A Reinvestigation of the Reductive Ring-opening of a 3-Substituted *exo*-4,5-Epoxytricyclo[5.2.1.$0^{2,6}$]dec-8-en-3α-ol to the Corresponding 3,5-Diol

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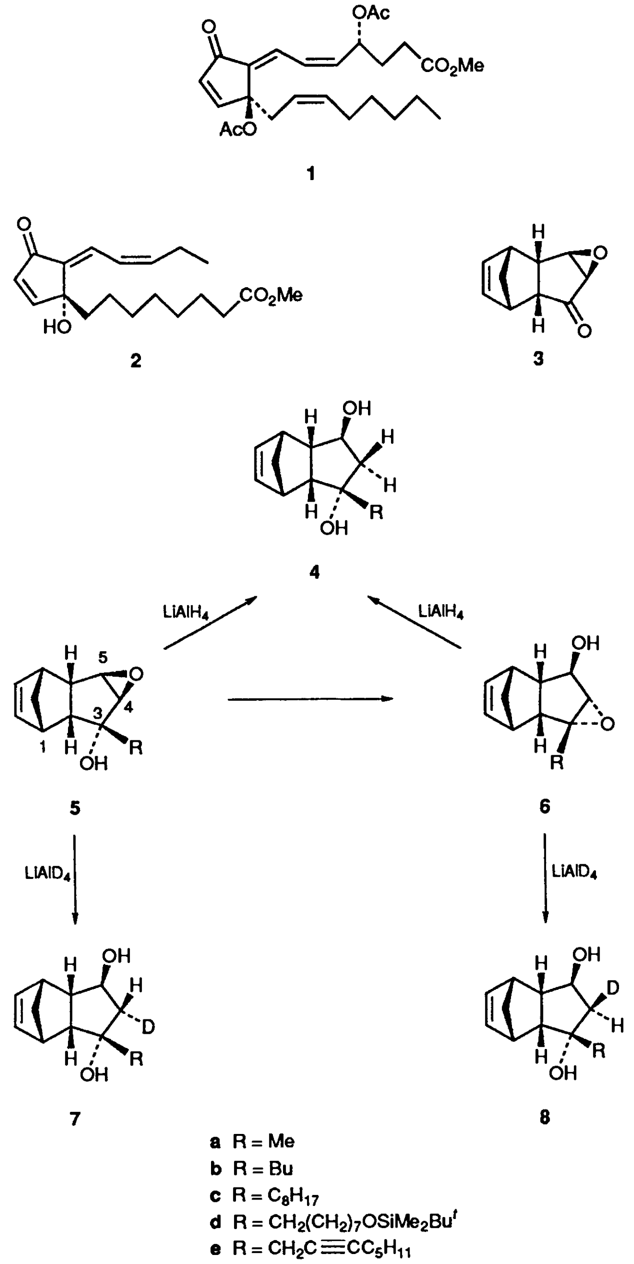
Regio- and stereo-specific reduction of the *exo*-epoxy alcohol **5** with $LiAlD_4$ produced the 4α-D-*trans*-3,5-diol **7** and the 4β-D-*trans*-3,5-diol **8** in varying ratios, an indication that in spite of epoxide rearrangement between **5** and **6** direct epoxide ring-opening of **5** to afford the 3,5-diol **4** is the primary pathway.

During the course of our studies on the syntheses of natural products involving a retro Diels–Alder reaction, it was found that both 3-substituted *exo*-4,5-epoxytricyclo[5.2.1.$0^{2,6}$]dec-8-en-3α-ol **5**[1] and 3-substituted *endo*-3,4-epoxytricyclo[5.2.1.$0^{2,6}$]-dec-8-en-5β-ol **6**[2] upon reduction by $LiAlH_4$ yielded the same *trans*-diol **4** (Scheme 1); this was then converted into natural products clavulone **1** and chromomoric acid DI methyl ester **2**. It was also observed that while the *endo*-epoxy alcohol **6** was quite easily reduced to the *trans*-3,5-diol **4**, the *exo*-epoxy alcohol **5** underwent only very slow reduction. Since the epoxy alcohols **5** and **6** equilibrate under basic conditions[3] and there is steric blocking by the olefinic bridge,[1,3] it was generally assumed that the *exo*-epoxy alcohol **5** does not itself undergo reductive epoxide ring-opening with $LiAlH_4$ to give the diol **4**. Rather, the reaction path involves formation and subsequent reduction of the inverted epoxy alcohol **6**.[1,3] However, since we had found that the *exo*-epoxide **9** is reduced exclusively to the diol **10** with $LiAlH_4$ in refluxing THF[4] (Scheme 2), we thought that the *exo*-epoxy alcohol **5** should behave similarly. Here, we report our results using an isotopic technique which sheds light on this process.

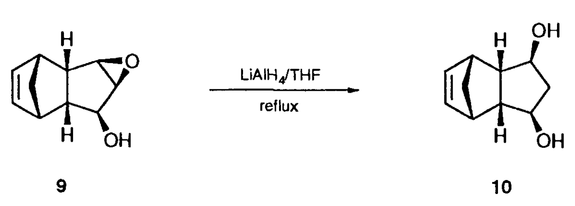
Our work was based on the following considerations. While both **5** and **6** were reduced by $LiAlH_4$ to give the diol **4**, the stereochemistry of the hydride attack would be different if the epoxy alcohol **5** underwent direct reduction. With the *endo*-epoxy alcohol **6**, hydride would approach from the *exo* side, while in the *exo*-epoxy alcohol **5**, the hydride attack would be from the *endo* side. Therefore, if lithium aluminium deuteride ($LiAlD_4$) was used in place of $LiAlH_4$ and the epoxide ring in **5** could be directly opened, the 4α-D-*trans*-3,5-diol **7** should be formed; otherwise, only the 4β-D-*trans*-3,5-diol **8** would be given by way of epoxide migration of **5** to **6** followed by epoxide ring-opening (Scheme 1). The structures of the diols **7** and **8** were then expected to be distinguished by analysis of their ^1H NMR data.

The epoxy alcohols **5a**, **b** and **6a**, **b** were prepared by treatment of the epoxy ketone **3** with MeLi or BuLi at 0 °C for 0.5–1 h; **5c**, **d** were prepared by rapid addition of **3** to the corresponding lithium reagent and then quenching; **6c**, **d** were obtained after reaction overnight at room temp.; **5e** was given as the only adduct when **3** was treated with oct-2-ynylzinc bromide, no inverted epoxy alcohol **6e** being isolated.

$LiAlH_4$ reduction of **5a**–**e** and **6a**–**d** gave the diols **4a**–**e**, the ^1H NMR data for which were analysed; the 4-H_2 assignments were made by use of the double resonance technique. Taking **4a** for example: on irradiation of the signal at δ 2.69 (6-H) the signal at δ 3.76 remained a doublet of doublets (J 6.3 and 2.1), showing very little coupling of 5-H with 6-H, with the signals of 4-H_2 and 5-H forming an ABX system. On irradiation of the signal at δ 3.76 (5-H) the doublet of doublets at δ 1.91 (J 13.8 and 6.3) and 1.63 (J 13.8 and 2.1) was simplified to doublets at δ 1.91 (J 13.8) and 1.63 (J 13.8), a result of 4-H_2, appearing as an AB system.



Scheme 1



Scheme 2

Table 1 $LiAlD_4$ Reductive ring-opening of the *exo*-epoxy alcohols **5a–e**

		Products		
Entry	Epoxy alcohol	7:8	Ratio	Yield (%)
1	**5a**, R = Me	**7a**:**8a**	63:37	92
2	**5b**, R = Bu	**7b**:**8b**	51:49	90
3	**5c**, R = C_8H_{17}	**7c**:**8c**	53:47	87
4	**5d**, R = $(CH_2)_8OSiMe_2Bu^t$	**7d**:**8d**	45:55	77
5	**5e**, R = $CH_2C{\equiv}CC_5H_{11}$	**7e**:**8e**	65:35	81

$LiAlD_4$ reduction of **6a–d** exclusively afforded the 4β-D-*trans*-3,5-diol **8** having a 4α-H. Comparison of the spectra of **4** and **8** permits unequivocal assignment of the 4α-H and 4β-H in **4**. If R = Me, for example, the doublet of doublets at δ 1.91 (*J* 13.8 and 6.3) in **4a** was simplified to a doublet at δ 1.89 (*J* 6.2) in **8a**, whereas the doublet of doublets at δ 1.63 (*J* 13.8 and 2.1) in **4a** disappeared in **8a**, suggesting that the signal at δ 1.89 in **8a** must arise from the resonance of 4a-H. Therefore, the signals at δ 1.91 and 1.63 in **4a** must be due to the protons 4α-H and 4β-H respectively.

With complete assignment of 4α-H and 4β-H in **4**, we next investigated the $LiAlD_4$ reduction of **5a–e**. An analysis of the spectra of the deuteriated diols so formed showed that they were a mixture of **7** and **8**. With R = Me for example, the doublets of doublets at δ 1.91 (4α-H) and 1.63 (4β-H) in **4a** collapsed to a doublet at δ 1.88 (*J* 6.3) and a singlet at δ 1.61, respectively, in the mixture of **8a** and **7a**. The ratio of the two signals, that is, the ratio of **8a** to **7a**, was 37 to 63%. Likewise, an analysis of the ^1H NMR results of the mixtures formed by $LiAlD_4$ reduction of **5b–e** are summarized in Table 1.

It is clear from the Table that $LiAlD_4$ reduction of **5** does afford **7** through direct epoxide ring-opening as the primary pathway, although it is accompanied by **8** as a result of epoxide migration to the inverted epoxide **6**. Furthermore, although an increase of the bulkiness of the R group enhances the tendency of epoxide migration,[3] the yield of the diol **8** does not increase significantly. This $LiAlH_4$ reduction of the *exo*-epoxy alcohol **5** may be attributed to the initial complexation of the reducing agent with the *endo*-alcoholic group, followed by intramolecular hydride attack at the *exo*-epoxide from its rear side.

In conclusion, in spite of the epoxide rearrangement of **5** to **6** and the steric blocking of hydride attack from the *endo* side, the epoxy alcohol **5** can still undergo direct reductive ring-opening to yield the diol **4**. This stereochemical feature is of considerable help in our synthetic studies of other chromomoric acids.

Experimental

General Details.—M.p.s were determined in open capillaries using a Mel-Temp apparatus and are uncorrected. IR spectra were recorded as neat films for oils or as KBr discs for solids on a Schimadzu IR-440 spectrometer. ^1H NMR spectra were determined with TMS as an internal standard in $CDCl_3$ at 200 MHz on a Varian XL-200 spectrometer or at 300 MHz on a Bruker AM-300 spectrometer; *J* values are given in Hz. Mass spectra were obtained on a Finnigan 4021 spectrometer using the electron impact technique. High resolution mass spectra (HRMS) were recorded with Finnigan MAT 8430 spectrometer. Microanalyses were performed using an Italian Carlo-Erba 1106 elemental analyser. All the reactions were carried out under dry N_2 atmosphere. Dry diethyl ether and THF were distilled over sodium–benzophenone ketyl under N_2 atmosphere. Flash column chromatography was conducted on silica gel H (10–40 mesh) from Qingdao Haiyang Chemical Works, with light petroleum (b.p. 60–90 °C, LP) and ethyl acetate (EA) as eluent in appropriate ratios.

3-*Methyl*-exo-4,5-*epoxytricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*en*-3-*ol* **5a** *and* 3-*Methyl*-endo-3,4-*epoxytricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*en*-5-*ol* **6a**.—To a solution of the epoxy ketone **3** (1.046 g, 6.46 mmol) in dry THF (30 cm^3) was added dropwise a solution of MeLi (1.00 mol dm^{-3} in ether; 9.1 cm^3, 9.1 mmol) at 0 °C. The reaction mixture was stirred at this temp. for 35 min and then quenched with saturated aqueous NH_4Cl (15 cm^3). The mixture was extracted with EtOAc (3 × 30 cm^3) and the combined extracts were washed with brine (3 × 10 cm^3), dried (Na_2SO_4) and evaporated under reduced pressure to afford crude **5a** and **6a**. Flash chromatography purification (LP–EA, 80:20) afforded the pure epoxy alcohols: **5a** (883 mg, 77%) and **6a** (177 mg, 15%) as a white solid and an oil respectively. Epoxy alcohol **5a**: m.p. 103.5–104.5 °C (hexane) (Found: C, 74.25; H, 8.0. $C_{11}H_{14}O_2$ requires C, 74.13; H, 7.92%); ν_{max}/cm^{-1} 3400, 3050, 1460, 1130, 1020, 860, 760 and 740; δ_H 6.32 (1 H, dd, *J* 5.6 and 2.8, 8-H or 9-H), 6.16 (1 H, dd, *J* 5.6 and 2.8, 9-H or 8-H), 3.18 (1 H, d, *J* 2.2, 4-H or 5-H), 3.10 (1 H, d, *J* 2.2, 5-H or 4-H), 3.02–2.86 (3 H, m), 2.54 (1 H, dd, *J* 7.7 and 4.0), 1.62 (1 H, s, OH), 1.42 (2 H, m, 10-H) and 1.40 (3 H, s, 3-CH_3); *m*/*z* 178 (M^+, 16%), 161 (28), 160 (15), 112 (100) and 66 (4). Epoxy alcohol **6a**: (Found: C, 74.0; H, 8.05. $C_{11}H_{14}O_2$ requires C, 74.13; H, 7.92%); ν_{max}/cm^{-1} 3200, 3050, 1470, 1380, 1060, 1050, 790, 740 and 720; δ_H 6.21 (1 H, dd, *J* 5.8 and 3.0, 8-H or 9-H), 5.90 (1 H, dd, *J* 5.8 and 3.0, 9-H or 8-H), 3.80 (1 H, d, *J* 3.0, 5-H), 3.05 (1 H, s, 4-H), 3.02–2.88 (3 H, m), 2.81 (1 H, dd, *J* 10.4 and 3.5), 1.41 (1 H, br, OH), 1.43 (2 H, m, 10-H) and 1.44 (3 H, s, 3-CH_3); *m*/*z* 165 (48%), 145 (15), 90 (15) and 66 (100).

3-*Butyl*-exo-4,5-*epoxytricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*en*-3-*ol* **5b** *and* 3-*Butyl*-endo-3,4-*epoxytricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*en*-5-*ol* **6b**.—The same procedure as described for preparation of **5a** and **6a** was used. Epoxy alcohol **5b**: m.p. 64.5–66.0 °C (hexane) (Found: C, 76.4; H, 9.4. $C_{14}H_{20}O_2$ requires C, 76.32; H, 9.15%); ν_{max}/cm^{-1} 3400, 2980, 2850, 1470, 1380, 1005, 860 and 840; δ_H 6.34 (1 H, dd, *J* 6.0 and 3.0, 8-H or 9-H), 6.18 (1 H, dd, *J* 6.0 and 2.8, 9-H or 8-H), 3.22 (1 H, d, *J* 2.2, 4-H or 5-H), 3.14 (1 H, d, *J* 2.2, 5-H or 4-H), 3.04–2.84 (3 H, m), 2.55 (1 H, dd, *J* 8.0 and 4.0), 1.58 (1 H, s, OH), 1.76–1.30 (8 H, m) and 0.94 (3 H, t, *J* 7.0, CH_3); *m*/*z* 220 (M^+, 3%), 203 (7), 154 (7), 137 (34), 97 (71) and 66 (100). Epoxy alcohol **6b**: (Found: C, 76.5; H, 9.3. $C_{14}H_{20}O_2$ requires C, 76.32; H, 9.15%); ν_{max}/cm^{-1} 3400, 3050, 1470, 1330, 1050, 1030, 800, 740 and 720; δ_H 6.23 (1 H, dd, *J* 5.5 and 3.0, 8-H or 9-H), 5.91 (1 H, dd, *J* 5.5 and 2.9, 9-H or 8-H), 3.80 (1 H, d, *J* 3.1, 5-H), 3.04 (1 H, s, 4-H), 3.02–2.80 (4 H, m), 2.10 (1 H, br, OH), 1.86 (1 H, m), 1.64–1.26 (7 H, m) and 0.94 (3 H, t, *J* 7.0, CH_3); *m*/*z* 220 (M^+, 9%), 203 (22), 155 (20), 137 (28), 97 (28) and 66 (100).

3-(8-tert-*Butyldimethylsiloxyoctyl*)-exo-4,5-*epoxytricyclo*-[5.2.1.$0^{2,6}$]*dec*-8-*en*-3-*ol* **5d**.—A solution of 8-*tert*-butyldimethylsiloxyoctyllithium was prepared from 8-*tert*-butyldimethylsiloxyoctyl bromide (2.10 g, 6.4 mmol) and lithium (176 mg, 25.6 mmol) in dry Et_2O (30 cm^3) at −5–0 °C for 2 h. To this lithium reagent was rapidly added the epoxy ketone **3** (930 mg, 5.74 mmol) in dry Et_2O (5 cm^3) at −10 °C with vigorous stirring. After the mixture had been stirred at this temp. for 20 min it was quenched with saturated aqueous NH_4Cl (20 cm^3). The resulting mixture was extracted with EtOAc (4 × 30 cm^3) and the combined extracts were washed with aqueous NH_4Cl (2 × 10 cm^3) and brine (3 × 10 cm^3) and dried (Na_2SO_4). Removal of the solvent followed by flash chromatography (LP–EA, 90:10 to 80:20) afforded **4d** (2.22 g, 95%) as a colourless oil (Found: C, 70.9; H, 10.3. $C_{24}H_{42}O_3Si$ requires C, 70.88; H, 10.41%); ν_{max}/cm^{-1} 3450, 1245, 1100, 830 and 770; δ_H 6.27 (1 H, dd, *J* 6.0 and 3.0, 8-H or 9-H), 6.12 (1 H, dd, *J* 6.0 and 3.0, 9-H or 8-H), 3.57 (2 H, t, *J* 7.0, CH_2OR), 3.15 (1 H, d, *J* 2.0, 4-H or 5-H), 3.07 (1 H, d, *J* 2.0, 5-H or 4-H), 2.94–2.86 (2 H, m), 2.82 (1 H, m), 2.48 (1 H, m), 1.70–1.22 (16 H, m), 1.53 (1 H, s, OH), 0.85 (9 H, s, Bu^tSi) and 0.04 (6 H, s, Me_2Si); *m/z* 389 (17%), 349 (17), 331 (23), 283 (62), 265 (26), 209 (10), 75 (100) and 66 (78).

3-(8-tert-*Butyldimethylsiloxyoctyl*)-endo-3,4-*epoxytricyclo*-[5.2.1.0^{2,6}]*dec*-8-*en*-5-*ol* **6d**.—To a solution of epoxy ketone **3** (5.85 g, 36.1 mmol) in dry ether (45 cm^3) was added dropwise a solution of 8-*tert*-butyldimethylsiloxyoctyllithium (40 mmol) over 50 min at −10 °C. The reaction mixture was then stirred at −10–0 °C for 2.5 h and then at room temp. overnight. The resulting yellow solution was then quenched by aqueous NH_4Cl (50 cm^3) and extracted with EtOAc (4 × 40 cm^3). The combined extracts were washed with aqueous NH_4Cl (3 × 20 cm^3) and brine (3 × 20 cm^3), dried (Na_2SO_4) and concentrated under reduced pressure. The residue was subjected to flash chromatography (LP–EA, 90:10 to 70:30) to afford the epoxy alcohol **6d** (13.0 g, 89%) as a colourless oil (Found: C, 71.0; H, 10.5. $C_{24}H_{42}O_3Si$ requires C, 70.88; H, 10.41%); ν_{max}/cm^{-1} 3400, 1460, 1095 and 840; δ_H 6.18 (1 H, dd, *J* 5.4 and 2.8, 8-H or 9-H), 5.87 (1 H, dd, *J* 5.4 and 3.0, 9-H or 8-H), 3.77 (1 H, d, *J* 2.5, 5-H), 3.60 (2 H, t, *J* 6.8, CH_2OR), 3.01 (1 H, s, 4-H), 3.00–2.73 (4 H, m), 1.68–1.20 (16 H, m), 1.70 (1 H, br, OH), 0.90 (9 H, s, Bu^t) and 0.05 (6 H, s, Me_2Si); *m/z* 406 (M^+, 1%), 349 (34), 325 (6), 283 (100), 265 (20) and 257 (10).

3-*Octyl*-exo-4,5-*epoxytricyclo*[5.2.1.0^{2,6}]*dec*-8-*en*-3-*ol* **5c**.—The reaction was carried out as described for the preparation of **5d** to afford **5c** as colourless oil (83%); ν_{max}/cm^{-1} 3450, 1470, 1340, 1240, 1020, 860 and 760; δ_H 6.23 (1 H, dd, *J* 5.4 and 2.8, 8-H or 9-H), 6.07 (1 H, dd, *J* 5.5 and 3.0, 9-H or 8-H), 3.11 (1 H, d, *J* 2.2, 4-H or 5-H), 3.03 (1 H, d, *J* 2.2, 5-H or 4-H), 2.86 (2 H, m), 2.78 (1 H, m), 2.45 (1 H, m), 1.44 (1 H, s, OH), 1.62–1.40 (4 H, m), 1.27–1.12 (12 H, m) and 0.81 (3 H, t, *J* 6.6, CH_3); *m/z* 276 (M^+, 3%), 258 (2), 210 (3), 193 (13), 163 (2), 97 (45) and 67 (100) (Found: M^+, 276.2078. $C_{18}H_{28}O_2$ requires M^+, 276.2089).

3-*Octyl*-endo-3,4-*epoxytricyclo*[5.2.1.0^{2,6}]*dec*-8-*en*-5-*ol* **6c**.—The same procedure as described for the preparation of **6d** was used to yield **6c** as a colourless oil (91%); ν_{max}/cm^{-1} 3400, 1470, 1330, 1240, 1050 and 720; δ_H 6.11 (1 H, dd, *J* 6.0 and 2.5, 8-H or 9-H), 5.80 (1 H, dd, *J* 6.0 and 3.0, 9-H or 8-H), 3.69 (1 H, d, *J* 2.5, 5-H), 2.93 (1 H, s, 4-H), 2.91–2.81 (3 H, m), 2.74 (1 H, m), 1.90 (1 H, br s, OH), 1.73 (1 H, m), 1.49–1.16 (15 H, m) and 0.81 (3 H, t, *J* 6.5, CH_3); *m/z* 276 (M^+, 9%), 258 (2), 247 (4), 210 (13), 193 (15), 178 (13), 163 (6), 97 (61) and 66 (100) (Found: M^+, 276.2084. $C_{18}H_{28}O_2$ requires M^+, 276.2089).

3-(*Oct*-2-*ynyl*)-exo-4,5-*epoxytricyclo*[5.2.1.0^{2,6}]*dec*-8-*en*-3-*ol* **5e**.—A solution of oct-2-ynylzinc bromide in THF was prepared[5] from 1-bromooct-2-yne (4.0 g, 21.2 mmol) and Zn–Cu couple (138 mmol, 6.5 equiv.) at 40 °C for 2 h. To this oct-2-ynylzinc bromide was added dropwise a solution of the epoxy ketone **3** (1.52 g, 9.4 mmol) in dry THF (10 cm^3). After the addition the reaction mixture was stirred at room temp. for 3 h, quenched with aqueous NH_4Cl (20 cm^3) and filtered. The aqueous layer was separated out and extracted with EtOAc (3 × 30 cm^3). The combined extracts were washed with brine (3 × 10 cm^3), dried (Na_2SO_4) and concentrated under reduced pressure to give a brown oil which was subjected to flash chromatography (LP–EA, 97:3) to afford pure **5e** as an oil (2.10 g, 82%); ν_{max}/cm^{-1} 3530, 1190, 1070 and 860; δ_H 6.30 (1 H, m, 8-H or 9-H), 6.08 (1 H, m, 9-H or 8-H), 3.18 (1 H, d, *J* 2.3, 4-H or 5-H), 3.16 (1 H, d, *J* 2.3, 5-H or 4-H), 2.92 (2 H, m), 2.84 (1 H, m), 2.58 (1 H, dt, *J* 14 and 2, $C\mathit{H}HC\equiv CC_5H_{11}$), 2.53 (1 H, m), 2.46 (1 H, dt, *J* 14 and 2, $CH\mathit{H}C\equiv CC_5H_{11}$), 2.18 (2 H, tt, *J* 7 and 2, $C\equiv CC\mathit{H}_2C_4H_9$), 1.62 (1 H, br s, OH), 1.54–1.29 (8 H, m) and 0.90 (3 H, t, *J* 7.1, CH_3); *m/z* 273 (M^+ + 1, 18%), 255 (20), 206 (20), 189 (30), 163 (34) and 67 (100).

General Procedure for $LiAlH_4$ *Reduction of the* exo-4,5-*Epoxy Alcohols* **5a–e** *and the* endo-3,4-*Epoxy Alcohols* **6a–d**.—To a solution of the epoxy alcohol (1 mmol) in dry THF (20 cm^3) under a N_2 atmosphere was rapidly added $LiAlH_4$ (8.2 mmol) and the suspension was stirred at room temp. (10 °C) for 4–6 d (for **5a–e**) or 20–30 h (for **6a–d**). To the mixture was then added, dropwise and successively at 0 °C, water (0.4 cm^3), aqueous 15% NaOH (0.4 cm^3) and water (1.2 cm^3). The resulting mixture was filtered and the granular precipitate was thoroughly washed with EtOAc. The filtrate was concentrated under reduced pressure and the crude diol was purified by flash chromatography to afford the pure diol **4**.

3-*Methyltricyclo*[5.2.1.0^{2,6}]*dec*-8-*ene*-3,5-*diol* **4a**. White solid, 90% yield, m.p. 108–109 °C (ether) (Found: C, 73.4; H, 9.0. $C_{11}H_{16}O_2$ requires C, 73.30; H, 8.95%); ν_{max}/cm^{-1} 3300, 3050, 1360, 1320, 1140, 1125, 750 and 725; δ_H 6.30 (1 H, dd, *J* 5.5 and 3.0, 8-H or 9-H), 6.08 (1 H, dd, *J* 5.5 and 3.0, 9-H or 8-H), 3.76 (1 H, dd, *J* 6.3 and 2.1, 5-H), 2.97 (1 H, m, 1-H or 7-H), 2.92 (1 H, m, 7-H or 1-H), 2.69 (2 H, m, 2-H and 6-H), 1.91 (1 H, dd, *J* 13.8 and 6.3, 4α-H), 1.63 (1 H, dd, *J* 13.8 and 2.1, 4β-H), 1.61 (2 H, s, two OH), 1.45 (3 H, s, CH_3) and 1.34 (2 H, m, 10-H); *m/z* 165 (48%), 145 (15), 97 (33), 96 (15) and 66 (100).

3-*Butyltricyclo*[5.2.1.0^{2,6}]*dec*-8-*ene*-3,5-*diol* **4b**. White solid, 90% yield, m.p. 114.0–115.5 °C (ether) (Found: C, 75.6; H, 10.2. $C_{14}H_{22}O_2$ requires C, 75.63; H, 9.97%); ν_{max}/cm^{-1} 3300, 1340, 1140, 1100 and 730; δ_H 6.34 (1 H, dd, *J* 5.6 and 3.0, 8-H or 9-H), 6.11 (1 H, dd, *J* 5.6 and 3.1, 9-H or 8-H), 3.73 (1 H, m, 5-H), 2.96 (1 H, m, 1-H or 7-H), 2.86 (1 H, m, 7-H or 1-H), 2.73 (1 H, m, 2-H or 6-H), 2.66 (1 H, m, 6-H or 2-H), 1.85 (1 H, dd, *J* 13.7 and 6.2, 4α-H), 1.73 (1 H, dd, *J* 13.7 and 4.7, 4β-H), 1.67–1.62 (2 H, m), 1.52–1.30 (6 H, m), 1.40 (2 H, s, two OH) and 0.92 (3 H, t, *J* 7.5, CH_3); *m/z* 204 (2%), 187 (3), 165 (30), 147 (3), 139 (20) and 66 (100).

3-*Octyltricyclo*[5.2.1.0^{2,6}]*dec*-8-*ene*-3,5-*diol* **4c**. White solid, 80% yield, m.p. 105.0–106.0 °C (ether) (Found: C, 77.7; H, 11.0. $C_{18}H_{30}O_2$ requires C, 77.65; H, 10.86%); ν_{max}/cm^{-1} 3300, 1340, 1320, 1260, 1100, 1020, 810 and 740; δ_H 6.34 (1 H, dd, *J* 5.6 and 2.8, 8-H or 9-H), 6.11 (1 H, dd, *J* 5.6 and 3.0, 9-H or 8-H), 3.73 (1 H, m, 5-H), 2.95 (1 H, m, 1-H or 7-H), 2.86 (1 H, m, 7-H or 1-H), 2.73 (1 H, m, 2-H or 6-H), 2.65 (1 H, m, 6-H or 2-H), 1.85 (1 H, dd, *J* 13.6 and 6.2, 4α-H), 1.72 (1 H, dd, *J* 13.6 and 4.7, 4β-H), 1.66–1.61 (s H, m), 1.52–1.23 (16 H, m, including two OH at 1.36) and 0.88 (3 H, t, *J* 7.0, CH_3); *m/z* 260 (2%), 242 (2), 211 (13), 195 (21), 165 (75) and 67 (100).

3-(8-tert-*Butyldimethylsiloxyoctyl*)*tricyclo*[5.2.1.0^{2,6}]*dec*-8-*ene*-3,5-*diol* **4d**. White solid, 80% yield, m.p. 80.0–81.0 °C (hexane) (Found: C, 70.4; H, 10.75. $C_{24}H_{44}O_3Si$ requires C, 70.53; H, 10.85%); ν_{max}/cm^{-1} 3270, 1240, 1120, 1090, 835 and 745; δ_H 6.34 (1 H, dd, *J* 5.6 and 2.5, 8-H or 9-H), 6.11 (1 H, dd, *J* 5.6 and 3.0, 9-H or 8-H), 3.73 (1 H, m, 5-H), 3.60 (2 H, t, *J* 6.6, CH_2OR), 2.96 (1 H, m, 1-H or 7-H), 2.86 (1 H, m, 7-H or 1-H), 2.73 (1 H, m, 2-H or 6-H), 2.65 (1 H, m, 6-H or 2-H), 1.85 (1 H, dd, *J* 13.6 and 6.2, 4α-H), 1.72 (1 H, dd, *J* 13.6 and 4.7, 4β-H), 1.67–1.61 (2 H, m), 1.56–1.30 (16 H, m, including two OH at 1.54), 0.90 (9 H, s, Bu^t) and 0.05 (6 H, s, Me$_2$Si); *m*/*z* 391 (38%), 373 (42), 351 (20), 333 (100), 325 (22), 307 (7) and 165 (62).

3-(*Oct*-2-*ynyl*)*tricyclo*[5.2.1.0^{2,6}]*dec*-8-*ene*-3,5-*diol* **4e**. White solid, 94% yield, m.p. 70.0–71.0 °C (hexane) (Found: C, 78.7; H, 9.6. C$_{18}$H$_{26}$O$_2$ requires C, 78.79; H, 9.55%); ν_{max}/cm^{-1} 3300, 3050, 1320, 1130, 1110 and 740; δ_H 6.30 (1 H, dd, *J* 5.5 and 2.6, 8-H or 9-H), 6.03 (1 H, dd, *J* 5.5 and 3.0, 9-H or 8-H), 3.78 (1 H, d, *J* 6.3, 5-H), 2.97 (1 H, m, 1-H or 7-H), 2.91 (1 H, m, 7-H or 1-H), 2.82 (1 H, m, 2-H or 6-H), 2.65 (1 H, m, 6-H or 2-H), 2.62 (1 H, dt, *J* 13.8 and 2.2, C*H*HC≡CC$_5$H$_{11}$), 2.54 (1 H, dt, *J* 13.8 and 2.2, CH*H*C≡CC$_5$H$_{11}$), 2.19 (2 H, tt, *J* 7.0 and 2.3, C≡CC*H*$_2$C$_4$H$_9$), 2.04 (1 H, s, OH), 1.92 (1 H, dd, *J* 14.2 and 6.3, 4α-H), 1.72 (1 H, d, *J* 14.2, 4β-H), 1.63 (1 H, br s, OH), 1.53–1.31 (8 H, m) and 0.90 (3 H, t, *J* 7.1, CH$_3$); *m*/*z* 275 (M$^+$ + 1, 4.22%), 257 (37), 239 (32), 208 (17), 191 (23), 166 100) and 173 (23).

General Procedure for LiAlD$_4$ *Reduction of* exo-4,5-*Epoxy Alcohols* **5a–e** *and* endo-3,4-*Epoxy Alcohols* **6a–d**.—To a solution of the epoxy alcohol (0.5 mmol) in dry THF (10 cm^3) under an N$_2$ atmosphere was rapidly added LiAlD$_4$ (4.1 mmol) and the suspension was stirred at room temp. (15 °C) for 6–8 d. To the mixture was then added, dropwise and successively at 0 °C, water (0.2 cm^3), aqueous 15% NaOH (0.2 cm^3) and water (0.6 cm^3). The resulting mixture was filtered and the granular precipitate was thoroughly washed with EtOAc. The filtrate was concentrated under reduced pressure and the crude diol was purified by flash chromatography to afford the pure diol **8** or a mixture of **7** and **8**.

4β-D-3-*Methyltricyclo*[5.2.1.0^{2,6}]*dec*-8-*ene*-3,5-*diol* **8a**. White solid, 91% yield, m.p. 107.5–108.0 °C (ether) (Found: C, 72.8; H + D, 9.5. C$_{11}$H$_{15}$DO$_2$ requires C, 72.89; H + D, 9.45%); ν_{max}/cm^{-1} 3300, 1360, 1315, 1140, 1125, 1100, 1000, 750 and 725; δ_H 6.32 (1 H, dd, *J* 5.6 and 3.0, 8-H or 9-H), 6.10 (1 H, dd, *J* 5.6 and 3.0, 9-H or 8-H), 3.78 (1 H, d, *J* 6.1, 5-H), 2.97 (1 H, m, 1-H or 7-H), 2.93 (1 H, m, 7-H or 1-H), 2.74–2.66 (2 H, m, 2-H and 6-H), 2.33 (2 H, br s, two OH), 1.89 (1 H, d, *J* 6.2, 4α-H), 1.45 (3 H, s, CH$_3$) and 1.34 (2 H, m, 10-H); *m*/*z* 181 (M$^+$, 1%), 166 (11), 164 (30), 146 (38), 99 (27) and 97 (100).

Mixture of 4α-D-3-*methyltricyclo*[5.2.1.0^{2,6}]*dec*-8-*ene*-3,5-*diol* **7a** *and* 4β-D-3-*methyltricyclo*[5.2.1.0^{2,6}]*dec*-8-*ene*-3,5-*diol* **8a**. White solid, 92% yield, m.p. 107.0–108.0 °C (ether) (Found: C, 72.95; H + D, 9.4. C$_{11}$H$_{15}$DO$_2$ requires C, 72.89; H + D, 9.45%); ν_{max}/cm^{-1} 3300, 3050, 1140, 1120, 1100, 1000 and 720; δ_H 6.29 (1 H, dd, *J* 5.6 and 3.0, 8-H or 9-H), 6.07 (1 H, dd, *J* 5.6 and 3.2, 9-H or 8-H), 3.74 (1 H, m, 5-H), 2.96 (1 H, m, 1-H or 7-H), 2.92 (1 H, m, 7-H or 1-H), 2.68 (2 H, m, 2-H and 6-H), 2.04 (2 H, br s, two OH), 1.88 (0.37 H, d, *J* 6.3, 4α-H), 1.61 (0.63 H, s, 4β-H), 1.44 (3 H, s, CH$_3$) and 1.32 (2 H, m, 10-H); *m*/*z* 181 (M$^+$, 5%), 166 (100), 164 (6), 146 (3), 99 (27) and 97 (100).

4β-D-3-*Butyltricyclo*[5.2.1.0^{2,6}]*dec*-8-*ene*-3,5-*diol* **8b**. White solid, 85% yield, m.p. 113.5–114.5 °C (ether) (Found: C, 75.35; H + D, 10.3. C$_{14}$H$_{21}$DO$_2$ requires C, 75.29; H + D, 10.38%); ν_{max}/cm^{-1} 3300, 3050, 1340, 1145, 1090, 1060, 1020 and 735; δ_H 6.34 (1 H, dd, *J* 5.6 and 3.0, 8-H or 9-H), 6.11 (1 H, dd, *J* 5.6, 3.2, 9-H or 8-H), 3.72 (1 H, dd, *J* 6.2 and 3.2, 5-H), 2.95 (1 H, m, 1-H or 7-H), 2.86 (1 H, m, 7-H or 1-H), 2.73 (1 H, m, 2-H or 6-H), 2.65 (1 H, m, 6-H or 2-H), 1.83 (1 H, d, *J* 6.2, 4α-H), 1.67–1.62 (2 H, m), 1.52–1.32 (6 H, m), 1.50 (2 H, s, two OH) and 0.92 (3 H, t, *J* 7.0, CH$_3$); *m*/*z* 224 (3%), 206 (22), 204 (8), 188 (58), 166 (49), 157 (3), 141 (14), 123 (10) and 109 (10).

Mixture of 4α-D-3-*butyltricyclo*[5.2.1.0^{2,6}]*dec*-8-*ene*-3,5-*diol* **7b** *and* 4β-D-3-*butyltricyclo*[5.2.1.0^{2,6}]*dec*-8-*ene*-3,5-*diol* **8b**. White solid, 90% yield, m.p. 113–114 °C (ether) (Found: C, 75.2; H + D, 10.4. C$_{14}$H$_{21}$DO$_2$ requires C, 75.29; H + D, 10.38%); ν_{max}/cm^{-1} 3300, 3050, 1330, 1140, 1080, 1060, 1020 and 730; δ_H 6.34 (1 H, dd, *J* 5.6 and 3.0, 8-H or 9-H), 6.10 (1 H, dd, *J* 5.6 and 3.2, 9-H or 8-H), 3.72 (1 H, m, 5-H), 2.95 (1 H, m, 1-H or 7-H), 2.86 (1 H, m, 7-H or 1-H), 2.73 (1 H, m, 2-H or 6-H), 2.64 (1 H, m, 6-H or 2-H), 1.83 (0.49 H, d, *J* 6.2, 4α-H), 1.71 (0.51 H, d, *J* 3.6, 4β-H), 1.67–1.62 (2 H, m), 1.52–1.32 (8 H, m, including two OH at 1.48) and 0.92 (3 H, t, *J* 6.9, CH$_3$); *m*/*z* 206 (3%), 188 (3), 166 (100), 140 (43), 121 (5), 100 (11) and 66 (36).

4β-D-3-*Octyltricyclo*[5.2.1.0^{2,6}]*dec*-8-*ene*-3,5-*diol* **8c**. White solid, 83% yield, m.p. 104.5–105.0 °C (ether) (Found: C, 77.4; H + D, 11.15. C$_{18}$H$_{29}$DO$_2$ requires C, 77.37; H + D, 11.18%); ν_{max}/cm^{-1} 3300, 1330, 1090, 1060 and 730; δ_H 6.34 (1 H, dd, *J* 5.6 and 2.6, 8-H or 9-H), 6.11 (1 H, dd, *J* 5.6 and 3.0, 9-H or 8-H), 3.73 (1 H, dd, *J* 6.3 and 3.4, 5-H), 2.96 (1 H, m, 1-H or 7-H), 2.86 (1 H, m, 7-H or 1-H), 2.76–2.63 (2 H, m, 2-H and 6-H), 1.84 (1 H, d, *J* 6.3, 4α-H), 1.64 (2 H, m), 1.51–1.24 (16 H, m, including two OH at 1.39) and 0.88 (3 H, t, *J* 7.1, CH$_3$); *m*/*z* 261 (1%), 196 (15), 166 (65), 100 (23) and 67 (100).

Mixture of 4α-D-3-*octyltricyclo*[5.2.1.0^{2,6}]*dec*-8-*ene*-3,5-*diol* **7c** *and* 4β-D-3-*octyltricyclo*[5.2.1.0^{2,6}]*dec*-8-*ene*-3,5-*diol* **8c**. White solid, 87% yield, m.p. 105.5–107.5 °C (ether) (Found: C, 77.4; H + D, 11.05. C$_{18}$H$_{29}$DO$_2$ requires C, 77.37; H + D, 11.18%); ν_{max}/cm^{-1} 3280, 1090, 1060 and 725; δ_H 6.34 (1 H, dd, *J* 5.5 and 2.9, 8-H or 9-H), 6.11 (1 H, dd, *J* 5.4 and 3.0, 9-H or 8-H), 3.73 (1 H, m, 5-H), 2.96 (1 H, m, 1-H or 7-H), 2.86 (1 H, m, 7-H or 1-H), 2.75–2.62 (2 H, m, 2-H and 6-H), 1.83 (0.47 H, d, *J* 6.2, 4α-H), 1.71 (0.53 H, d, *J* 4.5, 4β-H), 1.67–1.58 (2 H, m), 1.54–1.21 (16 H, m, including two OH at 1.36 and 1.38) and 0.88 (3 H, t, *J* 6.4, CH$_3$); *m*/*z* 261 (2%), 212 (8), 196 (13), 166 (55), 100 (22) and 67 (100).

4β-D-3-(8-tert-*Butyldimethylsiloxyoctyl*)*tricyclo*[5.2.1.0^{2,6}]-*dec*-8-*ene*-3,5-*diol* **8d**. White solid, 80% yield, m.p. 79.5–80.5 °C (hexane) (Found: C, 70.3; H + D, 11.2. C$_{24}$H$_{43}$DO$_3$Si requires C, 70.36; H + D, 11.07%); ν_{max}/cm^{-1} 3300, 3050, 1260, 1100, 840 and 775; δ_H 6.34 (1 H, dd, *J* 5.5 and 2.9, 8-H or 9-H), 6.11 (1 H, dd, *J* 5.5 and 3.1, 9-H or 8-H), 3.73 (1 H, dd, *J* 6.2 and 3.3, 5-H), 3.60 (2 H, t, *J* 6.5, CH$_2$OR), 2.96 (1 H, m, 1-H or 7-H), 2.86 (1 H, m, 7-H or 1-H), 2.73 (1 H, m, 2-H or 6-H), 2.65 (1 H, m, 6-H or 2-H), 1.82 (1 H, d, *J* 6.2, 4α-H), 1.66–1.61 (2 H, m), 1.53–1.30 (16 H, m, including two OH at 1.41), 0.90 (9 H, s, Bu^t) and 0.05 (6 H, s, Me$_2$Si); *m*/*z* 392 (3%), 374 (2), 352 (9), 335 (100) and 269 (31).

Mixture of 4α-D-3-(8-tert-*butyldimethylsiloxyoctyl*)*tricyclo*-[5.2.1.0^{2,6}]*dec*-8-*ene*-3,5-*diol* **7d** *and* 4β-D-3-(8-tert-*butyldimethylsiloxyoctyl*)*tricyclo*[5.2.1.0^{2,6}]*dec*-8-*ene*-3,5-*diol* **8d**. White solid, 77% yield, m.p. 78.0–81.5 °C (hexane) (Found: C, 70.4; H + D, 11.0. C$_{24}$H$_{43}$DO$_3$Si requires C, 70.36; H + D, 11.07%); ν_{max}/cm^{-1} 3300, 3050, 1260, 1100, 840 and 775; δ_H 6.34 (1 H, dd, *J* 5.6 and 3.0, 8-H or 9-H), 6.11 (1 H, dd, *J* 5.5 and 3.2, 9-H or 8-H), 3.73 (1 H, m, 5-H), 3.60 (2 H, t, *J* 6.8, CH$_2$OR), 2.96 (1 H, m, 1-H or 7-H), 2.87 (1 H, m, 7-H) or 1-H), 2.74 (1 H, m, 2-H or 6-H), 2.66 (1 H, m, 6-H or 2-H), 1.83 (0.55 H, d, *J* 6.2, 4α-H), 1.72 (0.45 H, d, *J* 4.6, 4β-H), 1.67–1.62 (2 H, m), 1.56–1.31 (16 H, m, including two OH at 1.54), 0.90 (9 H, s, Bu^t) and 0.05 (6 H, s, Me$_2$Si); *m*/*z* 392 (2%), 374 (5), 353 (14), 334 (100), 308 (5), 268 (56) and 166 (7).

Mixture of 4α-D-3-(*oct*-2-*ynyl*)*tricyclo*[5.2.1.0^{2,6}]*dec*-8-*ene*-3,5-*diol* **7e** *and* 4β-D-3-(*oct*-2-*ynyl*)*tricyclo*[5.2.1.0^{2,6}]*dec*-8-*ene*-3,5-*diol* **8e**. White solid, 81% yield, m.p. 69.0–71.5 °C (light petroleum, b.p. 60–90 °C) (Found: C, 78.5; H + D, 9.9. C$_{18}$H$_{25}$DO$_2$ requires C, 78.50; H + D, 9.88%); ν_{max}/cm^{-1} 3400, 3050, 1330 and 1115; δ_H 6.30 (1 H, dd, *J* 5.6 and 3.2, 8-H or 9-H), 6.02 (1 H, dd, *J* 5.6 and 3.1, 9-H or 8-H), 3.78 (1 H, m, 5-H), 2.97 (1 H, m, 1-H or 7-H), 2.91 (1 H, m, 7-H or 1-H), 2.83 (1 H, m, 2-H or 6-H), 2.66 (1 H, m, 6-H or 2-H), 2.62 (1 H, dt, *J* 13.8 and 2.4, C*H*HC≡CC$_5$H$_{11}$), 2.54 (1 H, dt, *J* 13.8 and 2.4, CH*H*C≡CC$_5$H$_{11}$), 2.19 (2 H, tt, *J* 6.9 and 2.4, C≡CC*H*$_2$C$_4$H$_9$), 1.90 (0.35 H, d, *J* 6.4, 4α-H), 1.73 (2 H, s, two OH), 1.70 (0.65 H, s, 4β-H), 1.53–1.31 (8 H, m) and 0.90 (3 H, t, *J* 6.8, CH$_3$); *m*/*z* 209 (6%), 166 (46), 101 (100) and 67 (79).

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