$_{13}$H$_{16}$OS: C, 70.87; H, 7.32. Found: C, 70.34; H, 7.10.

Alcohol 5a. To a stirred solution of 2-propenyllithium in ether was added to aldehyde **4** (4.6 g, 20.9 mmol) at 0 °C over a period of 1 h. The reaction mixture was poured into cold saturated ammonium chloride solution and extracted with ether. The extracts were successively washed with water and brine, dried ($MgSO_4$), and concentrated. Column chromatography of the residue (silica gel, 5:1 hexane–ether) gave the alcohol **5a** (4.38 g, 80%): ^{1}H NMR δ 1.30–1.78 (m, 2 H, CH$_2$), 1.66 (s, 3 H, CH$_3$), 1.81–2.44 (m, 4 H, CH$_2$), 2.68 (s, 1 H, OH), 2.96 (t, 2 H, CH$_2$S, *J* = 7 Hz), 3.92 (t, 1 H, CHO, *J* = 6 Hz), 4.77 (br s, 3 H, C=CH), 4.86 (br s, 1 H, C=CH), 6.95–7.35 (m, 5 H, SPh); IR (film) 3360 (OH), 1645 and 1585 (C=C). Anal. Calcd for C$_{16}$H$_{22}$OS: C, 73.23; H, 8.45. Found: C, 73.23; H, 8.21.

Acetate 5b. The alcohol **5a** (4.38 g, 16.7 mmol) was treated with acetic anhydride and pyridine (each 5 mL) at room temperature for 12 h to give the acetate **5b**, which was pure enough for further use (4.98 g, 98 %): ^{1}H NMR δ 1.70 (s, 3H, CH$_3$), 1.40–2.10 (m, 4 H, C=CH$_2$ and CH$_2$), 2.00 (s, 3 H, CH$_3$CO), 2.28 (t, 2 H, C=CCH$_2$, *J* = 8 Hz), 2.95 (t, 2 H, CH$_2$S, *J* = 8 Hz), 4.70–4.90 (m, 4 H, C=CH$_2$), 5.05 (t, 1 H, CHO, *J* = 6 Hz), 6.95–7.24 (m, 5 H, SPh); IR (film) 1735 (C=O).

Carboxylic Acid 6a. To a solution of *N*-isopropylcyclohexylamine (880 mg, 6.24 mmol) in THF (10 mL) was added *n*-BuLi (6.24 mmol) dropwise at 0 °C, and the mixture was stirred for 20 min at 0 °C. Then the acetate **5b** (1.60 g, 5.26 mmol) in THF (10 mL) was added to this solution at −78 °C during 5 min, and the resulting yellowish brown solution was stirred at −78 °C for 30 min. After addition of HMPA (1.12 g, 6.24 mmol) followed by *t*-BuMe$_2$SiCl (1.10 g, 7.28 mmol) in THF (5 mL), the mixture was warmed to room temperature over a period of 2 h and then heated under reflux for 4 h. The reaction mixture was quenched with 1 N HCl at 0 °C and stirred at room temperature for 2 h. The mixture was extracted with ether, and the extracts were washed with 1 N HCl and water and dried ($MgSO_4$). Concentration of the solvent gave an oil, which was purified by column chromatography (silica gel, 3:1 hexane–ether) to afford **6a** (1.33 g, 83%): ^{1}H NMR δ 1.58 (s, 3 H, CH$_3$), 1.81–2.46 (m, 10 H, C=CCH$_2$, CH$_2$CO), 2.92 (t, 2 H, CH$_2$S, *J* = 8 Hz), 4.69 (br s, 2 H, C=CH$_2$), 4.84–5.26 (m, 1 H, C=CH), 6.86–7.26 (m, 5 H, SPh), 9.40 (br s, 1 H, OH); IR (film) 3600–2400 (OH), 1700 (C=O), 1640 and 1580 (C=C).

The GLC analysis of the corresponding methyl ester **6b** (SE-30, 2 m × 3 mm i.d., 270 °C) exhibited a single peak assignable to the *E* isomer (t_r = 6.5 min for the *Z* isomer and 7.2 min for the *E* isomer, respectively): ^{1}H NMR δ 1.56 (s, 3 H, CH$_3$), 1.82–2.47 (m, 10 H, C=CH$_2$, CH$_2$CO), 2.92 (t, 2 H, CH$_2$S, *J* = 8 Hz), 3.52 (s, 3 H, OCH$_3$), 4.68 (br s, 2 H, C=CH$_2$), 4.82–5.22 (m, 1 H, C=CH), 6.89–7.30 (m, 5 H, SPh). Anal. Calcd for C$_{19}$H$_{26}$O$_2$S: C, 71.66; H, 8.23. Found: C, 71.46; H, 8.05.

Alcohol 6c. To a stirred suspension of LiAlH$_4$ (380 mg, 10 mmol) in THF (10 mL) was added dropwise the carboxylic acid **6a** (2.47 g, 8.13 mmol) at 0 °C. The resulting mixture was extracted with ethyl acetate, and the extracts were successively washed with 1 N HCl, saturated sodium bicarbonate solution, and brine. Drying ($MgSO_4$) and concentration of the solvent gave an oil, which was chromatographed (silica gel, 3:1 hexane–ether) to provide the alcohol **6c** (1.93 g, 82%): ^{1}H NMR δ 1.58 (s, 3 H, CH$_3$), 1.36–1.79 (m, 2 H, CH$_2$), 1.80–2.44 (m, 8 H, C=CCH$_2$), 2.95 (t, 2 H, CH$_2$S, *J* = 8 Hz), 3.47 (t, 2 H, CH$_2$O, *J* = 6 Hz), 4.74 (br s, 2 H, C=CH$_2$), 4.90–5.30 (m, 1 H, C=CH), 6.94–7.40 (m, 5 H, SPh); IR (film) 3320 (OH), 1642 and 1585 (C=C).

Aldehyde 6d. To a suspension of *N*-chlorosuccinimide (267 mg, 2.0 mmol) in toluene (10 mL) was added dimethyl sulfide (0.293 mL, 4.0 mmol) at 0 °C, and the resulting mixture was stirred at 0 °C for 2 h. A solution of the alcohol **6c** (290 mg, 1.0 mmol) in toluene (10 mL) was added dropwise at −23 °C, and the mixture was stirred for 2 h. After addition of triethylamine (2 mL), the stirring was continued at −23 °C for 10 min. The mixture was extracted with ether, washed with 1 N HCl and saturated sodium bicarbonate solution, dried ($MgSO_4$), and concentrated. The residue was chromatographed (silica gel, 10:1 hexane–ether) to give aldehyde **6d** (271 mg, 94%): ^{1}H NMR δ 1.59 (s, 3 H, CH$_3$), 1.94–2.48 (m, 10 H, C=CCH$_2$, CH$_2$CO), 2.97 (t, 2 H, CH$_2$S, *J* = 8 Hz), 4.78 (br s, 2 H, C=CH$_2$), 4.92–5.2 (m, 1 H, C=CH), 6.99–7.39 (m, 5 H, SPh), 9.66 (br s, 1 H, CHO); IR (film) 1720 (C=O).

Sulfide 7a. To a suspension of isopropyltriphenylphosphonium iodide (432 mg, 1.0 mmol) in THF (10 mL) was added *n*-BuLi (1.0 mmol) at 0 °C. After the wine-red solution was stirred at room temperature for 5 min, the aldehyde **6d** (144 mg, 0.5 mmol) in THF (5 mL) was added dropwise over a period of 5 min. After being heated under reflux for 1 h, the reaction mixture was diluted with hexane to precipitate triphenylphosphine oxide. Then the mixture was poured into ice–water and extracted with hexane.

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The hexane extracts were washed with water, dried ($MgSO_4$), and concentrated to give an oil, which was passed through a short column (silica gel, 100:1 hexane–ether) to afford **7a** (147 mg, 94%): ^1H NMR δ 1.59 (s, 6 H, CH_3), 1.67 (s, 3 H, CH_3), 1.86–2.48 (m, 10 H, C=CCH_2), 2.99 (t, 2 H, CH_2S, J = 8 Hz), 4.97 (s, 2 H, C=CH_2), 4.80–5.25 (m, 2 H, C=CH), 7.00–7.40 (m, 5 H, SPh).

Sulfoxide 7b. The sulfide **7a** (147 mg, 0.47 mmol) was oxidized to the sulfoxide **7b** in the mixed solution of MeOH–H_2O_2 (30% solution) (10 mL and 3 mL) at room temperature for 12 h. The mixture was extracted with ethyl acetate, and the extracts were washed with saturated sodium bicarbonate solution and brine. Drying ($MgSO_4$) and removal of the solvent gave an oil, which was purified by a column chromatography (silica gel, 1:1 hexane–ether) (137 mg, 89 %): ^1H NMR δ 1.58 (s, 6 H, CH_3), 1.66 (s, 3 H, CH_3), 1.76–2.46 (m, 10 H, C=CCH_2), 2.56–2.96 (m, 2 H, CH_2SO), 4.74 (br s, 2 H, C=CH_2), 4.81–5.16 (m, 2 H, C=CH), 7.30–7.70 (m, 5 H, SPh).

Farnesene (1a). A toluene solution (10 mL) of the sulfoxide **7b** (137 mg, 0.42 mmol) was heated under reflux for 2 h in the presence of $NaHCO_3$ powder (200 mg). The mixture was poured into water and extracted with hexane. The organic layer was washed with water, dried ($MgSO_4$), and concentrated. The residue was purified by column chromatography (silica gel, hexane) to give farnesene (**1a**), 76 mg, 90%): ^1H NMR δ 1.58 (s, 6 H, CH_3), 1.65 (s, 3 H, CH_3), 1.87–2.27 (m, 8 H, C=CCH_2), 4.85–5.35 (m, 6 H, C=CH), 6.26 (dd, 1 H, C=CH, J = 17 and 11 Hz). These spectral data along with GLC and TLC data of **1a** were consistent with those of an authentic specimen.[3]

Aldehyde 7c. Freshly distilled propylidenecyclohexylamine (695 mg, 5.0 mmol) in dry ether (5 mL) was added to a stirred solution of lithium isopropylamide (4.5 mmol) at 0 °C, and the mixture was stirred for 20 min. Then a solution of the aldehyde **6d** (271 mg, 0.94 mmol) in ether (5 mL) was added dropwise over a period of 10 min at −78 °C, and the resulting mixture was allowed to stand overnight at room temperature. The mixture was poured into ice–water, extracted with ether, washed with 1 N HCl and water, and dried ($MgSO_4$). Concentration of the solvent gave an oil, which was again diluted with ether (30 mL). To this solution was added oxalic acid (3 g) in water (10 mL) at room temperature for 5 h. The organic layer was separated and washed with saturated sodium bicarbonate solution and dried ($MgSO_4$). Removal of the solvent left an oil, which was chromatographed (silica gel, 10:1 hexane–ether) to give the aldehyde **7c** (160 mg, 52%): ^1H NMR δ 1.59 (s, 3 H, CH_3), 1.68 (s, 3 H, CH_3), 1.85–2.55 (m, 10 H, C=CCH_2, CH_2CO), 2.95 (t, 2 H, CH_2S, J = 8 Hz), 4.75 (s, 2 H, C=CH_2), 4.90–5.25 (m, 1 H, C=CH), 6.30 (t, 1 H, C=CH, J = 7 Hz), 7.00–7.35 (m, 5 H, SPh), 9.31 (s, 1 H, CHO); IR (film) 1680 (C=O).

β-Sinensal (1b). The aldehyde **7c** (43 mg, 0.13 mmol) was converted to **7d** in a solution of MeOH–H_2O_2 (10 mL and 2 mL) at room temperature for 12 h. The mixture was extracted with ethyl acetate, and the extracts were successively washed with saturated sodium bisulfite solution and brine, dried ($MgSO_4$), and concentrated to give an oil, which was pure enough for the use in the next step. A mixture of the sulfoxide **7d** (40 mg, 0.116 mmol) and $NaHCO_3$ powder (200 mg) in toluene (10 mL) was heated under reflux for 3 h. The reaction mixture was washed with water, dried ($MgSO_4$), and concentrated. The residue was passed through a short column (silic gel, 100:1 hexane–ether) to give β-sinensal (**1b**) (24.9 mg, 88 %): ^1H NMR δ 1.58 (s, 3 H, CH_3), 1.68 (s, 3 H, CH_3), 1.85–2.60 (m, 8 H, C=CCH_2), 4.80–5.30 (m, 5 H, C=CH), 5.98–6.53 (m, 2 H, C=CH, CH=CCO) 9.24 (s, 1 H, CHO); IR (film) 2700 (CHO), 1685 (C=O), 1642 and 1595 (C=C). These spectral data along with GLC and TLC results of **1b** were consistent with those of an authentic specimen.[4]

α-Acetoxy Sulfide 8a. To a mixed solution of the sulfoxide **7b** (357 mg, 1.08 mmol) in $(CH_3CO)_2O$ (20 mL) was added $(CF_3CO)_2O$ (0.3 mL) at room temperature. After being stirred at room temperature for 72 h, the mixture was diluted with benzene (150 mL). The mixture was poured into ice–water (300 mL) and stirred for 30 min. The sodium bicarbonate powder was added slowly to this mixture. The organic layer was washed with sodium bicarbonate solution and water and dried ($MgSO_4$). Removal of the solvent gave an oil, which was chromatographed (silica gel, 20:1 hexane–ether) to provide **8a** (281 mg, 70%): ^1H NMR δ 1.52 (s, 6 H, CH_3), 1.58 (s, 3 H, CH_3), 1.78–2.18 (m, 8 H, C=CCH_2), 2.40 (d, 2 H, C=CCH_2, J = 7 Hz), 4.72 (br s, 2 H, C=CH_2), 4.84–5.20 (m, 2 H, C=CH), 6.14 (t, 1 H, OCH, J = 7 Hz), 6.93–7.48 (m, 5 H, SPh); IR (film) 1740 (C=O), 1640 and 1580 (C=C), 1220 (C—O).

Alcohol 8b. An excess of $NaBH_4$ (380 mg, 10 mmol) was added to a solution of α-acetoxy sulfide **8a** (281 mg, 0.756 mmol) in wet ethanol (20 mL) at room temperature, and the mixture was stirred for 12 h. The reaction mixture was poured into ice–water and extracted with ether. The organic layer was wahsed with water, dried ($MgSO_4$), and concentrated. The residue was chromatographed (silica gel, 3:1 hexane–ether) to give **8h** (124 mg, 74%): ^1H NMR δ 1.62 (s, 6 H, CH_3), 1.68 (s, 3 H, CH_3), 1.88–2.40 (m, 11 H, C=CCH_2, OH), 3.61 (t, 2 H, CH_2O, J = 6 Hz), 4.80 (br s, 2 H, C=CH_2), a 4.86–5.25 (m, 2 H, C=CH); IR (film) 3320 (OH) and 1640 (C=C). Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 81.00; H, 11.93.

Epoxy Alcohol 9. To a solution of the alcohol **8b** (585 mg, 2.64 mmol) and vanadyl acetylacetonate (50 mg, 0.189 mmol) in refluxing benzene (20 mL) was added dropwise 85% *tert*-butyl hydroperoxide (360 mg, 3.4 mmol) over a period of 20 min. The resulting deep red solution was heated under reflux for 2 h and then poured into a saturated sodium bisulfite solution. Concentration of the organic layer followed by column chromatography (silica gel, 3:1 hexane–ether) afforded **9** (497 mg, 79 %): ^1H NMR δ 1.60 (s, 6 H, CH_3), 1.66 (s, 3 H, CH_3), 1.45–2.32 (m, 10 H, C=CCH_2, CH_2), 2.50 (d, 1 H, OCH, J = 4.2 Hz), 2.62 (d, 1 H, OCH, J = 4.2 Hz), 3.01 (br s, 1 H, OH), 3.40–3.80 (m, 2 H, CH_2O), 4.90–5.30 (m, 2 H; C=CH); IR (film) 3300 (OH).

Dendrolasin (1c). To a stirred solution of **9** (235 mg, 0.987 mmol) in CH_2Cl_2 (10 mL) was added CrO_3–2py complex (4 equiv) in CH_2Cl_2 at 0 °C. After being stirred at room temperature for 1.5 h, the mixture was diluted with ether (30 mL) and the organic layer was filtered. The filtrate was concentrated, and the residue was passed through a column (silica gel, 2:1 hexane–ether) to give dendrolasin (**1c**) (86 mg, 34 %): ^1H NMR δ 1.59 (s, 6 H, CH_3), 1.68 (s, 3 H, CH_3), 1.90–2.60 (m, 8 H, C=CCH_2), 4.80–5.30 (m, 2 H, C=CH), 6.16 (br s, 1 H, C=CH), 7.10 (br s, 1 H, C=CH), 7.21 (br s, 1 H, C=CH); IR (film) 2840, 1560, 1500, 1440, 1380, 1260, 1105, 1062, 1023, 875 cm^{-1}. These spectral data along with GLC and TLC results of **1c** were consistent with those of an authentic specimen.[12]

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Registry No. **1a**, 18794-84-8; **1b**, 3779-62-2; **1c**, 23262-34-2; **2**, 72445-15-9; **3**, 78791-55-6; **4**, 78791-56-7; **5a**, 87639-58-5; **5b**, 87639-59-6; **6a**, 87639-60-9; **6b**, 87655-10-5; **6c**, 87655-11-6; **6d**, 87655-12-7; **7a**, 72445-08-0; **7b**, 72445-10-4; **7c**, 87639-61-0; **7d**, 87639-62-1; **8a**, 87639-63-2; **8b**, 55050-41-4; **9**, 83637-41-6; CH_2=CHOEt, 109-92-2.

(12) Nokami, J.; Mandai, T.; Imakura, Y.; Nishiuchi, K.; Kawada, M.; Wakabayashi, S. *Tetrahedron Lett.* **1981**, *22*, 4489.