22. The Synthesis of a Novel Epoxycyclohexane from the Fungus *Eutypa lata* (Pers: F.) Tul.

by **Eric Defrancq, John Gordon**[1], **André Brodard**, and **Raffaele Tabacchi***

Institut de Chimie de l'Université de Neuchâtel, Avenue de Bellevaux 51, CH–2000 Neuchâtel

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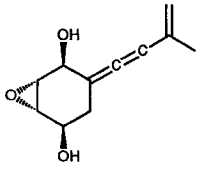
The synthesis of the novel (1'*R**,2'*S**,3'*R**,4'*S**,5'*R**)-1-(3',4'-epoxy-2',5'-dihydroxycyclohexyl)-3-methylbut-2-enone (**2**), recently isolated from the culture medium of the fungus *Eutypa lata*, is described.

Introduction. – The fungus *Eutypa lata* is the pathogen responsible for the vineyard dieback observed in recents years in Switzerland and France [1]. In the course of our search for the pathogenetically active secondary metabolites in the culture medium of *Eutypa lata*, a series of novel epoxycyclohexanes **1–4** have been isolated [2].



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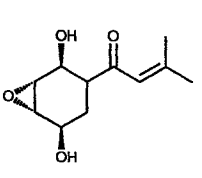

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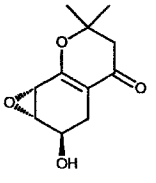

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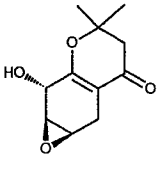

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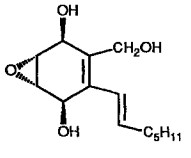
The structures of compounds **1–4** were elucidated by spectroscopic analysis and, in the case of **1**, confirmed by X-ray analysis and total synthesis [2]. It seems that compound **2** is biogenetically related to compound **1**. Thus, to confirm its structure and also to study the biosynthetic relationship between these new compounds, the synthesis of **2** is of interest. Furthermore, highly oxygenated cyclohexane compounds have been reported to show a wide range of biological activity [3].

Results and Discussion. – A similar synthetic strategy applied for **1** and for the eupenoxide [3], a compound which contains the same epoxycyclohexane-1,4-diol system, was followed for the synthesis of **2**.

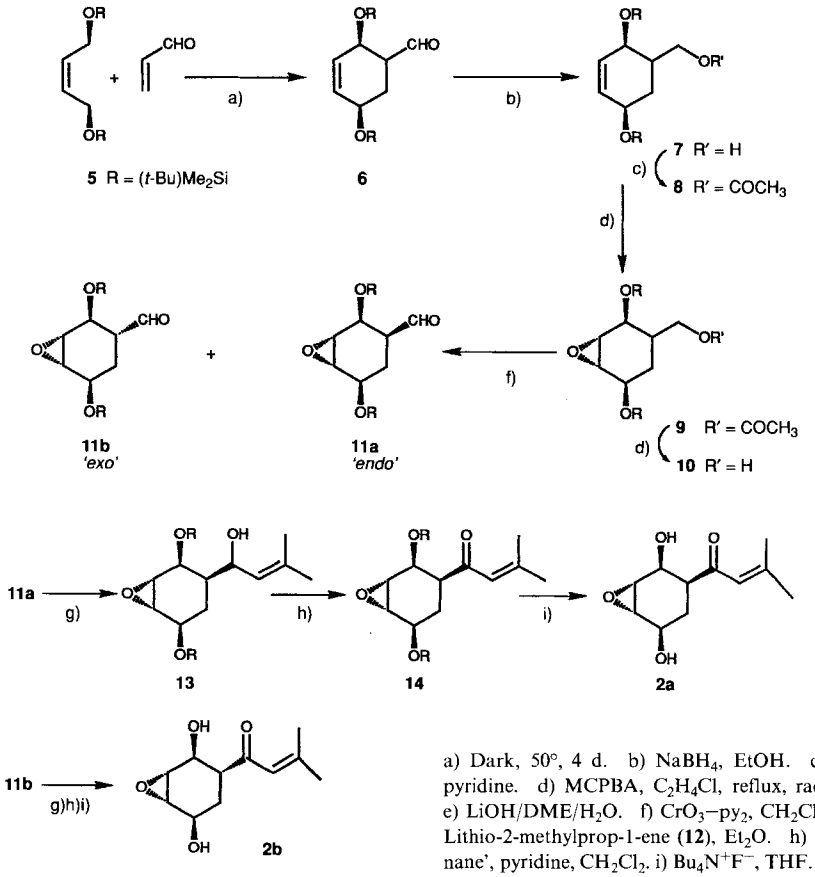


Eupenoxide

[1]) Present address: *Lonza AG*, CH–3930 Visp.

Retrosynthetic analysis of **2** suggested as a key intermediate the cyclohexanecarbaldehyde of the type **11** which could be generated by *Diels-Alder* addition of 1,4-dioxygenated butadiene to acrolein, followed by epoxidation. The build-up of the side chain by the reaction with a lithio compound and removal of the protecting groups would yield compound **2** (*Scheme*).

Scheme



a) Dark, 50°, 4 d. b) $NaBH_4$, EtOH. c) Ac_2O, pyridine. d) MCPBA, C_2H_4Cl, reflux, rad. inhib. e) LiOH/DME/H_2O. f) CrO_3–py_2, CH_2Cl_2. g) 1-Lithio-2-methylprop-1-ene (**12**), Et_2O. h) 'Periodinane', pyridine, CH_2Cl_2. i) $Bu_4N^+F^-$, THF.

The diene chosen was bis(silyloxy)butene **5** which *Duke* and *Rickards* used in their synthesis of eupenoxide [3]. Reaction of **5** with acrolein (50°, 4 d) afforded the corresponding cycloadduct **6** as a mixture of *r*-1,*c*-2,*c*-5/*r*-1,*t*-2,*t*-5-compounds (ratio 10:1) which is normally expected from secondary orbital considerations of the *Diels-Alder* reaction. At this stage, we decided to continue the syntheses with the mixture of the two diastereoisomers. Due to the rather drastic conditions used for the epoxidation, the aldehyde must be protected. First, we protected the aldehyde as a ketal. However, neither the ethyleneglycol protecting group nor bromo-methyl-glycol developed by *Corey* and *Ruden* [4] proved to be suitable. These results led us to look for a simpler, higher yielding route to **11**.

Reduction of aldehyde **6** with $NaBH_4$ in MeOH gave the primary alcohol **7** in good yield, but **7** could not be epoxidized directly. Thus, **7** was first protected as an acetyl derivative **8** which was then epoxidized cleanly by heating under reflux in 1,2-dichloroethane with *m*-chloroperoxybenzoic acid (MCPBA) and a radical inhibitor [5] to give the epoxide **9**. To show that epoxidation indeed took place on the rear face of the molecule, due to the directing influence of the two bulky (*t*-Bu)Me_2Si groups, we conducted NMR experiments not on **9** but directly on the intermediate **11a** (see later). The acetoxy group of **9** was hydrolyzed (LiOH, 1,2-dimethoxyethane/H_2O) without affecting the (*t*-Bu)Me_2Si groups to give **10**. Compound **10** was then oxidized with *Collins'* reagent CrO_3–py_2 [6] to give the target epoxy-aldehyde **11a**/**11b**. Although this sequence may appear laborious, all steps were accomplished smoothly and in high yields. The whole procedure could be carried out without purification of the intermediates.

At this point, we decided to separate the two diastereoisomers **11a** and **11b** by column chromatography. The stereospecific *trans*-epoxidation of compound **8** from the rear face of the molecule was confirmed by the ^{1}H-NMR of **11a**. For eupenoxide [3], the authors confirmed the configuration by considering the coupling constants $J(4,5)$ and $J(2,3)$. The *Karplus* equation [7] predict J values of 3.2 (dihedral angle of 50°) or 2.1 (dihedral angle of 120°) and 8.2 Hz (dihedral angle of 0°) or 0.8 Hz (dihedral angle of 70°) for *trans*- and *cis*-configuration, respectively. The observed coupling constant for eupenoxide was 2.3 Hz thereby etablishing a *trans*-configuration. Homodecoupling experiments on **11a** showed $J(2,3) = 1.6$ and $J(4,5) = 2.6$ Hz. These results, similar to those observed by *Duke* and *Rickards,* confirmed the *trans*-epoxidation. The influence of the bulky (*t*-Bu)MeSi group on the selectivity of epoxidation, whereby epoxidation occurs generally *trans* to the (*t*-Bu)Me_2Si group, had been recently reported [8]. Homodecoupling experiments likewise led to the configuration at C(6). Compound **11a** showed $J(1,2) = 3.6$ Hz, thereby revealing an '*endo*'-configuration based on *Karplus* rules. On the other hand, the observed $J(1,2)$ value for **11b** was 9.6 Hz, typical for a dihedral angle of 180°.

The build-up of the side chain was first attempted on the major product **11a**. Addition of the 1-lithio-2-methylprop-1-ene (**12**) on compound **11a** produced in good yields a diastereoisomeric mixture of allylic alcohols **13**. Oxidation of the allylic alcohols **13** proved extremely difficult. Using the standard reagents (CrO_3–py_2 [6], PDC [9], *Swern* oxidation [10], MnO_2 [11]), a complicated mixture of products was obtained in which **14** was a minor component. We found that 'periodinane' (described by *Dess* and *Martin* [12]) gave superior results to those obtained using other oxidants. To prevent decomposition products observed in the oxidation of **13** due to AcOH ('periodinane' obtained smelt very strongly of AcOH), we added some pyridine to the reaction mixture to trap the free acid. We obtained the required product pure after a simple aqueous workup in an reasonable yield. Removal of the (*t*-Bu)Me_2Si groups was achieved under nonacidic conditions with $Bu_4N^+F^-$ affording in good yields compound **2a**.

The same reaction sequence (addition of the lithio compound, oxidation, and desilylation) was performed on the minor component **11b** to give compound **2b**. Compounds **2a** and **2b** were then compared with the natural material by NMR and GC/MS. It was shown that the natural product corresponds to the compound **2b**, especially as the natural product showed the same large coupling constant $J(1,2) = 9.6$ Hz.

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Experimental Part

General. All commercially available chemical reagents were used without purification. THF and Et_2O were distilled over $LiAlH_4$ and CH_2Cl_2 over P_2O_5. The starting material *(E,s-trans, s-trans)-1,4-bis{[(tert-butyl)dimethylsilyl]oxy}but-2-ene* (**5**) was obtained from (*E*)-but-2-ene-1,4-diyl diacetate according to [3]. The 'periodinane' reagent was prepared from 2-iodobenzoic acid according to [12] and *1-lithio-2-methylprop-1-ene* (**12**) from 1-bromo-2-methylprop-1-ene according to [13]. M.p.: *Gallenkamp MFB-595-010M*. TLC: Aluminum sheets silica gel *60 F_{254}* (*Merck*). Prep. column chromatography: silica gel (*Merck 60*, 0.063–0.200 mm). FT-IR [cm^{-1}]: *Perkin-Elmer 1720X*, samples were measured as thin films on NaCl disks unless otherwise indicated. ^{1}H-NMR: *Bruker AMX 400*, δ in ppm using TMS as internal standard. MS: DCI (NH_3, positive mode) were recorded on a *Nermag R-3010* spectrometer, and HR-MS measurements were performed at Mass Spectrometry Laboratory of the University of Geneva. The microanalyses were done at the Laboratory for Organic Chemistry of ETH Zurich.

(2R,5R*)-2,5-Bis{[(*tert*-butyl)dimethylsilyl]oxy}cyclohex-3-ene-1-carbaldehyde* (**6a** and **6b**). Compound **5** (6.50 g, 20.6 mmol), freshly distilled acrolein (45 cm^3), and hydroquinone (0.40 g) were heated at 50° for 4 d in darkness. Then, unreacted dienophile was removed by distillation (50°/10 mm Hg). The yellow residual oil was chromatographed on a silica-gel column using toluene as eluant. The unreacted diene was first eluted followed by the mixture of the two diastereoisomers **6a** and **6b** as a pale yellow oil (5.80 g, 76%). TLC (toluene): R_f 0.55. FT-IR: 3035, 2955, 2930, 2885, 2860, 1715 (C=O, aldehyde), 1475, 1390, 1360, 1255, 1095, 835, 775. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.07 (*s*, 4 MeSi); 0.85, 0.90 (2*s*, 2 (*t*-Bu)Si); 1.90–2.05 (*m*, 2 H–C(6)); 2.45 (*m*, H–C(1)); 4.19 (*m*, H–C(5)); 4.57 (*t*, H–C(2)); 5.74–5.78 (*m*, H–C(3), H–C(4)); 9.74 (*d*, J = 1.7, CHO). DCI-MS: 372 (20), 371 (20, $[M + H]^+$), 313 (30, $[M - (t\text{-Bu})]^+$), 256 (60, $[M - (t\text{-Bu})Me_2Si]^+$), 239 (100, $[M - (t\text{-Bu})Me_2SiO]^+$), 181. Anal. calc. for $C_{19}H_{38}O_3Si_2$ (370.68): C 61.56, H 10.33; found: C 61.83, H 10.58.

(2R,5R*)-2,5-Bis{[(*tert*-butyl)dimethylsilyl]oxy}cyclohex-3-ene-1-methanol* (**7**). To a soln. of **6a**/**6b** (8.60 g, 23 mmol) in EtOH was added $NaBH_4$ (1.70 g, 45 mmol) and the mixture stirred at r.t., until all the starting material had been consumed (1 h). The mixture was then quenched by addition of a soln. of NH_4Cl and extracted with Et_2O. The org. layer was washed with sat. aq. NaCl soln., dried ($MgSO_4$), and evaporated to yield a pale yellow oil (7.8 g, 90%). TLC (toluene): R_f 0.1. FT-IR: 3390 (OH), 3030, 2955, 2930, 2855, 1470, 1390, 1360, 1255, 1075, 1025, 835, 775. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.09, 0.10, 0.11, 0.13 (4*s*, 4 MeSi); 0.88 (*s*, 2 (*t*-Bu)Si); 1.69–1.83 (*m*, H–C(1), 2 H–C(6)); 2.53 (br. *s*, OH); 3.74–3.76 (*m*, CH_2OH); 4.18 (*m*, H–C(5)); 4.28 (*t*, H–C(2)); 5.66–5.70 (*m*, H–C(3), H–C(4)). DCI-MS: 373 (2, $[M + H]^+$), 315 (10, $[M - (t\text{-Bu})]^+$), 241 (100, $[M - (t\text{-Bu})Me_2SiO]^+$), 225, 183.

{[(2R,5R*)-2,5-Bis{[(*tert*-butyl)dimethylsilyl]oxy}cyclohex-3-enyl}methyl Acetate* (**8**). To a soln. of **7** (7.82 g, 21 mmol) in CH_2Cl_2 (100 cm^3) was added Ac_2O (7.3 cm^3), pyridine (8.5 cm^3), and 4-(pyrrolidin-1-yl)pyridine (100 mg). After stirring for 1 h at r.t., all the starting material had been consumed. The soln. was diluted with CH_2Cl_2, washed twice with aq. 5% HCl soln., sat. aq. $NaHCO_3$ soln., and sat. aq. NaCl soln. The org. layer was dried ($MgSO_4$) and evaporated to give **8** as a pale yellow oil (7.74 g, 89%). TLC (toluene): R_f 0.5. FT-IR: 3030, 2955, 2930, 2895, 2860, 1745 (C=O, ester), 1475, 1390, 1360, 1255, 840, 775. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.05, 0.06, 0.08, 0.09 (4*s*, 4 MeSi); 0.87, 0.9 (2*s*, 2 (*t*-Bu)Si); 1.60–1.65 (*m*, 2 H–C(6)); 1.88 (*m*, H–C(1)); 2.05 (*s*, $COCH_3$); 4.03–4.07 (*m*, CH_2OAc); 4.12 (*m*, H–C(5)); 4.20 (*t*, H–C(2)); 5.70 (*m*, H–C(3), H–C(4)). DCI-MS: 416, 415 (5, $[M + H]^+$), 283 (100, $[M - (t\text{-Bu})Me_2SiO]^+$), 223.

{(2R,3R*,4S*,5S*)-2,5-Bis{[(*tert*-butyl)dimethylsilyl]oxy}-3,4-epoxycyclohexyl}methyl Acetate* (**9**). A soln. of **8** (0.54 g, 1.3 mmol), MCPBA (0.60 g) and 3-(*tert*-butyl)-4-hydroxy-5-methyl phenyl sulfide (0.08 g) in $C_2H_4Cl_2$ (30 cm^3) was heated under reflux. After 3 h, the soln. was diluted with CH_2Cl_2, washed with sat. aq. $NaHCO_3$ soln. and sat. aq. NaCl soln., dried ($MgSO_4$), and evaporated. The residual oil was purified by CC (toluene) to give **9** (0.46 g, 82%) as a pale yellow oil. TLC (toluene): R_f 0.20. FT-IR: 2955, 2930, 2890, 2860, 1745 (C=O, ester), 1475, 1385, 1370, 1255, 1090, 925, 835, 775. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.08, 0.09, 0.11, 0.14 (4*s*, 4 MeSi); 0.91, 0.93 (2*s*, 2 (*t*-Bu)Si); 1.42–1.48 (*m*, 2 H–C(6)); 1.80 (*m*, H–C(1)); 2.04 (*s*, CH_3CO); 3.10–3.13 (*m*, H–C(3), H–C(4)); 3.92–3.97 (*m*, CH_2OAc, H–C(5)); 4.25 (*t*, H–C(2)). DCI-MS: 432, 431 (100, $[M + H]^+$), 373 (20, $[M - (t\text{-Bu})]^+$), 313 (15, $[M - (t\text{-Bu})Me_2Si]^+$), 299, 239.

(2R,3R*,4S*,5S*)-2,5-Bis{[(*tert*-butyl)dimethylsilyl]}oxy}-3,4-epoxycyclohexane-1-methanol* (**10**). Compound **9** (1 g, 2.4 mmol) and LiOH (0.1 g, 4.6 mmol) were added to a soln. of 1,2-dimethoxyethane (60 cm^3) in H_2O

(20 cm^3) at r.t. After 6 h, more LiOH (0.11 g) was added, and the reaction was stirred overnight. The soln. was then diluted with Et_2O (200 cm^3) and washed with aq. 5% HCl soln. and sat. aq. NaCl soln., dried ($MgSO_4$), and evaporated to dryness. The residue was purified by CC (CH_2Cl_2) to give **10** (0.63 g, 67%). TLC (CH_2Cl_2): R_f 0.20. FT-IR: 3370 (OH), 2955, 2930, 2890, 2860, 1475, 1390, 1360, 1255, 1090, 920, 840, 775. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.10, 0.11, 0.13, 0.16 (4*s*, 4 MeSi); 0.91, 0.93 (2*s*, 2 (*t*-Bu)Si); 1.45–1.60 (*m*, 2 H–C(6)); 1.70 (*m*, H–C(5)); 2.08 (br. *s*, OH); 3.08–3.10 (*m*, H–C(3), H–C(4)); 3.57–3.70 (*m*, CH_2OH); 3.97 (*t*, H–C(5)); 4.20 (*m*, H–C(2)). DCI-MS: 389 (100, $[M + H]^+$), 331 (20, $[M - (t\text{-Bu})]^+$), 257 (10, $[M - (t\text{-Bu})Me_2SiO]^+$), 239, 199, 169.

*(2*R*,*3*R*,*4*S*,*5*S*)-2,5-Bis{[(*tert*-butyl)dimethylsilyl]oxy}-3,4-epoxycyclohexanecarbaldehyde* (**11a**/**11b**). To a soln. of **10** (0.51 g, 1.3 mmol) in dry CH_2Cl_2 (100 cm^3) was added CrO_3–py_2 (2 g, 7.7 mmol). After 2 h, the mixture was filtered, and the precipitate was washed thoroughly with CH_2Cl_2. The combined washings were evaporated to give a brown oil which was purified on CC. Elution with toluene gave first **11b** then **11a** (combined yield 0.38 g, 75%). Compound **11a** was recrystallized in CH_2Cl_2/hexane as white needles. M.p. 76°. TLC (toluene): R_f 0.35. FT-IR (KBr): 3010 (CH, epoxy), 2960, 2930, 2890, 2890, 2855, 1725 (C=O, aldehyde), 1475, 1380, 1085, 925, 840, 775. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.08, 0.11, 0.12, 0.14 (4*s*, 4 MeSi); 0.87, 0.91 (2*s*, 2 (*t*-Bu)Si); 1.67–1.90 (2*m*, 2 H–C(6)); 2.36 (*m*, H–C(1)); 3.15–3.20 (*m*, H–C(3), H–C(4)); 3.96–4.00 (*m*, $J(4,5) = 2.6$ Hz, H–C(5)); 4.59 (*m*, $J(2,3) = 1.6$ Hz, $J(1,2) = 3.6$ Hz, H–C(2)); 9.65 (*s*, CHO). DCI-MS: 387 (100, $[M + H]^+$), 329 (50, $[M - (t\text{-Bu})]^+$), 272, 255, 197, 169, 155. Anal. calc. for $C_{19}H_{38}O_4Si_2$ (386.68): C 59.02, H 9.91; found: C 58.92, H 9.94.

Compound **11b** was obtained as a white oil: TLC (toluene): R_f 0.39. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.10, 0.11 (2*s*, 4 MeSi); 0.87, 0.90 (2*s*, 2 (*t*-Bu)Si); 1.47–1.69 (*m*, 2H–C(6)); 2.67 (*m*, H–C(1)); 3.10–3.13 (*m*, H–C(3), H–C(4)); 4.20 (*d*, $J(1,2) = 9.6$ Hz, H–C(2)); 4.30 (*m*, H–C(5)); 9.71 (*s*, CHO). DCI-MS: as for **11a**.

*{(1'*R*,*2'*R*,*3'*R*,*4'*S*,*5'*S*)-2',5'-Bis{[(*tert*-butyl)dimethylsilyl]oxy}-3',4'-epoxycyclohexyl}(2-methylprop-1-enyl)methanol* (**13**). To a soln. of **11a** (0.41 g, 1.1 mmol) in dry Et_2O (15 cm^3) at 0° under N_2 was added dropwise a soln. of **12** in Et_2O (11 cm^3 of an 0.1N soln.). After 30 min, the mixture was diluted with Et_2O and washed twice with sat. aq. NH_4Cl soln., then twice with sat. aq. NaCl soln., and dried ($MgSO_4$). The org. layer was evaporated to give a diastereoisomer mixture of **13** (0.39 g, 84%) as a white oil. TLC (CH_2Cl_2): R_f 0.28. FT-IR: 3465 (OH), 2955, 2930, 2890, 2860, 1695 (C=C), 1475, 1380, 1360, 1260, 1100, 920, 840, 775. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.12, 0.13, 0.15, 0.18 (4*s*, 4 MeSi); 0.92, 0.94 (2*s*, 2 (*t*-Bu)Si); 1.45–1.75 (*m*, 2 H–C(6'), H–C(1')); 1.68–1.72 (2*s*, 2 CH_3); 2.65 (br. *s*, OH); 3.10 (*m*, H–C(3'), H–C(4')); 3.92–3.96 (*m*, H–C(5')); 4.26 (*m*, H–C(2')); 4.44 (*q*, C*H*OH); 5.27 (*d*, $J = 8$, H–C=C). DCI-MS: 443 (2, $[M + H]^+$), 387 (5, $[M - (t\text{-Bu})]^+$), 311 (15, $[M - (t\text{-Bu})Me_2SiO]^+$), 293, 253 (100), 235, 225, 211, 199. Anal. calc. for $C_{32}H_{46}O_4Si_2$ (442.79): C 62.39, H 10.47; found: C 62.35, H 10.51.

*(1'*R*,*2'*R*,*3'*R*,*4'*S*,*5'*S*)-1-{2',5'-Bis{[(*tert*-butyl)dimethylsilyl]oxy}-3',4'-epoxycyclohexyl}-3-methylbut-2-enone* (**14**). To a soln. of **13** (0.15 g, 0.34 mmol) in CH_2Cl_2 (10 cm^3) was added 'periodinane' (0.18 g, 0.42 mmol) and pyridine (1 cm^3). After 20 min, more 'periodinane' was added (0.1 g). The mixture was then diluted with Et_2O, washed thoroughly with 1N aq. NaOH soln., aq. 5% HCl soln., sat. aq. NaCl soln., and dried ($MgSO_4$). The solvent was evaporated and the yellow oil obtained was purified by CC (toluene) to give **14** as a white oil (0.075 g, 72%). TLC (toluene): R_f 0.31. FT-IR: 2955, 2930, 2890, 2860, 1735 and 1690 (α, β-unsat. ketone), 1625 (C=C), 1475, 1380, 1250, 1085, 925, 870, 780. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.14, 0.16, 0.17, 0.18 (4*s*, 4 MeSi); 0.90, 0.98, (2*s*, 2 (*t*-Bu)Si); 1.79–1.86 (*m*, 2 H–C(6')); 1.96, 2.26 (2*s*, 2 CH_3); 2.42–2.47 (*m*, H–C(1')); 3.17–3.22 (*m*, H–C(3'), H–C(4')); 3.93 (*t*, H–C(5')); 4.68 (*t*, H–C(2')); 6.19 (*s*, H–C=C). DCI-MS: 441 (40, $[M + H]^+$), 383 (10, $[M - (t\text{-Bu})]^+$), 309 (5, $[M - (t\text{-Bu})Me_2SiO]^+$), 293, 251, 209. HR-MS (EI): 440.2773 (M^+).

*(1'*R*,*2'*R*,*3'*S*,*4'*R*,*5'*S*)-1-(3',4'-Epoxy-2',5'-dihydroxycyclohexyl)-3-methylbut-2-en-1-one* (**2a**). To a soln. of **14** (0.085 g, 0.193 mmol) in THF was added $Bu_4N^+F^-\cdot 3H_2O$ (0.24 g, 0.76 mmol). After 2 h, all the starting material had been consumed, and the reaction soln. was diluted with AcOEt, washed with sat. aq. NaCl soln., dried ($MgSO_4$), and evaporated to give a yellow oil which was purified by CC. Elution with AcOEt/$CHCl_2$ 1:1 gave **2a** as a white oil. TLC (AcOEt): R_f 0.28. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.50, 1.75 (*m*, 2 H–C(6')); 1.94–2.17 (2*s*, 2 CH_3); 2.55 (*m*, H–C(1')); 3.22–3.34 (*m*, H–C(3'), H–C(4')); 4.07 (*m*, H–C(5')); 4.56 (*m*, H–C(2')); 6.08 (*s*, H–C=C). DCI-MS: 213 (100, $[M + H]^+$), 195, 161, 127, 83.

*(1'*R*,*2'*S*,*3'*R*,*4'*S*,*5'*R*)-1-(3',4'-Epoxy-2',5'-dihydroxycyclohexyl)-3-methylbut-2-en-1-one* (**2b**). The same procedure utilized for **2a** was used to prepare **2b**. TLC (AcOEt): R_f 0.26. FT-IR (KBr): 3420 (OH), 2930, 2855, 1710 and 1680 (α, β unsat. ketone), 1615 (C=C), 1445, 1385, 1250, 1115, 1070, 1045, 840, 800. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.51, 1.80 (2*m*, 2 H–C(6')); 1.68 (br. *s*, OH); 1.92, 2.16 (2*s*, 2 CH_3); 2.67 (*m*, H–C(1')); 2.85 (br. *s*, OH); 3.22–3.26 (*m*, H–C(3'), H–C(4')); 4.26 (*d*, H–C(5')); 4.38 (*d*, $J(1',2') = 9.6$, H–C(2')); 6.15 (*s*, H–C=C). DCI-MS: as for **2a**. HR-MS (EI): 212.1048 (M^+).

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