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A Total Synthesis of Racemic and Optically Active Terrein (trans-4,5-Dihydroxy-3-[(E)-1-propenyl]-2-cyclopenten-1-one).

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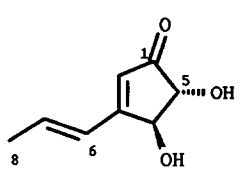
Abstract - Two routes to terrein (**1**), employing a novel ring contraction of 6-alkoxy-2,3-dihydro-6*H*-pyran-3-ones (**5**, **13**) are described. Separation into enantiomers was carried out by classical resolution *via* diastereomeric camphanic acid ester intermediates (**14**, **15**). A new method for cleavage of the 2-(trimethylsilyl)ethyl protecting group in the presence of acid and base sensitive functionality is reported.

The mould metabolite (+)-terrein was discovered by Raistrick and Smith[1] from *Aspergillus terreus* in 1935. Subsequent work showed that it is widely spread, appearing in other moulds, e.g. Aspergillus fischeri,[2] Aspergillus stellatus,[3] Aspergillus pulvinus[4] and Penicillium raistrickii.[5] Japanese workers have shown[6] that (+)-terrein inhibits plant growth, reducing the root elongation of lettuce and rice seedlings. (+)-Terrein has also been shown to have antibacterial activity.[4] Early work on the structure was carried out by Raistrick et al.,[7] but the correct structure **1** was not proposed until 1954 by Grove[5] and also by Barton and Miller.[8]



(+)-terrein
(+)-1

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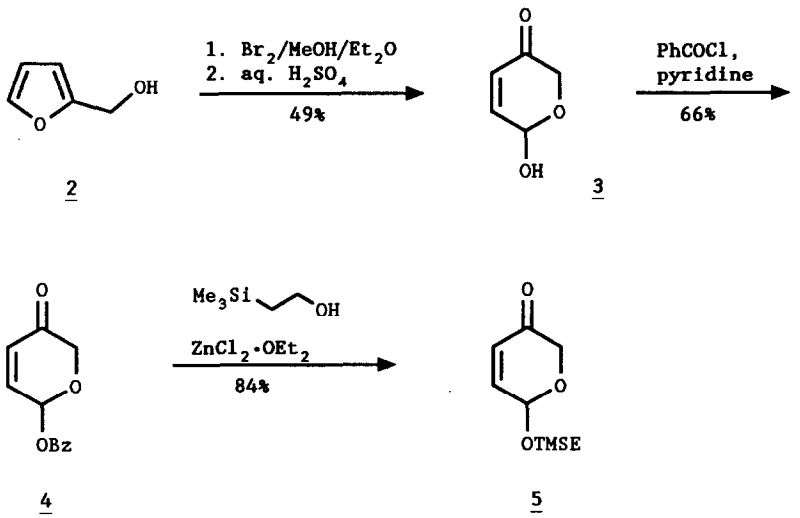
Early synthesis was impeded presumably by the sensitivity of **1** to base and acid. In 1974 Auerbach and Weinreb[9] reported the synthesis of racemic terrein in a multistep sequence and in low overall yield. Three years later Barton and Hulshoff[10] obtained rac-**1** *via* a photochemical ring contraction of a 5-hydroxy-4-pyrone derivative in the key step. Although this is a very short approach, it has the drawback of being non-stereoselective with respect to the configuration of the double bond and the trans arrangement of the hydroxy groups. The key step of the synthesis by Zwanenburg et al.[11] is the retro Diels-Alder reaction of a suitably elaborated mono epoxycyclopentadienone adduct. More recently, a kinetic enzymatic resolution of an early cyclopentadienone Diels-Alder adduct has provided the first formal synthesis of optically active terrein.[12]

Employing a novel ring contraction route,[13] we here record the complete total synthesis of natural and also non-natural terrein in simple fashion.

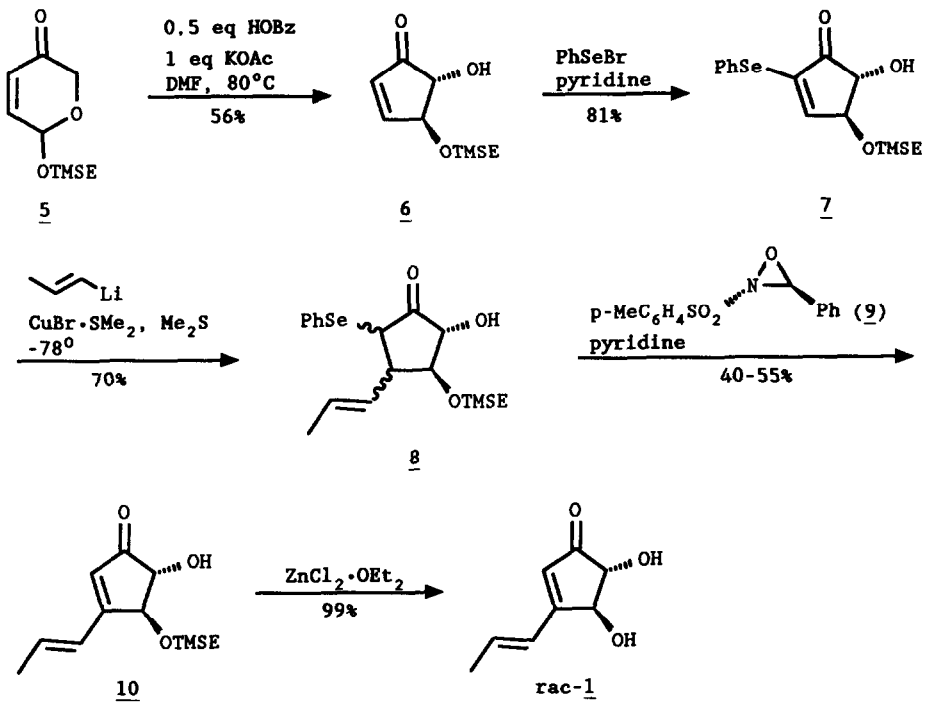
Racemic Terrein. Reaction of 2-furanmethanol (**2**) with bromine in methanol/ether followed by treatment with aqueous sulfuric acid gave hemiketal **3** as reported by Achmatowicz, Zamojski et al.[14] Conversion into the desired acetal **5** was accomplished *via* benzoate **4** by treatment with 2-(trimethylsilyl)ethanol in the presence of 10 mol% $ZnCl_2 \cdot OEt_2$.[13,15] The sequence **2** → **5** was amenable to multigram preparation of **5** in good overall yield from inexpensive reagents.

Scheme 1. Preparation of Precursor **5**.



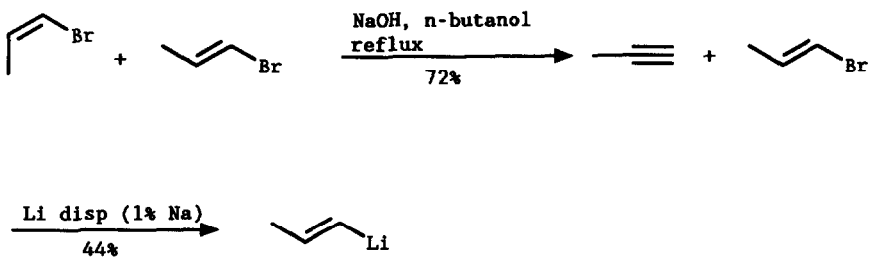
Educt **5** was elaborated to terrein following two strategies (approach A and B) as outlined in Schemes 2 and 4.

Scheme 2. Approach A.



Approach A envisaged the direct ring contraction of pyranone **5**, which under optimized conditions[15] furnished cyclopentenone **6** (56%). α-Benzeneselenenylation under Liotta conditions[16] provided **7** in high yield (81%). Introduction of the side chain by addition of E-1-propenyl cuprate (from E-1-propenyllithium,[17] prepared as shown in Scheme 3) gave selenide **8** as a

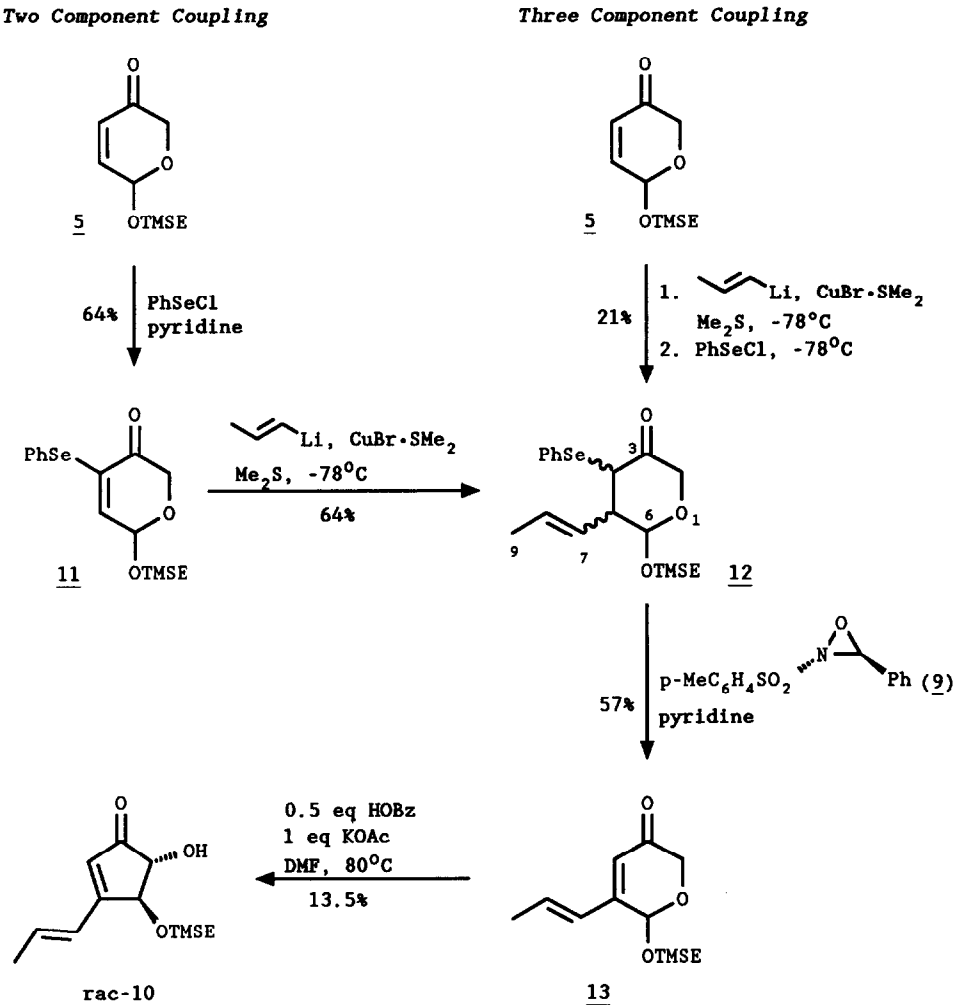
Scheme 3.



mixture of diastereomers. Oxidation of **8** with hydrogen peroxide under two phase conditions[18] produced dienone **10** in poor yield (10%); a slight improvement of the yield (25%) was achieved with m-chloroperbenzoic acid.

Furthermore, complete purification of **10** by column chromatography proved difficult. In contrast, oxidation with oxaziridine **9**[19] afforded pure dienone **10** in preparatively simple fashion (40 - 55%). Attempted deprotection of 2-(trimethylsilyl)ethyl ether **10** with anhydrous tetrabutylammonium fluoride under various conditions resulted in complete decomposition. However, treatment of **10** with Mayr catalyst[20] (zinc chloride monoetherate) afforded racemic terrein (rac-**1**) in almost quantitative (99%) yield. This constitutes a new method for the removal of a 2-(trimethylsilyl)ethyl protecting group from a base and acid sensitive alcohol.

Scheme 4. Approach B.

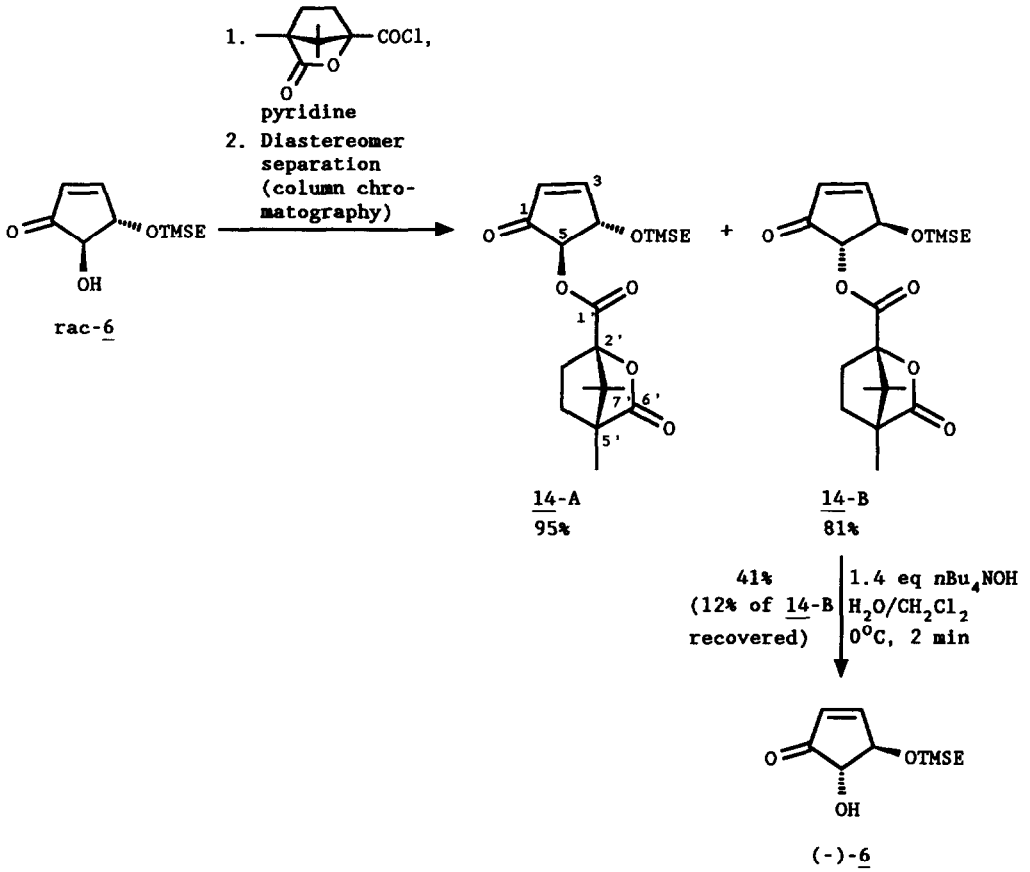


In approach B, the propenyl chain was appended first (**5** → **13**), followed by ring contraction of the resulting E-propenylpyranone **13**, giving protected terrein (rac-**10**) directly (Scheme 4).

Of the two routes to selenide **12** the two step route (**5** → **11**[21] → **12**) gave higher yields than the one step conversion of **5** into **12** (three component coupling of **5** with propenyl cuprate and trapping of the resulting enolate with PhSeCl). Again, oxidation of **12** was advantageously carried out with oxaziridine **9**. Ring contraction of **13**, unlike that of **5**, proceeded in low yield (14%).

Preparation of Natural and Non-natural Enantiomers. The resolution of racemic intermediates succeeded with early enone rac-**6** (Scheme 5 and 6) and also with the later dienone rac-**10** (Scheme 7). In both cases the preparation of enantiomers involved separation of diastereomeric camphanic acid esters.

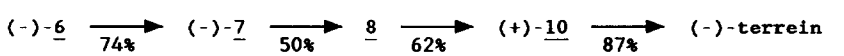
Scheme 5. Classical Resolution of **6** *via* Camphanates **14**-A (less polar) and **14**-B (more polar).



Esterification gave **14-A** (less polar) and **14-B** (more polar) in high yield. Column chromatography on silica gel (ether/light petroleum, 1:1) effected separation (Δ R_F = 0.03). Because of tailing of the less polar **14-A**, the more polar **14-B** could not be freed completely from **14-A** . However, camphanate **14-A** was obtained diastereomerically pure. Saponification of **14-B** was tested under various conditions. Best results were obtained under two phase conditions ($n\text{-}Bu_4N^+OH^-$, H_2O/CH_2Cl_2, 0°C, 2 min), giving optically active (-)-**6** (90% ee).

Cyclopentenone (-)-**6** was converted into non-natural (-)-terrein [(-)-**1**] (90% ee) as outlined in Scheme 6.

Scheme 6. Conversion of (-)-**6** into (-)-Terrein (for Experimental Conditions see Scheme 2).



yield: 20% from (-)-6

Esterification of rac-**10** with camphanic acid chloride and diastereomeric separation of **15-A** and **15-B** were carried out (Scheme 7) as described for the earlier intermediate rac-**6**. Saponification of ester **15-A** proceeded more smoothly than that of less substituted ester **14-B**, giving optically active (96% ee) dienone (-)-**10**. Deprotection of the alcohol function with $ZnCl_2 \cdot OEt_2$ afforded naturally occurring (+)-terrein [(+)-**1**], identical to the literature,[10] including optical rotation ($[\alpha]_D^{22}$ = +161.8° ± 5.5°, c 0.62, H_2O. Lit[10] $[\alpha]_D^{25}$ = +163.3°, c 0.97, H_2O).

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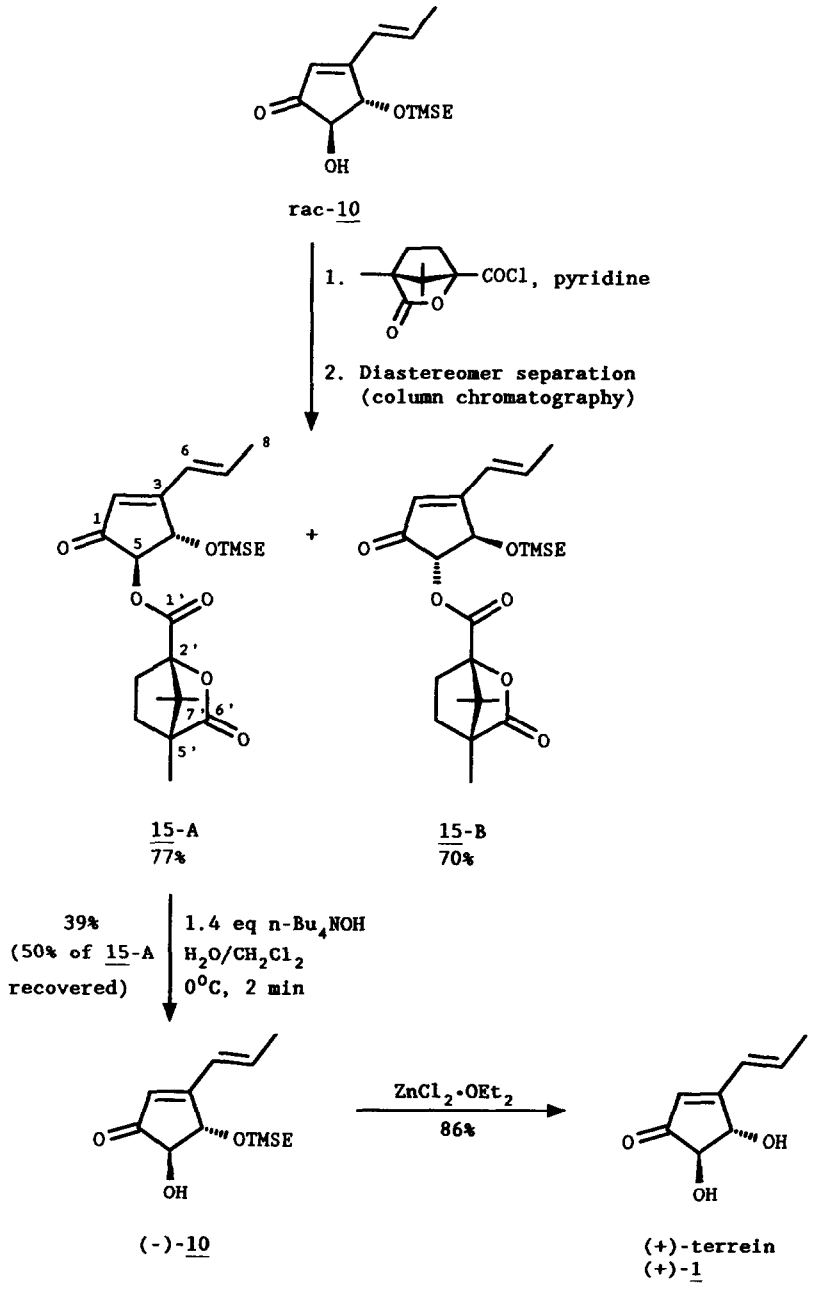
Scheme 7. Separation of Esters 15-A and 15-B.



Experimental Section

Melting points were determined on a Büchi apparatus. Infrared spectra were obtained with a Perkin-Elmer 1710 spectrometer. ^{1}H NMR spectra were recorded in $CDCl_3$ unless otherwise stated at either 80 or 200 MHz on a Bruker WP 80 or WP 200 SY spectrometer. Chemical shifts are reported in ppm downfield from tetramethylsilane, and splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad. ^{13}C NMR spectra were obtained on either a Bruker WP 200 SY or a Bruker AM 300 at 50.3 MHz or 75.5 MHz. Chemical shifts are reported in ppm downfield from tetramethylsilane. Low and high resolution electron impact mass spectra were recorded on a Finnigan MAT 312 spectrometer with an ionization potential of 70 eV at room temperature, unless otherwise stated. Optical rotations were measured with a Perkin-Elmer 241 polarimeter. Microanalyses were performed in the Department of Organic Chemistry of the University of Hannover.

Preparative column chromatography was performed on J.T. Baker silica gel (particle size 30 -60 μm). Analytical tlc was carried out on aluminium-backed 0.2 mm silica gel 60 F_{254} plates (E. Merck).

THF and diethyl ether (ether) were distilled from sodium benzophenone ketyl prior to use, CH_2Cl_2 from P_4O_{10}. Petrol refers to light petroleum, bp 30 - 60°C, and was redistilled prior to use.

***trans*-5-Hydroxy-4-(2-trimethylsilylethoxy)-2-cyclopenten-1-one (rac-6).** Benzoic acid (80 mg, 0.655 mmol) and potassium acetate (128.5 mg, 1.31 mmol) were added to a solution of pyranone **5** (283 mg, 1.32 mmol) in dry DMF (34 mL) under N_2. The mixture was stirred at 80°C for 135 min and then concentrated *in vacuo* at the same temperature. The residue was taken up with ether (25 mL) and the mixture was washed with aqueous sodium bicarbonate solution (5%, 15 mL). After extraction of the aqueous phase with ether (3 x 10 mL), the combined organic layers were washed with brine (15 mL), dried ($MgSO_4$) and evaporated *in vacuo*. Column chromatography on silica gel (15 g, ether/petrol, 1:1) afforded cyclopentenone rac-**6** as a yellowish oil (159 mg, 56%). IR (cap film) 3530, 2960, 2900, 1730, 1590, 1350, 1320, 1250, 1180, 1120, 1080, 1030, 1000, 950, 860, 785, 720 cm^{-1}. 200 MHz ^{1}H NMR δ 7.44 (dd, $J_{2,3}$ = 6 Hz, $J_{3,4}$ = 2 Hz, 1 H, H-3), 6.21 (dd, $J_{2,3}$ = 6 Hz, $J_{2,4}$ = 2 Hz, 1 H, H-2), 4.40 (m, 1 H, H-4), 4.15 (d, $J_{4,5}$ = 2 Hz, 1 H, H-5), 4.02 - 3.53 (m, 3 H, AB part of ABX system, $CH_2CH_2SiMe_3$ and OH), 0.96 (dd, J_{AX} = 8 Hz, J_{BX} = 8 Hz, X part of ABX system, 2 H, $CH_2CH_2SiMe_3$), -0.01 (s, 9 H, $SiMe_3$). 50 MHz ^{13}C NMR δ 204.89 (s, C-1), 159.14 (d, C-3), 131.88 (d, C-2), 82.72 (d, C-4), 80.02 (d, C-5), 67.87 (t, $CH_2CH_2SiMe_3$), 18.26 (t, $CH_2CH_2SiMe_3$), -1.48 (q, $SiMe_3$). MS, *m/e* (rel intensity): 214 (M^+, 0), 185 (13), 170 (15), 157 (8), 141 (15), 113 (5), 96 (19), 75 (63), 73 (100), 68 (8). Exact mass calcd for M^+-101 ($CH_2CH_2SiMe_3$): 113.0238. Found 113.0238.

(±)-*trans*-2-Benzeneselenenyl-5-hydroxy-4-(2-trimethylsilylethoxy)-2-cyclopenten-1-one (rac-7). Pyridine (0.2 mL, 2.47 mmol) was added to a solution of benzeneselenenyl bromide (557 mg, 2.36 mmol) in CH_2Cl_2 (11.2 mL) under N_2. The mixture was stirred at room temperature for 10 min, then a solution of cyclopentenone rac-**6** (483 mg, 2.25 mmol) in CH_2Cl_2 (4 mL) was added rapidly. The mixture was stirred for 30 min, diluted with CH_2Cl_2 and washed with water (3x). The aqueous layers were extracted with CH_2Cl_2, the combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo*. Column chromatography on silica gel (45 g, ether/petrol, 1:1) afforded pure selenenylenone rac-**7** as a slightly yellow oil (677 mg, 81%). IR (cap film) 3425, 3059, 2953, 2894, 1723, 1568, 1250, 1078, 860, 838, 744, 692 cm^{-1}. 200 MHz ^{1}H NMR δ 7.62 (m, 2 H, aryl-H), 7.39 (m, 3 H, aryl-H), 6.77 (d, $J_{3,4}$ = 2 Hz, 1 H, H-3), 4.31 (t, J = 2 Hz, 1 H, H-4), 4.25 (bd, $J_{4,5}$ = 2 Hz, 1 H, H-5), 3.79 (dt, J_t = 9 Hz, J_d = 7.6 Hz, 1 H, $CHHCH_2SiMe_3$), 3.66 (dt, J_t = 9 Hz, J_d = 7.6 Hz, 1 H, $CHHCH_2SiMe_3$), 3.04 (bs, 1 H, OH), 0.96 (t, J = 9 Hz, 2 H, $CH_2CH_2SiMe_3$), 0.0 (s, 9 H, Me_3Si). 50 MHz ^{13}C NMR δ 201.35 (s, C-1), 151.90 (d, C-3), 138.93 (s, C-2), 135.83 (d, C_{aryl}-2,6), 129.71 (d, C_{aryl}-3,5), 129.05 (d, C_{aryl}-4), 124.54 (s, C_{aryl}-1), 82.89

(d, C-5), 80.03 (d, C-4), 67.77 (t, $CH_2CH_2SiMe_3$), 18.29 (t, CH_2CH_2-$SiMe_3$), -1.42 (q, Me_3Si). MS (50°C), *m/e* (rel intensity): 370 (M^+, ^{80}Se, 6.5), 368 (M^+, ^{78}Se, 3), 342 ($M^+-C_2H_4$, ^{80}Se, 10), 340 ($M^+-C_2H_4$, ^{78}Se, 5.3), 327 ($M^+-C_2H_4-CH_3$, ^{80}Se, 5.3), 325 ($M^+-C_2H_4-CH_3$, ^{78}Se, 3), 185 (47), 101 (25), 75 (99), 73 (100). Exact mass calcd. for $C_{16}H_{22}O_3Si^{80}Se$: 370.0504. Found 370.0502.

(±)-*trans*-5-Hydroxy-3-(E-1-propenyl)-4-(2-trimethylsilylethoxy)-2-cyclopenten-1-one (rac-10). A suspension of $CuBr \cdot SMe_2$ complex[22] (961 mg, 4.68 mmol) and dimethyl sulfide (0.1 mL) in anhydrous ether (6.8 mL) under argon was cooled to -78°C and then E-1-propenyl lithium[17] (19 mL of a 0.5 M solution in ether, 9.5 mmol) was added, dropwise and with stirring, during 15 min. After 2 h a solution of selenenylenone rac-7 (770 mg, 2.08 mmol) in ether (2.5 mL) was added dropwise during 15 min to the grey solution of the organocuprate, while the temperature was maintained at -78°C. The mixture was stirred for 45 min, then a solution of acetic acid (0.58 mL, 10.1 mmol) in ether (3 mL) was added at -78°C, giving a black precipitate. After allowing the mixture to warm to room temperature it was diluted with ether and washed twice with aqueous ammonium chloride/ammonia solution (sat. NH_4Cl/1.7M NH_3, 2:1). The aqueous layers were extracted with ether (3x), the combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo*. The residual orange oil (820 mg) was filtered through silica gel (11 g), eluting with ether/petrol (4:6) to obtain crude selenide **8** (597 mg, 70%) as an orange oil.

Oxaziridine **9** (479 mg, 1.74 mmol) was added to a stirred solution of selenide **8** (597 mg, 1.45 mmol) and pyridine (0.59 mL, 7.3 mmol) in $CHCl_3$ (2 mL). After 1 h the mixture was evaporated to dryness and purified by flash chromatography on silica gel (90 g, ether/ petrol/CH_2Cl_2, 4:3:3). Repeated column chromatography of the crude dienone on silica gel (7 g), eluting with ether/petrol (6:4) afforded dienone rac-**10** (147 mg, 28% from **7**) as a slightly yellow oil. IR ($CHCl_3$) 2955, 2925, 1705, 1638, 1250, 1092, 968, 860, 839 cm^{-1}. 200 MHz ^1H NMR (C_6D_6) δ 6.39 (dq, $J_{6,7}$ = 15.8 Hz, $J_{7,8}$ = 6.5 Hz, 1 H, H-7), 5.99 (m, $J_{6,7}$ = 15.8 Hz, 1 H, H-6), 5.82 (s, 1 H, H-2), 4.50 (bd, $J_{4,5}$ = 2.3 Hz, 1 H, H-5), 4.30 (d, $J_{4,5}$ = 2.3 Hz, 1 H, H-4), 4.01 (dt, J_t = 9.1 Hz, J_d = 7.2 Hz, 1 H, C*H*HCH$_2$SiMe$_3$), 3.71 (dt, J_t = 9.1 Hz, J_d = 7.2 Hz, 1 H, CH*H*CH$_2$SiMe$_3$), 3.34 (bs, 1 H, OH), 1.51 (dd, $J_{7,8}$ = 6.5 Hz, $^4J_{6,8}$ = 1.5 Hz, 3 H, H-8), 0.99 (m, 2 H, CH$_2$C*H*$_2$SiMe$_3$), 0.02 (s, 9 H, Me_3Si). 50 MHz ^{13}C NMR (C_6D_6) δ 203.49 (s, C-1), 167.54 (s, C-3), 139.52 (d, C-7), 125.72 (d, C-2), 125.45 (d, C-6), 83.43 (d, C-5), 80.46 (d, C-4), 67.52 (t, $CH_2CH_2SiMe_3$), 19.01 (q, C-8), 18.50 (t, $CH_2CH_2SiMe_3$), -1.32 (q, Me_3Si). MS, *m/e* (rel intensity): 226 ($M^+-C_2H_4$, 13), 211 ($M^+-C_2H_4-CH_3$, 6), 197 (7.5), 136 (8.3), 121 (8.5), 75 (41), 73 (100). Exact mass calcd for $M^+-C_2H_4$ ($C_{11}H_{18}O_3Si$): 226.1025. Found 226.1022.

(±)-Terrein (rac-1). $ZnCl_2 \cdot OEt_2$ (0.06 mL of a 2.2 M solution in CH_2Cl_2, 0.132 mmol) was added to a stirred solution of 2-(trimethylsilyl)ethyl ether rac-**10** (30 mg, 0.118 mmol) in dry CH_2Cl_2 (0.5 mL) under N_2. A colorless precipitate was formed in the course of the reaction. After 16 h saturated sodium bicarbonate solution (0.1 mL) was added and the mixture extracted with ethyl acetate (3x). The combined extracts were dried ($MgSO_4$) and concentrated *in vacuo* to give a clear oil (60 mg) that was purified by column chromatography on silica gel (3.5 g, acetone/petrol, 1:1) and subsequent recrystallization from benzene. Racemic terrein (rac-**1**) (18 mg, 99%) was obtained as a colorless crystalline solid, mp 94 - 95°C (from benzene). IR (KBr) 3420, 2973, 1685, 1636, 1561, 1333, 1310, 1220, 1114, 1084, 975 cm^{-1}. 200 MHz ^1H NMR (acetone-d_6) δ 6.83 (dq, $J_{6,7}$ = 15.5 Hz, $J_{7,8}$ = 6.6 Hz, 1 H, H-7), 6.44 (m, $J_{6,7}$ = 15.5 Hz, 1 H, H-6), 5.96 (s, 1 H, H-2), 4.95 (bs, 1 H, OH), 4.73 (bs, 1 H, H-5), 4.62 (bs, 1 H, OH), 4.07 (d, $J_{4,5}$ = 2.5 Hz,1 H, H-4), 1.91 (dd, $J_{7,8}$ = 6.6 Hz, $^4J_{6,8}$ = 1.4 Hz, 3 H, H-8). 75 MHz ^{13}C NMR (acetone-d_6) δ 206.80 (C-1), 169.49 (C-3), 140.29 (C-7), 126.34 (C-2), 125.74 (C-6), 82.29 (C-5), 77.89 (C-4), 19.36 (C-8). MS (50°C), *m/e* (rel intensity): 154 (M^+, 10), 139 (M^+-CH_3, 100), 121 (54), 79 (86). Exact mass calcd for $C_8H_{10}O_3$: 154.063. Found 154.063.

4-Benzeneselenenyl-6-(2-trimethylsilylethoxy)-2,3-dihydro-6*H*-py-ran-3-one (11). Pyridine (0.08 mL, 0.99 mmol) was added to a solution of benzeneselenenyl chloride (187 mg, 0.97 mmol) in CH_2Cl_2 (4.6 mL) under N_2. The orange solution was stirred for 10 min, then a solution of enone **5** (200 mg, 0.93 mmol) in CH_2Cl_2 (1.7 mL) was added. After the reaction had gone to completion (11 h, tlc control), the mixture was diluted with CH_2Cl_2 and washed with water (3x). The aqueous layers were reextracted with CH_2Cl_2, the combined organic layers were dried ($MgSO_4$) and evaporated *in vacuo*. Purification of the residual orange oil (370 mg) by column chromatography on silica gel (11 g), eluting with CH_2Cl_2/petrol (1:1) afforded selenenylenone **11** as a slightly yellow oil (245 mg), which according to ^1H NMR data contained 10% (w/w) of 4-chloro-6-(2-trimethylsilylethoxy)-2,3-dihydro-6*H*-pyran-3-one (cf. footnote 21). Yield, calculated for pure **11**, was 64%. IR (cap film) 3059, 2953, 2896, 1708, 1688, 1605, 1579, 1477, 1329, 1250, 1134, 1044, 860, 837, 742, 694 cm^{-1}. 80 MHz ^1H NMR δ 7.7 - 7.25 (m, 5 H, aryl-H), 6.19 (d, $J_{5,6}$ = 3.8 Hz, 1 H, H-5), 5.07 (d, $J_{5,6}$ = 3.8 Hz, 1 H, H-6), 4.57 (d, J_{gem} = 16.8 Hz, 1 H, H-2), 4.17 (d, J_{gem} = 16.8 Hz, 1 H, H-2), 3.78 - 3.61 (m, 2 H, $CH_2CH_2SiMe_3$), 0.93 (t, J = 8.5 Hz, 2 H, $CH_2CH_2SiMe_3$), 0.0 (s, 9 H, Me_3Si). 50 MHz ^{13}C NMR δ 192.0 (s, C-3), 138.35 (d, C-5), 137.08 (d, C_{aryl}-2,6), 136.06 (s, C-4), 129.86 (d, C_{aryl}-3,5), 129.28 (d, C_{aryl}-4), 124.86 (s, C_{aryl}-1), 94.41 (d, C-6), 66.70 (t, C-2), 66.26 (t, $CH_2CH_2SiMe_3$), 18.13 (t, $CH_2CH_2SiMe_3$), -1.49 (q, Me_3Si). MS, *m/e* (rel intensity): 370 (M^+, ^{80}Se, 1.7), 368 (M^+, ^{78}Se, 0.9), 312 ($M-C_2H_2O_2$, ^{80}Se, 0.8), 310 ($M-C_2H_2O_2$, ^{78}Se, 0.4), 253 (4.5), 251 (2.1), 205 (8.4), 133 (29), 131 (86), 73 (100). Exact mass calcd for $C_{16}H_{22}O_3Si^{80}Se$: 370.0503. Found 370.0503.

5-(E-1-propenyl)-6-(2-trimethylsilylethoxy)-2,3-dihydro-6*H*-pyran-3-one (13). E-1-Propenyl lithium (4.95 mL of a 0.6 M solution in ether, 2.97 mmol) was added dropwise during 5 min to a stirred suspension of $CuBr \cdot SMe_2$ (304 mg, 1.48 mmol) and dimethyl sulfide (0.03 mL) in anhydrous ether (2.2 mL) under argon at -78°C. After 2 h a solution of selenenyl enone **11** (400 mg, 1.08 mmol) in ether (1.4 mL) was added, dropwise and with stirring, during 15 min to the grey solution of the cuprate, while the temperature was maintained at -78°C. After a further 90 min the reaction was quenched by pouring the mixture into aqueous ammonium chloride/ammonia solution (sat. NH_4Cl/1.7 M NH_3, 2:1) and extracting with ether (3x). The combined organic layers were dried ($MgSO_4$) and evaporated *in vacuo* to give a yellow oil (450 mg) that was purified by flash chromatography on silica gel (16 g, ether/petrol, 2:8) to yield selenide **12** (289 mg, 64%) as a 1:1 mixture of diastereomers. IR (cap film) 3058, 2953, 2921, 1729, 1715, 1605, 1579, 1478, 1249, 1044, 860, 838, 741, 693 cm^{-1}. 200 MHz ^1H NMR δ 7.65 - 7.45 (m, 4 H, aryl-H), 7.35 - 7.2 (m, 6 H, aryl-H), 5.74 - 5.48 (m, 3 H, *H-7*, H-8, *H-8*), 5.37 (ddq, $J_{7,8}$ = 15.2 Hz, $J_{5,7}$ = 8.4 Hz, $^4J_{7,9}$ = 1.2 Hz, 1 H, H-7), 4.85 - 4.65 (m, 3 H), 4.23 (d, J_{gem} = 16.2 Hz, 1 H, H-2 or *H-2*), 4.11 (d, J_{gem} = 16.2 Hz, 1 H, H'-2 or *H'-2*), 3.95 - 3.72 (m, 4 H), 3.63 - 3.44 (m, 3 H), 3.11 (m, $J_{5,7}$ = 8.4 Hz, 1 H, H-5), 2.85 (m, 1 H, *H-5*), 1.72 (d, $J_{8,9}$ = 5 Hz, 3 H, *H-9*), 1.63 (m, $J_{8,9}$ = 6 Hz, 3 H, H-9), 1.14 - 0.78 (m, 4 H, $CH_2CH_2SiMe_3$), 0.03 (s, 9 H, $SiMe_3$ or *$SiMe_3$*), -0.01 (s, 9 H, *$SiMe_3$* or $SiMe_3$). MS, *m/e* (rel intensity): 412 (M^+, ^{80}Se, 1.9), 410 (M^+, ^{78}Se, 0.9), 370 ($M^+-C_2H_2O$, ^{80}Se, 4), 368 ($M^+-C_2H_2O$, ^{78}Se, 2.3), 311 (3.3), 295 (1), 253 (11), 251 (6), 227 (33), 75 (35), 73 (100). Exact mass calcd for $C_{19}H_{28}O_3Si^{80}Se$: 412.0973. Found 412.0972.

Oxaziridine **9** (200 mg, 0.726 mmol) was added to a stirred solution of selenide **12** (270 mg, 0.655 mmol) and pyridine (0.26 mL, 3.22 mmol) in $CHCl_3$ (0.9 mL). After 1 h the mixture was evaporated *in vacuo* and the residual orange oil (485 mg) purified by column chromatography on silica gel (40 g, CH_2Cl_2) to give dienone **13** (95 mg, 57%) as a yellowish oil. IR ($CHCl_3$) 3010, 2960, 1708, 1671, 1637, 1597, 1318, 1269, 1250, 1038, 860, 838 cm^{-1}. 200 MHz ^1H NMR (C_6D_6) δ 5.92 (dq, $J_{7,8}$ = 16 Hz, $J_{8,9}$ = 6.5 Hz, 1 H, H-8), 5.90 (s, 1 H, H-4), 5.70 (m, $J_{7,8}$ = 16 Hz, 1 H, H-7), 5.27 (s, 1 H, H-6), 4.45 (d, J_{gem} = 17 Hz, 1 H, H-2), 4.12 (d, J_{gem} = 17 Hz, 1 H, H-2), 3.90 (dt, J_t= 9 Hz, J_d = 6.5 Hz, 1 H, $CHHCH_2SiMe_3$), 3.54 (dt, J_t = 9 Hz, J_d =

6.5 Hz, 1 H, CH*H*CH_2SiMe_3), 1.47 (m, $J_{8,9}$ = 6.5 Hz, 3 H, H-9), 1.0 - 0.78 (m, 2 H, $CH_2CH_2SiMe_3$), -0.03 (s, 9 H, Me_3Si). 50 MHz ^{13}C NMR (C_6D_6) δ 194.38 (s, C-3), 152.47 (s, C-5), 135.06 (d, C-8), 129.11 (d, C-4), 122.47 (d, C-7), 93.70 (d, C-6), 66.38 (t, C-2), 65.62 (t, $CH_2CH_2SiMe_3$), 18.83 (q, C-9), 18.21 (t, $CH_2CH_2SiMe_3$), -1.43 (q, Me_3Si). MS, *m/e* (rel intensity): 254 (M^+, 0.5), 226 ($M^+-C_2H_4$, 9.3), 211 (5.3), 196 (48), 183 (31), 137 (60), 75 (33), 73 (100). Exact mass calcd for $M^+-C_2H_4$ ($C_{11}H_{18}O_3Si$): 226.1025. Found 226.1025.

(±)-*trans*-5-Hydroxy-3-(E-1-propenyl)-4-(2-trimethylsilylethoxy)-2-cyclopenten-1-one (rac-10) by Ring Contraction of 13. Benzoic acid (10.6 mg, 0.087 mmol) and potassium acetate (17 mg, 0.173 mmol) were added to a solution of pyranone **13** (44 mg, 0.173 mmol) in dry DMF (4.4 mL) under N_2. The mixture was stirred at 80°C for 14 h, then concentrated *in vacuo* at the same temperature. The residue was taken up with CH_2Cl_2 (10 mL) and the mixture washed with aqueous sodium bicarbonate solution (5%). After extraction of the aqueous phase with CH_2Cl_2 (2x), the combined organic layers were washed with brine, dried ($MgSO_4$) and evaporated *in vacuo*. Column chromatography of the residue on silica gel (5 g, ether/petrol, 1:1) afforded starting material **13** (4.7 mg, 11%) and cyclopentenone rac-**10** (6 mg, 14%) as a yellowish oil, identical with the previously obtained material.

Camphanic Acid Esters 14-A and 14-B. Separation of Diastereoisomers. (-)-ω-Camphanic acid chloride (Fluka, 97%) (640 mg, 2.95 mmol) was added to a stirred solution of alcohol **rac-6** (550 mg, 2.57 mmol) and pyridine (0.41 mL, 5.1 mmol) in dry CH_2Cl_2 (6 mL) at 0°C. After 2 h the mixture was washed with water (3x) and the aqueous layers were extracted with CH_2Cl_2. The combined organic layers were dried ($MgSO_4$), evaporated *in vacuo* and the residual brown oil (1.26 g) was purified by flash chromatography on silica gel (25 g, ether/petrol/CH_2Cl_2, 3:5:2) to yield a mixture of esters **14-A** and **14-B** (980 mg, 97%) as a slightly yellow crystalline solid. MS (80°C), *m/e* (rel intensity): 394 (M^+,1.2), 379 (M^+-CH_3, 1.5), 366 ($M^+-C_2H_4$,13), 351 ($M^+-C_2H_4-CH_3$, 18), 306 (5.5), 226 (19), 211 (8), 169 (26), 125 (16), 109 (66), 97 (32), 83 (57), 73 (100). Column chromatography of the product on silica gel [165 g, ether/petrol, 1:1, R_F(**14-A**) > R_F(**14-B**)] gave pure ester **14-A** (272 mg) and a mixture of isomers (670 mg) that was subjected to further column chromatography (130 g silica gel), giving **14-A** (140 mg) and a mixed fraction (520 mg). Repeated column chromatography of the latter (100 g silica gel) afforded an additional batch of **14-A** (68 mg), ester **14-B** (410 mg) and a mixture of isomers (40 mg). The diastereomeric purities of camphanic acid esters **14-A** (480 mg, 95%) and **14-B** (410 mg, 81%), according to ^1H NMR data, were 100% de and 90% de, respectively. Data of **14-A**: $[\alpha]_D^{22}$ = +69.6°, $[\alpha]_{578}^{22}$ = +72.2°, $[\alpha]_{546}^{22}$ = +80.6°, $[\alpha]_{436}^{22}$ = +102.6° (c = 1.09 in CH_2Cl_2). IR ($CHCl_3$) 2958, 1789, 1748, 1734, 1275, 1168, 1106, 1063, 861, 839 cm^{-1}. 200 MHz ^1H NMR (C_6D_6) δ 6.87 (dd, $J_{2,3}$ = 6.2 Hz, $J_{3,4}$ = 2 Hz, 1 H, H-3), 5.84 (dd, $J_{2,3}$ = 6.2 Hz, $^4J_{2,4}$ = 1.5 Hz, 1 H, H-2), 5.37 (d, $J_{4,5}$ = 3 Hz, 1 H, H-5), 4.41 (ddd, $J_{4,5}$ = 3 Hz, $J_{3,4}$ = 2 Hz, $^4J_{2,4}$ = 1.5 Hz, 1 H, H-4), 3.54 (m, 2 H, $CH_2CH_2SiMe_3$), 2.27 (ddd, J_{gem} = 13.2 Hz, J = 10 Hz, J = 5 Hz, 1 H, H-3′), 1.82 (ddd, J_{gem} = 13.2 Hz, J = 9 Hz, J = 5 Hz, 1 H, H-3′), 1.38 (ddd, J_{gem} = 13.2 Hz, J = 10 Hz, J = 5 Hz, 1 H, H-4′), 1.27 (ddd, J_{gem} = 13.2 Hz, J = 9 Hz, J = 5 Hz, 1 H, H-4′), 1.10 (s, 3 H, CH_3), 0.89 (t, J = 8 Hz, 2 H, $CH_2CH_2SiMe_3$), 0.88 (s, 3 H, CH_3), 0.83 (s, 3 H, CH_3), 0.02 (s, 9 H, Me_3Si). 50 MHz ^{13}C NMR (C_6D_6) δ 196.87 (s, C-1), 177.35 (s, C-6′), 167.15 (s, C-1′), 157.89 (d, C-3), 132.77 (d, C-2), 90.59 (s, C-2′), 80.61 (d, C-5), 80.22 (d, C-4), 67.75 (t, $CH_2CH_2SiMe_3$), 54.81 (s, C-5′), 54.66 (s, C-7′), 30.87 (t, C-3′), 28.66 (t, C-4′), 18.24 (t, C-7), 16.70 (q, CH_3), 16.36 (q, CH_3), 9.75 (q, CH_3), -1.30 (q, Me_3Si). Exact mass calcd for $C_{20}H_{30}O_6Si$: 394.1812. Found 394.1813. Data of **14-B**: mp 89.5°C; $[\alpha]_D^{22}$ = -82.3°, $[\alpha]_{578}^{22}$ = -85.0°, $[\alpha]_{546}^{22}$ = -94.9°, $[\alpha]_{436}^{22}$ = -119.5° (c = 1.19 in CH_2Cl_2). IR (KBr) 2957, 2930, 1791, 1759, 1732, 1635, 1272, 1170, 1108, 1062, 861, 839 cm^{-1}. 200 MHz ^1H NMR (C_6D_6) δ 6.90 (dd, $J_{2,3}$ = 6.2 Hz, $J_{3,4}$ = 2 Hz, 1 H, H-3), 5.86 (dd, $J_{2,3}$ = 6.2 Hz, $^4J_{2,4}$ = 1.5 Hz, 1H, H-2), 5.32

(d, $J_{4,5}$ = 2.6 Hz, 1 H, H-5), 4.39 (ddd, $J_{4,5}$ = 2.6 Hz, $J_{3,4}$ = 2 Hz, $J_{2,4}$ = 1.5 Hz, 1 H, H-4), 3.61 (dt, J_{gem} = 9.5 Hz, J_t = 8 Hz, 1 H, C*H*HCH$_2$-SiMe$_3$), 3.49 (dt, J_{gem} = 9.5 Hz, J = 8 Hz, 1 H, CH*H*CH$_2$SiMe$_3$), 2.21 (ddd, J_{gem} = 13.2 Hz, J = 10 Hz, J = 5 Hz, 1 H, H-3'), 1.84 (ddd, J_{gem} = 13.2 Hz, J = 9 Hz, J = 5 Hz, H-3'), 1.47-1.2 (m, 2 H, H-4'), 1.06 (s, 3 H, CH$_3$), 0.90 (t, J = 8 Hz, CH$_2$C*H*$_2$SiMe$_3$), 0.89 (s, 3 H, CH$_3$), 0.83 (s, 3 H, CH$_3$), 0.02 (s, 9 H, Me$_3$Si). 50 MHz ^{13}C NMR (C_6D_6) δ 196.88 (s, C-1), 177.18 (s, C-6'), 167.02 (s, C-1'), 157.83 (d, C-3), 132.85 (d, C-2), 90.48 (s, C-2'), 80.53 (d, C-5), 80.37 (d, C-4), 67.81 (t, C-6), 54.68 (s, C-5'), 54.42 (s, C-7'), 30.93 (t, C-3'), 28.75 (t, C-4'), 18.30 (t, C-7), 16.63 (q, CH$_3$), 16.45 (q, CH$_3$), 9.72 (q, CH$_3$), -1.29 (q, Me$_3$Si). Anal. Calcd for $C_{20}H_{30}O_6Si$: C, 60.89; H, 7.66. Found: C, 60.75; H, 7.56.

(-)-(4R,5S)-5-Hydroxy-4-(2-trimethylsilylethoxy)-2-cyclopenten-1-one [(-)-6]. Tetrabutylammonium hydroxide (3.5 mL of a 0.1 M solution in methanol/isopropanol, E.Merck, 0.35 mmol) was added rapidly to a vigorously stirred solution of ester **14-B** (100 mg, 0.253 mmol) in CH_2Cl_2 (2.4 mL) and water (2.6 mL) at 0°C. After 120 sec the reaction was quenched by adding aqueous HCl (3.6 mL of a 0.1 M solution, 0.36 mmol) and extracting the mixture with ether (3x). The combined organic layers were washed with brine, dried ($MgSO_4$) and concentrated *in vacuo*. Flash chromatography of the residue on silica gel (10 g, ether/petrol/CH_2Cl_2, 3:4:3) afforded starting material **14-B** (12 mg) and crude alcohol **(-)-6** (41 mg). The latter was purified further by column chromatography on silica gel (5 g, ether/petrol, 6:4) to yield **(-)-6** (22 mg, 41%) as a colorless oil with spectroscopic data identical to those of the racemic compound **rac-6**. $[\alpha]_D^{22}$ = -42.2°, $[\alpha]_{578}^{22}$ = -42.4°, $[\alpha]_{546}^{22}$ = -41.9° (c = 1.2 in CH_2Cl_2).

Conversion of Cyclopentenone (-)-6 into (-)-Terrein. α-Benzeneselenenylation of enone **(-)-6** (67 mg, 0.313 mmol) was carried out as described for the racemic compound and afforded selenenylenone **(-)-7** (86 mg, 74%) as a slightly yellow oil. $[\alpha]_D^{22}$ = -10.9°, $[\alpha]_{578}^{22}$ = -10.1°, $[\alpha]_{546}^{22}$ = -6.6° (c = 1.01 in CH_2Cl_2). Addition of E-1-propenyl cuprate to selenenylenone **(-)-7** (84 mg, 0.227 mmol) and oxidation of the resulting selenide **8** (47 mg, 50%) with oxaziridine **9** was carried out as described, giving dienone **(+)-10** (18 mg, 31% from **(-)-6**). $[\alpha]_D^{22}$ = +1.2°, $[\alpha]_{578}^{22}$ = +2.8°, $[\alpha]_{546}^{22}$ = +10.2° (c = 1.57 in CH_2Cl_2). (-)-Terrein (9.5 mg, 87%) was obtained as colorless plates by treatment of **(+)-10** (18 mg, 0.071 mmol) with $ZnCl_2 \cdot OEt_2$ (0.04 mL of a 2.2 M solution in CH_2Cl_2, 0.088 mmol), followed by aqueous work up and purification by column chromatography and recrystallization from benzene, as described for the racemic compound, mp 117°C (from benzene). $[\alpha]_D^{22}$ = -141.5°, $[\alpha]_{578}^{22}$ = -146.3°, $[\alpha]_{546}^{22}$ = -161.0°, $[\alpha]_{436}^{22}$ = -121.8° (c = 0.40 in H_2O).

Camphanic Acid Esters 15-A and 15-B. Separation of Diastereoisomers. Esterification of alcohol **rac-10** (109 mg, 0.429 mmol) with camphanic acid chloride (107 mg, 0.494 mmol) and pyridine (0.07 mL, 0.867 mmol) gave a mixture of camphanates **15-A** and **15-B** (165 mg, 89%) as an oil. MS (90°C), *m/e* (rel intensity): 434 (M^+,1), 406 ($M^+-C_2H_4$, 10), 391 ($M^+-C_2H_4-CH_3$, 6.7), 347 (1), 317 (3.4), 271 (5.9), 209 (42), 183 (13), 136 (17), 109 (50), 97 (25), 83 (48), 73 (100). Column chromatography of the product on silica gel [65 g, ether/petrol, 1:1, R_F(**15-A**) > R_F(**15-B**)] afforded pure ester **15-A** (57 mg) and a mixture of isomers (87 mg). The latter was subjected to repeated column chromatography (40 g silica gel), to afford **15-A** (13 mg) and a mixed fraction (72 mg), which was chromatographed (25 g silica gel) to afford **15-A** (1.8 mg, total amount 71.8 mg, 77%) and pure diastereomer **15-B** (65 mg, 70%). The diastereomeric purities of esters **15-A** and **15-B**, according to ^{1}H NMR data, were 96% de and 97% de, respectively. Data of **15-A**, mp 115 -116°C (from ether/ petrol): $[\alpha]_D^{22}$ = +86.9°, $[\alpha]_{578}^{22}$ = +91.0°, $[\alpha]_{546}^{22}$ = +104.3°, $[\alpha]_{436}^{22}$ = +157.9° (c = 1.07 in CH_2Cl_2). IR (KBr) 2957, 2900, 1783, 1737, 1715, 1640, 1571, 1274, 1253, 1169, 1108, 1061, 862, 839 cm^{-1}. 200 MHz ^{1}H NMR (C_6D_6) δ 6.32 (dq, $J_{7,8}$ = 6.9 Hz, $J_{6,7}$ = 15.5 Hz, 1 H, H-7), 5.93 (m, $J_{6,7}$ = 15.5 Hz, 1 H, H-6), 5.81 (s, 1 H, H-2), 5.71 (d, $J_{4,5}$ = 2.5 Hz, 1 H, H-5), 4.65 (d, $J_{4,5}$ = 2.5 Hz, 1 H, H-4), 3.74 (dt, J_t = 9 Hz, J_d = 7.2 Hz, 1 H, C*H*HCH$_2$SiMe$_3$), 3.53

(dt, J_t = 9 Hz, J_d = 6.5 Hz, 1 H, CH*H*CH$_2$SiMe$_3$), 2.36 (ddd, J_{gem} = 13.5 Hz, J = 9.5 Hz, J = 6 Hz, 1 H, H-3′), 1.88 (ddd, J_{gem} = 13.5 Hz, J = 8.2 Hz, J = 5.3 Hz, 1 H, H-3′), 1.52 (dd, $J_{7,8}$ = 6.9 Hz, $^4J_{6,8}$ = 1.5 Hz, 3 H, H-8), 1.45 - 1.24 (m, 2 H, H-4′), 1.19 (s, 3 H, CH$_3$), 0.93 (dd, J = 9 Hz, J = 6.5 Hz, 1 H, CH$_2$CH*H*SiMe$_3$), 0.91 (dd, J = 9 Hz, J = 7.2 Hz, 1 H, CH$_2$CH*H*SiMe$_3$), 0.89 (s, 3 H, CH$_3$), 0.85 (s, 3 H, CH$_3$), 0.03 (s, 9 H, Me$_3$Si). 50 MHz ^{13}C NMR (C$_6$D$_6$) δ 195.74 (s, C-1), 177.34 (s, C-6′), 167.21 (s, C-1′), 166.58 (s, C-3), 139.80 (d, C-7), 126.74 (d, C-2), 125.41 (d, C-6), 90.69 (s, C-2′), 80.54 and 80.45 (2 d, C-4 and C-5), 67.31 (t, *C*H$_2$CH$_2$SiMe$_3$), 54.84 (s, C-5′), 54.68 (s, C-7′), 30.93 (t, C-3′), 28.63 (t, C-4′), 19.02 (q, C-8), 18.30 (t, CH$_2$*C*H$_2$SiMe$_3$), 16.82 (q, CH$_3$), 16.33 (q, CH$_3$), 9.79 (q, CH$_3$), -1.37 (q, Me$_3$Si). Anal. Calcd. for C$_{23}$H$_{34}$O$_6$Si: C, 63.56; H, 7.89. Found: C, 63.66; H, 7.62. Data of **15-B**, mp 98.5°C (from ether/petrol): $[\alpha]_D^{22}$ = -64.1°, $[\alpha]_{578}^{22}$ = -66.8°, $[\alpha]_{546}^{22}$ = -75.5°, $[\alpha]_{436}^{22}$ = -94.8° (c = 1.14 in CH$_2$Cl$_2$). IR (KBr) 2956, 2895, 1784, 1757, 1714, 1641, 1584, 1567, 1248, 1171, 1117, 1063, 864, 840 cm^{-1}. 200 MHz ^{1}H NMR (C$_6$D$_6$) δ 6.33 (dq, $J_{6,7}$ = 15.8 Hz, $J_{7,8}$ = 6.8 Hz, 1 H, H-7), 5.95 (m, $J_{6,7}$ = 15.8 Hz, 1 H, H-6), 5.83 (s, 1 H, H-2), 5.57 (d, $J_{4,5}$ = 2.6 Hz, 1 H, H-5), 4.63 (d, $J_{4,5}$ = 2.6 Hz, 1 H, H-4), 3.76 (dt, J_t = 8.9 Hz, J_d = 7.5 Hz, 1 H, *C*H*H*CH$_2$SiMe$_3$), 3.5 (dt, J_t = 8.9 Hz, J_d = 7.5 Hz, 1 H, CH*H*CH$_2$SiMe$_3$), 2.22 (ddd, J_{gem} = 13.4 Hz, J = 9.6 Hz, J = 5.8 Hz, 1 H, H-3′), 1.87 (ddd, J_{gem} = 13.4 Hz, J = 8.2 Hz, J = 5.4 Hz, 1 H, H-3′), 1.53 (dd, $J_{7,8}$ = 6.8 Hz, $^4J_{6,8}$ = 1.5 Hz, 3 H, H-8), 1.4 - 1.22 (m, 2 H, H-4′), 1.11 (s, 3 H, CH$_3$), 0.92 (m, 2 H, CH$_2$C*H*$_2$SiMe$_3$), 0.89 (s, 3 H, CH$_3$), 0.85 (s, 3 H, CH$_3$), 0.02 (s, 9 H, Me$_3$Si). 50 MHz ^{13}C NMR (C$_6$D$_6$) δ 195.76 (s, C-1), 177.18 (s, C-6′), 167.08 (s, C-1′), 166.35 (s, C-3), 139.73 (d, C-7), 126.86 (d, C-2), 125.47 (d, C-6), 90.52 (s, C-2′), 80.74 and 80.54 (2 d, C-4 and C-5), 67.41 (t, *C*H$_2$CH$_2$SiMe$_3$), 54.67 (s, C-5′), 54.40 (s, C-7′), 31.00 (t, C-3′), 28.77 (t, C-4′), 19.04 (q, C-8), 18.44 (t, CH$_2$*C*H$_2$-SiMe$_3$), 16.71 (q, CH$_3$), 16.47 (q, CH$_3$), 9.75 (q, CH$_3$), -1.35 (q, Me$_3$Si). Exact mass calcd for M$^+$-C$_2$H$_4$ (C$_{21}$H$_{30}$O$_6$Si): 406.1812. Found 406.1813. Anal. Calcd. for C$_{23}$H$_{34}$O$_6$Si: C, 63.56; H, 7.89. Found: C, 63.50; H, 7.83.

(-)-(4*S*,5*R*)-5-Hydroxy-3-(*E*-1-propenyl)-4-(2-trimethylsilylethoxy)-2-cyclopenten-1-one [(-)-10]. Tetrabutylammonium hydroxide (2.4 mL of a 0.1 M solution in methanol/isopropanol, E.Merck, 0.24 mmol) was added rapidly to a vigorously stirred solution of ester **15-A** (71 mg, 0.163 mmol) in CH$_2$Cl$_2$ (1.6 mL) and water (2 mL) at 0°C. After 120 sec aqueous HCl (2.4 mL of a 0.1 M solution) was added, followed by diluting the mixture with CH$_2$Cl$_2$ and extracting with aqueous sodium bicarbonate solution (5%). The aqueous phase was extracted with CH$_2$Cl$_2$ (3x), the combined organic layers were dried (MgSO$_4$) and evaporated *in vacuo*. Flash chromatography of the residue on silica gel (7 g, ether/petrol/CH$_2$Cl$_2$, 4:3:3) gave starting material **15-A** (35.5 mg, 50%) and crude alcohol **(-)-10** (19 mg). The latter was purified further by column chromatography on silica gel (5 g, ether/petrol, 1:1) to yield **(-)-10** (16.5 mg, 39%) as a colorless oil, with spectral data identical to the racemic compound **rac-10**. $[\alpha]_D^{22}$ = -9.3°, $[\alpha]_{578}^{22}$ = -11.4°, $[\alpha]_{546}^{22}$ = -21.3°, $[\alpha]_{436}^{22}$ = -221.2° (c = 1.19 in CH$_2$Cl$_2$).

Preparation of (+)-Terrein [(+)-1]. Deprotection of 2-(trimethylsilyl)-ethyl ether **(-)-10** (16.3 mg, 0.064 mmol) with ZnCl$_2$·OEt$_2$ (0.035 mL of a 2.2 M solution in CH$_2$Cl$_2$, 0.077 mmol) was carried out as described for **rac-10**, giving (+)-terrein **(+)-1** (8.5 mg, 86%) with spectral data identical to those of the racemic compound, mp 123°C (from benzene). $[\alpha]_D^{22}$ = +161.8°, $[\alpha]_{578}^{22}$ = +167.6°, $[\alpha]_{546}^{22}$ = +184.2°, $[\alpha]_{436}^{22}$ = +139.0° (c = 0.62 in H$_2$O).

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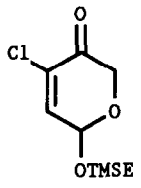

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